# Catalytic and Co-ordination Chemistry of Enolate Oxazoline $\kappa^{2}$-N,O-Ligands to Group 9 \& 11 Transition Metals 

by

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#### Abstract

The co-ordination chemistry and resulting catalytic potential of Group 9 and 11 transition metal centered complexes with the 2-acylmethyl-2-oxazoline skeleton are detailed. Each of the synthesized ligand species were treated with either a Copper (II) or Cobalt (II) salt to promote co-ordination, in all cases deprotonation of the ligand occurred. These complexes have, thereafter, been examined by infrared spectroscopy (IR), UV-Visible spectroscopy (UV-Vis), mass spectrometry (MS), cyclic voltammetry (CV), combustion analysis (EA) and x-ray diffraction and probed for their potential redox properties. In the case of $\mathrm{Cu}(\mathrm{II})$ chelated complexes, no desirable redox behaviour was observed. Although, with respect to $\mathrm{Co}(\mathrm{II})$ complexes, one complex displayed favourable redox potential. The redox active species have been shown to effectively catalyze the polymerization of methyl methacrylate with tosyl chloride as an initiator, through an ATRP-like mechanism. Work within also reflects preliminary co-ordination to Iridium and Rhodium metal centers. Successfully synthesized Iridium complexes have been tested with respect to their oxidative properties. Positive results have been observed in their ability to perform oxidative addition with both $\mathrm{HSnPh}_{3}$ and MeI. Both small molecule species have been effectively added to an $\operatorname{Ir}(\mathrm{I})$ complex, formally changing its oxidation state to $\operatorname{Ir}(\mathrm{III})$.


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## List of Abbreviations:

| Acetonitrile | ACN |
| :--- | :--- |
| Aluminum(III)chloride | $\mathrm{AlCl}_{3}$ |
| Aryl | Ar |
| Atom transfer radical polymerization | ATRP |
| Benzene-d | $\mathrm{C}_{6} \mathrm{D}_{6}$ |
| tertiary-Butyl | $t$-Bu |
| normal-Butlyllithium | $n-\mathrm{BuLi}^{2}$ |
| 2,2'-Bipyridine | $\mathrm{Bpy}^{\text {Carbon disulphide }}$ |
| Chloroform | $\mathrm{CS} 2_{2}$ |
| Chloroform-d | CHCl |
| 3 |  |


| Dimethyl formamide | DMF |
| :---: | :---: |
| Dimethyl sulphoxide | DMSO |
| Distilled water | $\mathrm{dH}_{2} \mathrm{O}$ |
| 1,1'-bis(Diphenylphosphino)ferrocene | dppf |
| Diethyl ether | $\mathrm{Et}_{2} \mathrm{O}$ |
| Elemental Analysis | EA |
| Electron volts | eV |
| Ethanol | EtOH |
| Ethyl acetate | EtOAc |
| Gel Permeation Chromatography | GPC |
| Heteronuclear multiple-bond correlation spectroscopy | HMBC |
| Heteronuclear single- quantum correlation spectroscopy | HSQC |
| Hertz | Hz |
| Infrared spectroscopy | IR |
| Ligand to metal charge transfer | LMCT |
| Magnesium sulphate | $\mathrm{MgSO}_{4}$ |
| Mass spectrometry | MS |
| Melting point | mp |
| Metal to ligand charge transfer | MLCT |
| Methanol | MeOH |
| Methyl iodide | MeI |
| Methyl methacrylate | MMA |
| N -bromosuccinamide | NBS |


| 1-Napthyl | nap |
| :---: | :---: |
| Nuclear magnetic resonance spectrosopy | NMR |
| Nuclear Overhauser effect spectroscopy | nOesy |
| The Oak Ridge Thermal Ellipsoid Plot | ORTEP |
| Parts per million | ppm |
| Poly(aniline) | PANi |
| Poly(methyl methacrylate) | PMMA |
| Poly(styrene) | PS |
| Poly(vinylchloride) | PVC |
| Polydispersity Index | PDI |
| Potassium hydroxide | KOH |
| Pyridine | py |
| Reversible Addition-Fragmentation Chain Transfer | RAFT |
| Room temperature | rt |
| Sodium carbonate | $\mathrm{Na}_{2} \mathrm{CO}_{3}$ |
| Sodium chloride | NaCl |
| Sodium sulphate | $\mathrm{Na}_{2} \mathrm{SO}_{4}$ |
| Sulphuric acid | $\mathrm{H}_{2} \mathrm{SO}_{4}$ |
| Tetrabutylammonium hexafluorophosphate | $\left[\mathrm{N}(\mathrm{n}-\mathrm{Bu})_{4}{ }^{+}\right]\left[\mathrm{PF}_{6}{ }^{-}\right]$ |
| Tetrahydrofuran | THF |
| $\mathrm{N}, \mathrm{N}, \mathrm{N}^{\prime}, \mathrm{N}^{\prime}$-Tetramethylethylenediamine | TMEDA |
| (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl | TEMPO |
| Thin Layer Chromatography | TLC |


| Thionyl chloride | $\mathrm{SOCl}_{2}$ |
| :---: | :---: |
| Trichloroacetyl chloride | TCAC |
| Triethylamine | $\mathrm{NEt}_{3}$ |
| Triethylamine hydrochloride | $\mathrm{NEt}_{3} \cdot \mathrm{HCl}$ |
| Triethylphosphite | $\mathrm{P}(\mathrm{OEt})_{3}$ |
| Trichlorosilane | $\mathrm{HSiCl}_{3}$ |
| Trifluoroacetic anhydride | TFAA |
| Triphenylphosphine | $\mathrm{PPh}_{3}$ |
| Triphenylphosphine oxide | $\mathrm{O}=\mathrm{PPh}_{3}$ |
| Triphenylsilane | $\mathrm{HSiPh}_{3}$ |
| Triphenylstannane | $\mathrm{HSnPh}_{3}$ |
| Tosyl chloride | TsCl |
| Ultraviolet-Visible spectroscopy | UV-Vis |
| Vaska's complex | $\operatorname{IrCl}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2}$ |
| Zinc Chloride | $\mathrm{ZnCl}_{2}$ |

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### 1.0 Introduction

### 1.1 Oxazolines

Oxazolines, or 4,5-dihydro-2-oxazoles, are five-membered heterocycles containing a nitrogen and oxygen between an $\mathrm{sp}^{2}$-hybridized carbon atom. They can differ sterically by substitution appended to any of its five vertices (expect the oxygen atom) or isomerically by positioning of the $\pi$-bond (Scheme 1).


Scheme 1: 2-, 3-, and 4- oxazolines (left to right)
Oxazolines can be manufactured in a variety of methods including the Witte-Seeliger reaction (metal-catalyzed cross-coupling), ${ }^{1}$ a ring-closing reaction with thionyl chloride, ${ }^{2}$ from oxidation of an oxazolinidine or by simply heating a carboxylic acid or aldehyde with a 1,2-amino alcohol (Scheme 2). ${ }^{3}$ Oxazolines have gained synthetic interest due to not only their relatively stable and inert nature but also their close relation to acyl derivatives of $\alpha$-amino acids. ${ }^{4}$ They are unreactive with most nucleophiles, radical species, bases and weak acids. Oxazolines were first used in the field of polymer chemistry as a monomer; the resulting poly(2-oxazolines) ${ }^{5}$ are like that of similar to poly(amides) making them strong candidates in biomedical applications. ${ }^{6}$ The aspect of this that is attractive to organic chemists is that the oxazoline protecting group can be installed during synthesis by using mild conditions and are moderately good precursors for functional later group transformation. ${ }^{4,6,7}$


Scheme 2: Three known routes to 2-oxazolines.
More recently, oxazolines have been widely studied for their role in polymerization and protecting group chemistry ${ }^{8,9}$ as well as their ability to be a respectable monodentate ligands in asymmetric and symmetric catalysis. ${ }^{10,11}$ Over the years, oxazolines have had, and continue to exhibit, a vast array of applications from polymer chemistry to organic chemistry to coordination chemistry. ${ }^{4-7}$

### 1.2 Coordination Chemistry

Coordination chemistry entails the formation of covalent/coordination bonds (usually dative interactions) between, normally, a metal ion and neutral or charged ligands. In the case that the resulting complex carries a charge, an ion with opposite change is present to balance it to a neutral state. As previously mentioned, ligands can be either neutral or charged (cationic or anionic). Neutral ligands include $N$-heterocyclic carbenes, pyridine, acetonitrile and water (Scheme 3).


Scheme 3: Examples of mono-charged and neutral ligands
Most charged ligands are anionic in nature as transition metal centers are generally cationic. Charged ligands can be mono-, di- or tri- anionic such as halogen species $\left(\mathrm{Cl}^{-}, \mathrm{Br}^{-}, \mathrm{F}^{-}, \mathrm{I}^{-}\right)$and deprotonated oxygen species (e.g., 8-hydroxyquinolinolate) (Scheme 3). Once coordinated, octahedral ligated metal complexes can exhibit different geometric isomers; mer/fac, cis/trans, as well as lambda/delta ( $\Lambda / \Delta$ ) rotational isomers (Scheme 4).




Scheme 4: Conformational and rotation isomers of cobalt complexes

### 1.2.1 Denticity

The number of donor groups from a specific ligand attached to a central metal atom denotes its denticity. ${ }^{12}$ Oxazolines on their own can act as monodentate ligands ${ }^{13-16}$ or polydentate ligands when functionalized with other groups, meaning they can be bound to the central atom through one or more bonds. ${ }^{17-19}$ There are multiple examples of oxazoline-based ligands with varying
denticity in the literature including mono- $(\mathbf{A})^{14}$, bi- $(\mathbf{B})^{20}$, and tridentate $(\mathbf{C})^{19}$ architectures

## (Scheme 5).



Scheme 5: Examples of Mono-, bi-, and tridentate oxazoline transition metal complexes
The examples given in Scheme 5 represent transition metal complexes containing chelating ligands. Strong donating interactions, such as in the case of the nitrogen in the oxazoline ring, readily form bonds with a formally cationic metal center. If the oxazoline ring is appended with another anionic functional group, the compound can form a chelate bond with the metal center effectively changing its bond mode from $\kappa^{1}$ to $\kappa^{2}$ (or higher).

## 1.3. $\kappa^{2}-\mathrm{N}, \mathrm{O}$ Chelating Ligands

There are several types of nitrogen-based bidentate chelating ligands such as those with NN, NS, NP, NC, or NO-donor atom functionality. N,O chelates have been targeted as a class of ligands in the fields of catalytic and coordination chemistry due to their variable bonding modes and binding affinities for cationic metal species. ${ }^{21}$ After being bound to a metal center the participating ligands are employed in applications ranging from small molecule activation to stoichiometric bond activation and catalysis. In an N,O donor ligand, the oxygen atom is often anionic in character, making it a hard (Lewis basic) donor to the metal center. ${ }^{22}$ The nitrogen is an intermediate donor, meaning it can exhibit properties of both a hard and soft donor. This gives the nitrogen atom freedom to bond then release itself from the metal. Overall, this hemilabile quality makes $\mathrm{N}, \mathrm{O}$ donor ligands attractive for use in catalysis when coordinated to a metal center.

### 1.3.1 Classes of N,O Chelating Ligands

A lot of focus in the literature has been put on N,O chelates, such as those derived from amino acids. ${ }^{23,24}$ More common to the field of inorganic coordination chemistry are the 1,3- and 1,4-N,O chelates. These functional groups (Scheme 6), most noticeably quinolinolates ${ }^{25-27}$ and picolinates, ${ }^{28-30}$ have seen a span of uses catalytically. Sulfonamidates ${ }^{31}$ and phosphoramidates ${ }^{32,33}$ have started to see more use in the field as well.




Scheme 6: Types of N,O-donor pro-chelates.

### 1.3.2 Synthesis of Ligands

A target of the Gossage groups' research has been centered around a $1,5-\mathrm{N}, \mathrm{O}$ pro-ligand, first synthesized by Meyers ${ }^{34}$ and later popularized by the simple synthesis of the series from Prof. Tohda in 1984. ${ }^{35}$ In his studies of these compounds, Tohda crafted clever, high yielding synthetic pathways to these compounds. ${ }^{36,37} \mathrm{He}$ later went on to continue his investigation of the formation of abnormal Michael adducts that these particular oxazoline based compounds can adopt. ${ }^{8} \mathrm{He}$ devised three simple synthetic pathways (Scheme 7); 2-step acylation and deacylation, a crossed Claisen condensation with $\mathrm{AlCl}_{3}$ coordination (for acid chloride compounds with $\alpha$-protons to the carbonyl), and a reaction that utilizes pyridine to synthesize compounds with more electron
withdrawing donor groups. Another, less popular method to make these types of compounds comes from the use of a dithio-ketene ${ }^{9,38,39}$ (vide infra).


Scheme 7: A general look at three of Tohda's procedures to make the target oxazoline ligand class

### 1.3.2.1 Ligands via Diacylation and Hydrolysis

The first, and most versatile, synthetic pathway developed by Tohda is a two-step reaction. ${ }^{35}$ The starting oxazoline is acylated at the $N$-position first, which then activates the methyl group on the oxazoline at position 2 (Scheme 8). This is done an in polar aprotic solvent as the transition state of the intermediate is very polar. The isolated intermediate material, in high yields (82-99 \%), is subjected to a basic mixture of excess potassium hydroxide dissolved in methanol ( 1.5 M $\mathrm{KOH})$. This cleaves the $\mathrm{C}-\mathrm{N}$ bond at the N -acetlyated position to give the desired compound in moderate to high yields (57-95 \%). This reaction has been optimized to the point where one can produce $>30$ grams of $\mathbf{D}$ without sacrificing yield or materials. ${ }^{35}$


Scheme 8: Tohda's diacylation and deacylation procedure to make the target compound, D

### 1.3.2.2 Ligands via Crossed-Claisen Reaction

The second pathway developed by Tohda in 1986 was a way to synthesize these oxazoline derived compounds if an alkyl-carbonyl substituent bonded to the heterocycle. The 2,4,4-trimethyl-2-oxazoline and triethylamine are added to a solution of aluminum chloride. ${ }^{36}$ After which an anhydride species is added over 30 minutes at $0^{\circ} \mathrm{C}$. Once obtained, but not isolated, the intermediates species is immediately dissolved in a basic potassium hydroxide/methanol solution to cleave the C-N bond on the 3-position of the oxazoline (Scheme 9 ). The pure product $(\mathbf{E})$ is obtained by via co-distillation with ethylene glycol. Although this method is effective for synthesizing these types of compounds with alkyl chains that have protons directly next to the carbonyl, yields do not exceed $75 \%{ }^{36}$


Scheme 9: Tohda's procedure for synthesis of the target compound, $\mathbf{E}$, via $\mathrm{AlCl}_{3}$

### 1.3.2.3 Ligands via S,S-dithio-Ketenes

A less popular route used in the synthesis of these oxazoline-appended compounds is the reaction of a $S, S$-dithio-ketene with an amino alcohol. The dithio ketene is generated in situ in a one-pot reaction between NaH , carbon disulphide $\left(\mathrm{CS}_{2}\right)$ and methyl iodide (MeI) (Scheme 10)..$^{9,38,39}$ In this reaction, a sample of a benzyl ketone is irreversibly deprotonated and reacted with $\mathrm{CS}_{2}$ and MeI to give the dithio intermediate ( $\mathbf{F}$ ). The intermediate compound is immediately dropped into a dispersion of Na and the chosen amino alcohol. After reflux, the target ring-closed compound is isolated as an off-white powder (G). ${ }^{40}$ Drawbacks of this reaction pathway is the overall technical difficulty of the synthesis and lower yields obtained of the targets (49-63 \%).



Scheme 10: Generation of the S,S-dithio ketene and synthesis of the target compound, G

### 1.3.2.4 Ligands via alternative methods - pyridine/lithiation

Two last methods are more uncommon as they can make a smaller range of such modified oxazoline compounds. The first method is by using a mixture of pyridine in acetonitrile with a strongly electron withdrawing anhydride. In this route, the reaction is kept at a temperature of 0 ${ }^{\circ} \mathrm{C}$ to prevent unwanted by-products and is mediated by pyridine (Scheme 11). After completion, the target compound can be isolated as an off-white powder in excellent yields (90-93 \%). ${ }^{8}$


Scheme 11: Reaction to make target compound, H, with cold pyridine.

The second method is by using $n$ - BuLi in an electrophilic substitution of a ketone species to obtain the target compound (Scheme 12). The starting 2-oxazoline compound is subjected to $n$ butyllithium. This lithiates the 2-position of the oxazoline, forming the supposed lithio-oxazoline intermediate. Afterwards the lithio-oxazoline is reacted with the ester of choice and can be isolated as an off-white powder (E) after extraction and work-up (85 \%). ${ }^{34}$


Scheme 12: Lithiation of the oxazoline and reaction with EtOAc to give the target compound, E.

### 1.3.3 Tautomers of the Target Ligand Series

This class of compounds display at least three different tautomers (resonance contributors); the enol, keto and enamine forms (Scheme 13). Although, in the solid state of the compound series, the enamine form is most prominently observed (Figure 1) and in the solution state a mix of the enamine and keto form can be observed. ${ }^{35}$


enol

keto


Scheme 13: Tautomers of this ligand class, along the $\mathrm{N}-\mathrm{C}-\mathrm{C}-\mathrm{C}-\mathrm{O}$ backbone.


Figure 1: Crystal structure of $\mathbf{D}$, seen in the enamine form.

### 1.4 Relevant Transition Metal N,O-complexes

### 1.4.1 Copper(II)/Cobalt(II/III) Complexes

The area of copper(II) and cobalt(II) complexes bearing $\mathrm{N}, \mathrm{O}$-donor ligands has been extensively researched with literature searches returning complexes bound to all classes of ligands, including a wide variety of amino acid functionalzed complexes. (Scheme 14, I). ${ }^{41-43}$ Other N,Odonor ligands that are commonly found bound to metals are those of the amidate, phosphoramidate, quinolinolate and the pyridonate classes (Scheme 6). Cobalt and copper have received increasing attention over the years as substitutes for heavier transition metals due to their cheaper cost and facile synthesis. ${ }^{44,45}$ Tendenborg in 1999 synthesized a small library of ligands (both N,O- and N,N-chelates) and coordinated them to both copper and cobalt metal salts (Scheme 14, J). ${ }^{46}$ They later tested those complexes in their ability to catalyze the asymmetric aziridination of styrene. They received high yields with modest enantiomeric excesses in short reaction times (10 minutes). In 2016, preliminary studies on copper(II) coordination polymers were disclosed by the Amo-Ochoa group and their pyridonate $\mathrm{N}, \mathrm{O}$-ligands showed their exceptional binding utility by attracting other copper complexes to form a polymeric substance (Scheme 14, K). ${ }^{47}$ More recently, in 2017 Shakdofa and coworkers presented their work on copper and cobalt anti-tumor complexes. The tested complexes [NNO, NN, OO-(dinuclear Cu species) and NO ligated complexes] showed a modest level of activity against the human leukemia, human liver cancer, and human breast cancer cell lines although not at active as a current anti-tumor drug, Doxorubicin (Scheme 14, L). ${ }^{48}$


I


K



L

Scheme 14: A few relevant copper and cobalt complexes (I-L)

### 1.4.2 Rhodium(I/III)/Iridium(I/III) Complexes

Further down Group 9 lies Iridium and Rhodium. In recent years (1960-present), there have been a plethora of studies surrounding their interesting properties. Rhodium, and Iridium to a degree, were initially used as hydrogenation catalysts (addition of $\mathrm{H}_{2}$ across a $\pi$-bond) ${ }^{49-52}$ as is in the case of Wilkinson's catalyst (Scheme 15, M). ${ }^{53}$

Both Rhodium and Iridium have gained significant interest in the research field as they can efficiently facilitate oxidative addition/reductive elimination-type reactions (redox). This lead to their increasingly popularity in the field of catalytic-coordination chemistry. One of the best candidates for studying hydrogen transfer, as well as other general oxidative addition reactions is Vaska's complex, $\operatorname{IrCl}(\mathrm{CO})\left(\mathrm{PPh}_{2}\right)($ Scheme 15, $\mathbf{N})$. These reactions can be visualized physically as well they tend to lose their bright yellow colour and through infrared spectroscopy as they observed to have higher stretching frequencies $\left(>2000 \mathrm{~cm}^{-1}\right.$ once oxidative addition occurs at the Ir center).


M


N

Scheme 15: Wilkinson's catalyst (M) and Vaska's complex (N).
Two coordination compounds to note are $\mathbf{O}^{54}$ and $\mathbf{P} .{ }^{32,33,55}$ Using a simple two-step method (use of an iridium-COD dimer ${ }^{56}$ then coordination of their ligand) then by the addition of a reaction nucleophilic species, the Carlton group has been able to synthesise an array of H-Ir-R complexes (see Scheme 16, O). This reactions series showcases the redox ability of the iridium centered complex as it oxidizes from an $\operatorname{Ir}(\mathrm{I})$ to $\operatorname{Ir}(\mathrm{III}) .{ }^{54}$ In a more recent example, the Love and Schafer groups have been able to synthesize 1,3-N,O-chelated phosphoramidate complexes (Scheme 16, $\mathbf{P})$. These complexes have shown to perform a variety of oxidative addition/reductive elimination reactions with various boron substrates. In doing so, they've demonstrated the versatility of these types of complexes by achieving a high yielding, selective hydroboration. ${ }^{32,33,55}$



Scheme 16: Carlton's and Love's chelated iridium complexes.

### 1.5 Polymers

Polymers are macromolecular structures or more simply explained as long chains with repeating units. There are two main different types of polymers, organic (PANi, PVC, PS) and inorganic polymers (polyphosphazenes, polysilanes, poly(ferrocenylsilanes)). These
macromolecules can consist of one singular repeat unit (homopolymer) to many different repeat units (co-polymer) arranged neatly (block co-polymer) or unpredictably (random co-polymer). Polymers are characterized the degree of their uniformity (Equation 1). This measurement is known as the polydispersity index (PDI). ${ }^{57}$

PDI $=\frac{\mathrm{M}_{\mathrm{w}}}{\mathrm{M}_{\mathrm{n}}} \begin{aligned} & \text { Weight-average } \\ & \text { molar mass }\end{aligned}$
Equation 1: Polydispersity Index.

### 1.5.1 Mechanisms of Polymer Growth

The two generally accepted mechanisms surrounding polymer growth are step-growth (condensation) and chain growth (addition). Step-growth polymerization occurs by the monomer units adding to each other in a more unpredictable fashion, having monomers reacting to make dimers, dimers reacting to form tetramers, or a monomer unit and a dimer reacting to form a trimer. These seemingly random chain length oligomers react with each other to increase the polymer chain length. A polymer polymerized with this mechanism generally produces low molecular weights, high percent conversion but also a more broad PDI. ${ }^{58}$

The other main accepted mechanism is by chain growth. With a chain growth mechanism, the reactive species, usually a radial species, initiates and facilitates the lengthening of the polymer chain. In this case a new monomer is added tip-to-tail or step by step to the polymer chain. High polymer molecular weights, along with a narrow PDI but low conversion rate are consistent with this mechanism.

### 1.5.2 Metal Catalyzed Atom Transfer Radical Polymerization (ATRP)

Atom transfer radical polymerization (ATRP) was simultaneously discovered by Mitsuo Sawamoto, ${ }^{59}$ Jin-Shan Wang and Krzysztof Matyjaszewski in $1995 .{ }^{60}$ ATRP starts off with the initiation of the catalytic species (see Scheme 17). The catalyst chosen for metal-based ATRP must be able to have a reasonable affinity for halogens, be able to accommodate the extra halogen in its coordination sphere as well as have an easily accessible oxidation state with typically a one electron difference. ${ }^{61}$


Scheme 17: General mechanism for Cu -mediated ATRP.
Afterwards the initiated radial species (R•) seeks out the olefinic monomer. Once found, the radical species bonds to the olefin, propagating along the backbone of the molecule (P•). ${ }^{61}$ This step occurs continuously and stops once all of the monomer units have been bonded together. The polymer is terminated by the halogen species that was originally bonded to the initiator as the catalyst "terminates" the initiator and the polymerization is ended. Additionally, ATRP is a living polymerization, meaning that the process can be stopped and restarted. This process is ideal for co-block polymerizations as one block can be polmerized, stopped, and a second monomer can be polymerized onto the first block. This facilitates an effective and controlled synthesis. ${ }^{60,61}$

Another type of radical polymerization is nitroxide mediated polymerization (NMP). This method is akin to ATRP although makes no use of metal species and is usually initiated and/or mediated by TEMPO, or other radical nitroxide functional molecules (nitroxide $=\mathrm{N}-\mathrm{O} \bullet$ ).

### 1.5.2.1 Copper(I/II) Catalysts in ATRP

ATRP, when it was first discovered, primarily used copper $(\mathrm{I})$ catalysts as they could accommodate the halogen initiative species in their coordination sphere, lead to minimal side reactions and its higher oxidation state $\left(\mathrm{Cu}^{2+}\right)$ can be easily accessed. The first copper complex to be used in this manner by Matyjaszewski is the in situ generated catalyst, copper(I)bipyridine chloride. ${ }^{60}$ Their catalyst worked efficiently, giving PDI's $<1.5$ (narrow molecular weight distributions). They noted that without the additive (bpy) the molecular weight and PDI were ill controlled and gave poor results. ${ }^{60}$ Matyjaszewski and co-workers have been building to expand this field with the use of their copper catalysts by varying the coordinated ligand. ${ }^{62}$ Different ligand scaffolds they've recently used (see, Scheme 18) contain four N -donor atoms, are potentially tetradentate ligands. Currently, their pre-catalyst $\left.\left[\mathrm{Cu}\left(\mathrm{TPMA}^{\mathrm{NMe} 2}\right) \mathrm{Br}\right)\right][\mathrm{Br}]$ exhibits the highest $\mathrm{k}_{\text {ATRP }}(=1)$, meaning the rate at which ATRP can be started and the rate at which it can be stopped are almost equal. A good ATRP catalyst has a $\mathrm{k}_{\text {ARTP }}$ value of 1 , meaning the ease of which polymerization and be started and stopped and started again is high, making an effective catalyst for co-block polymerizations. This means for a true reversible, radical polymerization. ${ }^{62}$


TPMA



Scheme 18: Matyjasewski's varying ligand design for copper ATRP catalysts.

### 1.5.2.2 Cobalt(II/III) Catalysts in ATRP

Since the discovery of ATRP, chemists have set out to find other metal containingcomplexes that can perform ATRP more efficiently that its copper predecessors. Simple systems such as $\mathbf{Q}$ and $\mathbf{R}$ (Scheme 19) as well as more complexes systems such as $\mathbf{S}$ have been recently explored.


Scheme 19: Relevant cobalt(II) ATRP catalysts
Matyjaszewski and co-workers have also tested a simple cobalt catalyst ( $\mathbf{R}$ ) analogue in the polymerization of MMA and styrene. ${ }^{63}$ This catalyst was specifically tested in the copolymerization of two different acrylate species, ultimately terminated by TEMPO. Here they observed narrow PDI's ( $<1.2$ ) at very high conversion rates with high molecular weights ( $\sim 40$ $000 \mathrm{Da}) .{ }^{63}$ The Zhang group have shown with their cobalt catalyst $(\mathbf{Q})$ they can achieve very high molecular weight with high conversion rates with narrow PDI's ( $<1.35$ ). What is interesting about their synthesis is that they've used RAFT agents to neatly facilitate polymerization via an ATRP mechanism. ${ }^{64}$ More recently, the Yan group have showcased the catalytic ability of the cobalt enriched polymer. With this macromolecule, they could polymerize a variety of acrylates (PMMA, $40 \%$ conversion, $\mathrm{PDI}=1.84)$ as well as styrene $(\mathrm{PS}, 42 \%$ conversion. $\mathrm{PDI}=1.92)$ in modest yields and narrow dispersities. ${ }^{65}$

### 1.6 Past Work

Previous work in the Gossage group on this project pertains to synthesis of the target ligand series as well as preliminary coordination work with copper ${ }^{20}$ and cobalt. ${ }^{66}$ Pertaining to ligand synthesis either Tohda's, or Meyer's procedures (Scheme 8, Scheme 9) were used to synthesize T1-4, D, E (Scheme 20).



Scheme 20: A library of ligands leading towards the formation of $\kappa^{2}-\mathrm{N}, \mathrm{O}-$ donor complexes
Compound $\mathbf{D}$ was selected as a candidate to test the coordination abilities of the ligand series. The compound was ligated to a copper metal center and is observed to be the deprotonated enolate form of the ligand. This work was repeated with a cobalt metal salt to receive T1-3, U1/2, D (Scheme 21). ${ }^{66}$ The reaction, although low yielding (in the case of $\mathrm{Co} / \mathrm{Cu}$ ), worked well enough to isolate single crystals of each of the synthesize species.


Scheme 21: Complexation of T1-4/U1-2/D to a cobalt(II) metal center

### 1.7 Objective of This Thesis

The purpose of this thesis is to synthesize, characterize and expand the already established library of $\kappa^{2}-\mathrm{N}, \mathrm{O}-$ bidentate oxazoline ligands. Varying the -R substituents as well as the substituents on the 4-position of the oxazoline (-R') will influence the electronic properties of the ligand therefore varying the redox properties of the metal complex. The series of $\kappa^{2}$-N,O-bidentate ligands will be coordinated to either cobalt, copper or iridium, to obtain novel Group 9 and 11 complexes (Scheme 22). All organic compounds will have their purity tested by a series of NMR techniques and melting point. All transition metal complexes will be characterized by UV-Vis, IR, CV, X-ray diffraction, MS, melting point, and a combination of NMR spectroscopy experiments. The complex series will be trialed as polymerization catalysts with monomers such as methyl methacrylate. Oxidation of an Iridium(I) centered complex giving two novel Iridium(III) complexes will be explored and characterized by IR, a combination of NMR spectroscopic experiments and X-ray diffraction where applicable. Synthesis of Rhodium complexes will also be attempted.

$R^{\prime}=H, M e$ R = aryl, alkyl (16 varieties)



V4

x

Scheme 22: Selected compounds/complexes synthesized during this thesis.

### 2.0 Results and Discussion

### 2.1 General Considerations

Each of the following reactions (Sec. 2.2-2.4) were completed in either the exact method or an adaption of the methods first used by Tohda et al.,,$^{8,35}$ Pittman and coworkers, ${ }^{9}$ or Meyers and collegues ${ }^{34}$ and are referenced appropriately to their article or origin. The metal complexation reactions were modified from a preparation by Gossage et al. to further optimize their synthesis. ${ }^{20}$ The ligands can be obtained in one to two steps and the metal complexes can be obtained in an additional one to two step(s). Samples of compounds 3i and 4i were obtained from J. Adjei (Ryerson University), synthesized by the same methods as described below. ${ }^{67}$

### 2.2 Synthesis and Characterization of Intermediate Compounds (3a-i, 5a-d)

The diacylated intermediate compounds (3a-i) were synthesized using commercially available 2,4,4-trimethyl-2-oxazoline (1a) and the corresponding acid chloride. In each case, 1 equivalent of $\mathbf{1 a}$ was heated to reflux with 2.2 equivalents of the acid chloride ( $\mathbf{2 a - i}$ ) and 3 equivalents of $\mathrm{NEt}_{3}$ in acetonitrile for three hours (Scheme 23). After which, the mixture is filtered to exclude the triethylammonium chloride salt formed. Once all volatile components have been removed, the mixture is subjected to two washes; the first with equal parts chloroform and distilled water, and the second wash with equal parts chloroform (previous wash) and a $5 \%$ solution of sodium carbonate in water $\left(\mathrm{Na}_{2} \mathrm{CO}_{3(\mathrm{aq})}\right)$. The washes extract excess triethylamine (and $\left.\left[\mathrm{NEt}_{3}\right][\mathrm{HCl}]\right)$ as well as by products such as benzoic acid derivatives. All impurities are assumingly removed in the washing process. The organic phases were dried $\left(\mathrm{MgSO}_{4}\right.$ or $\left.\mathrm{Na}_{2} \mathrm{SO}_{4}\right)$, filtered, then all remaining volatile components were removed under vacuum. Once removed, the crude product was revealed as a yellow-orange sludge. The crude mixture is purified by recrystallizing with a
$1: 1$ toluene $/ n$-hexanes combination, except for $\mathbf{3 d}$ which was done with a $1: 2$ mixture of toluene $/ n$ hexanes. Depending in on the " $R$ " substituent, the pure product emerged was either a light orange or a pale yellow solid. Yields ranged accordingly to the steric bulk associated with the " $R$ " group itself with seemingly little to no electronic influence of the substituents in the variable group. The obtained yields were moderate to excellent for the intermediate species (45-99 \%)



Scheme 23: General reaction conditions for the formation of 3a-i. Compound 3i was supplied by J. Adjei.

All compounds are novel, with the exception of $\mathbf{3 a} / \mathbf{c} / \mathbf{h} / \mathbf{i}^{20,35,67}$ which are known in the literature. For all the synthesized intermediate species, characterization was carried out by melting point (mp), NMR, TLC and in the case of the novel compounds by elemental analysis (EA). For these intermediate compounds, the ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectrum generally displays eight to eleven different proton environments for the aryl derivatives ( $\mathbf{3 a - g} / \mathbf{i}$ ) and five different proton environments for the alkyl derivative ( $\mathbf{3 h}$ ).


Figure 2: One of the intermediate compounds, $\mathbf{3 e}$, labeled for aid in NMR discussion.


Figure 3: ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectrum of $\mathbf{3 e}$.

Resonance signals indicative of the desired product are those of positions $\mathbf{1 , 3 , 5}$ and the overall 'doubling' of aryl resonance signals (Figure 2). These protons (1, 3, 5) resonate at approximately $\delta_{\mathrm{H}}=1.55,4.25,5.00 \mathrm{ppm}$ depending on the " $R$ " group attached to the carbonyl group at position 6. Specifically, 3e displays resonance signal at $\delta_{\mathrm{H}}=1.62,4.33$ and 4.95 ppm (Figure 3).

For this compound ( $\mathbf{3 e}$ ), there are six distinct aromatic signals which resonate between 7.08.0 ppm . Of these signals, two display doublet character due to their four-bond coupling $\left({ }^{4} J\right)$ with either the protons on the neighboring carbon's methyl group or from the other ortho carbon's
proton. The other four signals show a characteristic doublet of doublets splitting pattern. This splitting pattern is indicative of a proton interacting with an immediate neighboring proton $\left({ }^{3} \mathrm{~J}\right)$ and with second order effects from a further proton $\left({ }^{4 / 5} J\right)$.


Figure 4: ${ }^{13} \mathrm{C}$-NMR spectrum for $\mathbf{3 e}$.

In the carbon NMR ( $\left.{ }^{13} \mathrm{C}-\mathrm{NMR}\right)$ spectra, there are generally fifteen to twenty-three different carbon environments for the aryl species ( $\mathbf{3 a - g}$ ) and eleven different carbon environments for the alkyl species (3h). The frequency of which the carbons at positions 1, 3, and 5 (Figure 2) resonate are the first sign of the successful synthesis of the target intermediate species. In general, these positions resonate at approximately $\delta_{\mathrm{C}}=25,80$ and 100 ppm for $\mathbf{1}, 5$, and 3 respectively. Like the proton NMR spectrum, these signals vary greatly depending on the " $R$ " group attached to the enolic carbonyl. For this compound, $\mathbf{3 e}$, the carbons $\mathbf{1 , 5} 5$ and 3 resonate at $\delta_{\mathrm{C}}=22.8,79.8,85.4 \mathrm{ppm}$ respectively (Figure 4). By observing the coupling constants and a variety of two-dimensional

NMR experiments (COSY ${ }^{1} \mathrm{H}-{ }^{1} \mathrm{H}$, $\mathrm{HSQC}{ }^{1} \mathrm{H}-{ }^{13} \mathrm{C}, \mathrm{HMBC}{ }^{1} \mathrm{H}-{ }^{13} \mathrm{C}$ ) assignments have been made to each of the compounds.

The second variety of diacylated compounds (5a-d) were made in a similar manner where the only starting oxazoline differed to 2-methyl-2-oxazoline (1b). In each of the four cases, 1 equivalent of $\mathbf{1 b}$ was refluxed with 2.2 equivalents of the corresponding acid chloride and 3 equivalents of $\mathrm{NEt}_{3}$ in tetrahydrofuran for 3 hours (Scheme 24). This process differs from the synthesis of $\mathbf{3 a - 3} \mathbf{g}$ as described by Pittman and coworkers as the reaction leads to a ring-opened chlorinated intermediate, $\mathbf{5}$, as displayed. ${ }^{9}$


Scheme 24: General procedure on how to synthesize diacylated compounds 5a-d.

After completion of the reaction, the salt is filtered from the solution where then the volatile components can be removed. The sludge is afterwards subjected to two washes, once with equal part chloroform and water and the second wash with equal parts chloroform and a $5 \%$ solution of $\mathrm{Na}_{2} \mathrm{CO}_{3(\mathrm{aq})}$. All resulting impurities were removed during the washing process. The organic phases were dried $\left(\mathrm{MgSO}_{4}\right.$ or $\left.\mathrm{Na}_{2} \mathrm{SO}_{4}\right)$, filtered, then all remaining volatile components were removed. Once removed, the crude product was revealed as a yellow-orange sludge. The crude mixture was attempted purification by recrystallizing with a $1: 1$ mixture of toluene $/ n$-hexanes, as in the
methylated oxazoline compounds (3). All attempts in this matter lead to the mixture of compounds oiling out of solution together instead of solidifying and recrystallizing separately (Figure 5).


Figure 5: $\underline{A}$ - Prior to work-up, before filtering the salt $\left(\left[\mathrm{NEt}_{3}\right][\mathrm{HCl}]\right), \underline{B}$ - After work-up and attempted recrystallization (5a).

Thus, the intermediate species (5a-d) were attempted to be purified by column chromatography, although all attempts were met with failure as there were various impurities mixed together with similar retention factors in the case of $\mathbf{5 d}$. It is known as revealed by Pittman and co-workers ${ }^{9}$, that 2-methyl-2-oxazoline undergoes a ring opening mechanism when reacted under the same conditions as described above. ${ }^{35}$ This, most likely, gave the intermediate species as a ring open oxazoline (5) instead of the target ring closed oxazoline species (3). Although by careful column chromatography a sample of $\mathbf{5 d}$ was obtained. Compound $\mathbf{5 d}$ recrystallized from $\mathbf{4 5 \%} \mathrm{EtOAc} / n$ hexnaes and was obtained as a fully off-white powder. This sample was characterized only by ${ }^{1} \mathrm{H}-$ NMR spectroscopy. In the ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectrum signals corresponding to the proposed compound, 5d, have been observed (Figure 6).


Figure 6: ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectrum of $\mathbf{5 d}$.


Figure 7: Zoom in on the aromatic region in the ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectrum of $\mathbf{5 d}$. Coupling constants are displayed.

When looking at the coupling constants of the aromatic region, there are four resonance signals which coupling to other one other aromatic resonance signal. Their corresponding ${ }^{3} J$ values correlate to one other signal, which is indicative of a para substituted phenyl ring (Figure 7).

The use of these intermediate compounds will be detailed in Section 2.3 (compounds 3ai) and Section 2.4 (compounds 5a-d).

### 2.3 Synthesis and Characterization of a Ligand Series with $\mathbf{1 a}(\mathbf{4 a - i}$ and $\mathbf{4} \mathbf{j}-\mathbf{l})$

### 2.3.1 Synthesis and Characterization of ligands $\mathbf{4 a - i}$

Once the intermediate compounds have been obtained, they are subjected to a 1.5 M methanolic potassium hydroxide solution ( KOH dissolved in MeOH ).


Scheme 25: Formation of the ligand series with reacted initially with 1a. Compound $\mathbf{4 i}$ was made by J. Adjei.

These basic conditions cleave the C-N bonded acyl group. Typically, the reagents are stirred at room temperature for six hours. Once the reaction time elapsed, all volatiles are removed from the flask and are subjected to two washes with distilled water. During the second distilled water wash, sometimes a scoopula tip of brine is added to help separate the layers. The organic phase is dried
$\left(\mathrm{MgSO}_{4}\right)$, filtered and again volatile components are removed. The resulting pale yellow or light orange sludge is recrystallized with a $1: 4$ mixture of toluene $n$-hexanes. This reveals the target ligand as either pale yellow needles (4d-i) or white needles (4a-c) in moderate to high yields (23$99 \%$ ).

All compounds are novel, with the exception of $\mathbf{4 a} / \mathbf{c} / \mathbf{h}^{20,35}$ which are known in the literature and $\mathbf{4 b} / \mathbf{g} / \mathbf{i}^{67}$ which have been previously synthesized by our group. ${ }^{66}$ For all the synthesized ligand species, characterization was carried out using their melting point (mp), NMR spectroscopy (a combination of various $1 \mathrm{D} / 2 \mathrm{D}$ experiments), TLC and in the case of the novel compounds by elemental analysis (EA). The ligand series exhibits characteristic resonances in both the proton and carbon NMR spectra. Such as the case of $\mathbf{4 e}$ series (Figure 8), the proton NMR spectrum displays all the characteristic resonance signals for the target ligand series.

Resonance signals for the two-methyl groups ( $\sim 1.43 \mathrm{ppm}$ ) and the $\mathrm{CH}_{2}(\sim 4.15 \mathrm{ppm})$ on the heterocycle as well as the enolic resonance ( $\sim 5.50 \mathrm{ppm}$ ) support the formation of the ligand. For more evidence the aromatic region can be examined. In this case in the aromatic region there are three signals being split to observe a doublet ( $\sim 7.23 \mathrm{ppm}$ ), a doublet of doublets ( $\sim 7.62 \mathrm{ppm}$ ), and a singlet with distinguishable ${ }^{4} J$ coupling to another proton environment to give a doublet ( $\sim 7.82$ ppm).


Figure 8: ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectrum of $\mathbf{4 e}$, boxed in regions depict characteristic signals for $\mathbf{4}$ (red $=$ alkyl, green $=$ aromatic).

Positions 8, 10 and 11 have been assigned by a variety of 2D-NMR experiments (COSY, HSQC and HMBC). Using COSY and HSQC NMR spectra all positions except for those at 8, 1011 have been assigned, making it easier to focus on the three aromatic carbons without protons. An HMBC NMR spectrum (Figure 9) revealed all the positions in question which have neighboring carbons that have protons associated with them ( $\underline{\mathrm{C}}-\mathrm{C}-\underline{\mathrm{H}}$, an interaction with the adjacent carbons proton). Specifically, in the aromatic region it disclosed the strong interaction of proton 9 to carbons with chemical shifts of $\delta_{\mathrm{C}}=134.3$ and 138.5 ppm . Similarly, another strong interaction of proton 13 to carbons with the chemical shift of $\delta_{\mathrm{C}}=138.5 \mathrm{ppm}$. Lastly the proton at position 12 exhibited communication to carbons at chemical shifts of $\delta_{\mathrm{C}}=134.3$ and 139.3 ppm . For one last piece of evidence, the interactions between the carbonyl and the rest of the aromatic ring can be considered. The carbonyl group (7) is shown to be interacting with both protons at the

9 and 13 positions. Meaning those carbons interacting with position 12 must be situated opposite to the oxazoline. With this information one can deduce the correct assignments of positions $\mathbf{8 , 1 0}$ and 11. Position 8 lies next to the carbonyl as it interacts with protons 9 and 13 , position 11 is the chlorinated carbon in the para-position (this is supported by its very downfield shift), and position 10 (the only remaining assignment) is the methyl-carbon meta to the carbonyl.


Figure 9: HMBC-NMR spectrum of $\mathbf{4 e}$. (blue $=$ aromatic interactions, green $=$ carbonyl interactions)

### 2.3.2 Synthesis and Characterization of ligands $\mathbf{4 j} \mathbf{- I}$

To make shorter alkyl variants of the target ligands series different reaction pathways were explored. The first is the reaction of $1 \mathbf{1 a}$ with either trichloroacetyl chloride (TCAC) or with trifluoroacetic anhydride (TFAA). Once activated by the pyridine, the tri-halogenated species become very reactive and thus the reaction mixture is kept cold. This synthetic methodology has been described by Tohda et al. ${ }^{8}$ The reaction was done by cooling all reagents down in separate flasks then by adding the oxazoline and pyridine together in ACN . Once the tri-halogenated species was cooled it was added dropwise to the stirring solution of $\mathbf{1 a} / \mathrm{py}$. The reaction was stirred at 0 ${ }^{\circ} \mathrm{C}$ for 6 hours. After the reaction was completed the volatile components were removed in vacuo. The resulting sludge was dissolved in distilled water and washed with DCM twice. The organic
phased was dried $\left(\mathrm{MgSO}_{4}\right)$, filtered and again the volatile components were removed. The sludge was dissolved in hot $n$-hexanes and left to recrystallize. This revealed the product (both $\mathbf{4} \mathbf{j}$ and $\mathbf{4 k}$ ) as white powder. This reaction is done in a 1:2.2:2 ratio of 1a:TCAC/TFAA:py (Scheme 26).



Scheme 26: General reaction of tri-halogenated species with 1a to give the target alkyl ligands.

The alkyl ligands, $\mathbf{4 j} / \mathbf{k}$, were analyzed by both ${ }^{1} \mathrm{H}$ - and ${ }^{13} \mathrm{C}$-NMR spectroscopy where all characteristic resonance signals were observed as in the literature. ${ }^{8}$ In addition, compound $\mathbf{4} \mathbf{j}$ gave one resonance in the ${ }^{19} \mathrm{~F}$-NMR spectrum at $\delta_{\mathrm{F}}=-79.8 \mathrm{ppm}$ as expected $\left(\right.$ Figure 10). ${ }^{8}$


Figure 10: ${ }^{13} \mathrm{C}$ - and ${ }^{19} \mathrm{~F}$-NMR spectrum of $\mathbf{4} \mathbf{j}$.

The second reaction pathway known to produce alkyl derivative of $\mathbf{4}$ is the lithiation of $\mathbf{1 a}$ followed by nucleophilic substitution of ethyl acetate to form 41 (Scheme 27). ${ }^{34}$


Scheme 27: The synthetic route of 41.

This reaction was carried out by first chilling 1a in ACN to $-84^{\circ} \mathrm{C}$, this is done by creating a cold bath by freezing ethyl acetate with liquid nitrogen. Once chilled, $n-\mathrm{BuLi}$ is added dropwise with rapid stirring of the oxazoline solution. This would lithiate the methyl on the 2 position of the oxazoline (Scheme 27). This then was stirred, initially at $-84^{\circ} \mathrm{C}$ but was left to gradually warm to room temperature, overnight. Once completed, the lithio oxazoline species was cooled back down to $-84{ }^{\circ} \mathrm{C}$ where cold, dried $\mathrm{EtOAc}\left(4 \AA\right.$ sieves and MgSO 4 for $3 \mathrm{~d},-26^{\circ} \mathrm{C}$ ) was added dropwise. This solution was left to stir for 2 hours, where the solution was warmed to room temperature, to let it fully react. Upon completion, distilled degassed water was added slowly to the solution to quench excess $n$-BuLi. The mixture was washed with diethyl ether twice, the organic phased dried $\left(\mathrm{MgSO}_{4}\right)$, filtered and had all the volatile components removed. This left behind a white sludge which was attempted to be recrystallized by washing with cold $n$-heptanes. The isolated material was analyzed by ${ }^{1} \mathrm{H}$ - and ${ }^{13} \mathrm{C}-\mathrm{NMR}$ spectroscopy.


Figure 11: Crude ${ }^{1} \mathrm{H}$ - and ${ }^{13} \mathrm{C}$-NMR spectra of the mixture of $\mathbf{4 l}$ and $\mathbf{1 a} \mathbf{a}^{\mathbf{2}}$.

When analyzed by NMR spectroscopy, a mess of resonance signals sprouted in the alkyl region of the proton NMR spectrum and in the $\mathrm{sp}^{2}$-C/alkyl regions of the carbon NMR spectrum (Figure 11). This impurity, previously reported by Meyers and coworkers, is said to be a dimer (Scheme 27). ${ }^{34}$ This oxazoline dimer, $\mathbf{1 a}^{\mathbf{2}}$, is most likely synthesized in the lithiation step; presumably if a lithio-oxazoline species finds another molecule of 1a before it finds its target (EtOAc) and hence a dimer is formed. Compound $\mathbf{1 a}^{\mathbf{2}}$ was not isolated from this reaction but was instead treated with warm distilled water $\left(60^{\circ} \mathrm{C}\right)$ for four hours while stirring. ${ }^{34}$ The solution is washed again, with diethyl ether twice. The organic phase is dried $\left(\mathrm{MgSO}_{4}\right)$, filtered and had all the volatile components removed. This process cleaves the oxazolidine moiety and gives $\mathbf{4 1}$. When pure $\mathbf{4 1}$ is analyzed by ${ }^{1} \mathrm{H}$ - and ${ }^{13} \mathrm{C}$-NMR spectroscopy, both the enamine and the keto form of the ligand are observed in a 10:1 ratio (E:K) as noted by Meyers et al. (Figure 12). ${ }^{34}$


Figure 12: ${ }^{1} \mathrm{H}$ - and ${ }^{13} \mathrm{C}$-NMR spectra for $\mathbf{4 1}$. The enamine and keto forms are present in a 10:1 ratio.

### 2.4 Synthesis and Characterization of a Ligand Series with 2-methyl-2-oxazoline ( $\mathbf{6 a - d}$ )

All these compounds (Scheme 28) are known in the literature expect $\mathbf{6 b}$. Compounds $\mathbf{6 c} \mathbf{d}$ are known but have been synthesized by reacting a dithio ketene (made by reacting $\mathrm{CS}_{2}, \mathrm{NaH}$ with acetophenone [Sec 1.3.2.3]) with 2-amino-2-methyl-1-propanol. This way the target compounds are made in moderate yields ( $49-63 \%$ )..$^{7,8}$ In this study, Pittman and co-workers' procedure ${ }^{9}$ was more closely followed for the synthesis of $\mathbf{6 a}$, whereas Tohda's procedure was followed in an attempted to synthesize $\mathbf{6 b - d}$. ${ }^{35}$



Scheme 28: Formation of the ligand series with reacted initially with $\mathbf{1 b}$.

Just like prior routes to make 4a-i, 6a-d were synthesized by dissolving the crude mixture of 5, previously noted in Section 2.4, in a 1.5 M solution of potassium hydroxide $(\mathrm{KOH})$ dissolved
in methanol (MeOH) (Scheme 28). This basic mixture facilitates the cleavage of the $\mathrm{C}-\mathrm{O}$ and then the C-N acyl groups as well as reforming the heterocyclic ring. Once the 18 -hour reaction period is over, the solution is filtered so that any precipitated salts can be excluded. A 1.0 M solution of sulphuric acid in water $\left(\mathrm{H}_{2} \mathrm{SO}_{4(\mathrm{aq})}\right)$ is added dropwise with stirring to MeOH solution to obtain a pH neutral state. Once neutral, the solution is washed with distilled water twice. The organic phased is dried $\left(\mathrm{MgSO}_{4}\right)$, filtered and all volatile components are removed.


Figure 13: $\underline{A}$ - 6a after attempted recrystallization, $\underline{B}$ - before work-up of 5a to $\mathbf{6 a}$

The resulting dark red/brown sludge was attempted to be recrystallized with varying ratios of toluene $/ n$-hexanes although each time the ligand 'oiled' out of solution instead of solidifying (Figure 13). Column chromatography eluting with $30 \%$ acetone $/ n$-hexanes as in the Pittman procedure, was then employed for purification. The target, $\mathbf{6 a} / \mathbf{c}(33-64 \%)$, were isolated as palepink powders whereas $\mathbf{6 b}$ was isolated as a pale-yellow powder (83\%). Unfortunately, all attempts to synthesize compound $\mathbf{6 d}$ resulted in failure. Regardless of purity of $\mathbf{5 d}$, when subjected to the basic $\mathrm{KOH} / \mathrm{MeOH}$ mixture the compound was not able to be isolated. The reaction was tried several ways, including varying reaction time, KOH concentration, and purifying the intermediate species.


Scheme 29: Attempted synthesis of $\mathbf{6 d}$.

Once the reaction was completed and volatiles removed, the sludge was washed twice with water, although each wash became progressively harder and harder to separate. The addition of several milliliters of brine (and eventually replacing water with brine) aided in separation. Regardless of good separation of the phases, when it came to preforming the column (eluting with a $30 \%$ acetone $/ n$-hexanes gradually raised to $100 \%$ acetone in some cases), the well separated fractions did not contain the desired product (Figure 14). Due to time constraints, further attempts to yield 6d were abandoned.


Figure 14: An example of one of the repeated attempts to synthesize $\mathbf{6 d}$ by Tohda's method. ( ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectrum)

These compounds (6a-c) were analyzed by their characteristic resonance signals in their ${ }^{1} \mathrm{H}$ - and ${ }^{13} \mathrm{C}$-NMR spectra. In the ${ }^{1} \mathrm{H}$-NMR spectrum, the two methylene groups (both of those on the heterocycle $[1,2])$ resonate in the alkyl region at approximately $\delta_{\mathrm{H}}=3.86$ and 4.54 ppm for positions 1 and 2, respectively. The absolute assignment of these two protons can be affirmed by their coupling constants. Where the signal at $\delta_{\mathrm{H}}=3.86 \mathrm{ppm}$ has a ${ }^{3} J=8.54 \mathrm{~Hz}$ and the $\delta_{\mathrm{H}}=4.54$ ppm signal has also a ${ }^{3} J=8.54 \mathrm{~Hz}$. Since these two values are the same (as well as taking their splitting patterns into consideration) it can be assumed that they are indeed coupling to one another, making them neighbours and suggesting their assignments are correct.

For this compound, $\mathbf{6 b}$, another characteristic feature of its isolation lies within the aromatic region. In this region, there are three resonance signals with splitting patterns of a doublet, a doublet of doublets, and a doublet (due to long-range splitting with a close proton) (Figure 15). As before, these signals can be assigned by calculating their coupling constants. The coupling constants of those in Figure 15 labeled as $\mathbf{8 , 1 2}$ and $\mathbf{1 1}$ are $J=1.99 \mathrm{~Hz}, J=8.54,1.99 \mathrm{~Hz}, J=8.54$ Hz. Using the same path of thinking as before the protons can be properly assigned. Displaying a smaller coupling constant is indicative of coupling with a proton neighbor more than 3 bonds away. Here, protons 8 and 12 are interacting and because of this give the ${ }^{4} J$ coupling constant of 1.99 Hz . The same can be said for proton 11 , as it only interacts with proton 12 . Thus, giving the ${ }^{3} J$ coupling constant of 8.54 Hz . With the calculated coupling constants as well as analyzing their splitting pattern protons 8, 12 and 11 can be and have been correctly assigned. This method was taken into consideration when assigning the protons and carbons (above, Sec. 2.3.1) for both $\mathbf{6 a}$ and $\mathbf{6 c}$.


Figure 15: The ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectrum for $\mathbf{6 b}$

### 2.5 Synthesis and Spectrochemical Investigation of Transition Metal Complexes

Using the fifteen derivatives produced of the 2-acylmethyl-2-oxazoline scaffold, the synthesis of several copper and cobalt complexes were undertaken. These complexes were initially made using the preparation described by Gossage et al. but was later altered to further optimize reaction conditions. ${ }^{20}$ Two equivalents of $\mathbf{4}$ or $\mathbf{6}$ are dissolved in EtOH and 2.3 equivalents of $\mathrm{NEt}_{3}$ are added. Separately, 1 equivalent of a metal nitrate salt $\left(\mathrm{Co}\left(\mathrm{NO}_{3}\right)_{2} \cdot 6 \mathrm{H}_{2} \mathrm{O}\right.$ or $\left.\mathrm{Cu}\left(\mathrm{NO}_{3}\right)_{2} \cdot 2.5 \mathrm{H}_{2} \mathrm{O}\right)$ is dissolved in EtOH. The metal solution is syringed into the ligand solution while stirring. A noticeable colour change occurs and, in most cases, immediate formation of a coloured precipitate is noted (Scheme 30).


Scheme 30: A general metal complexation reaction of $\mathbf{4}$ or $\mathbf{6}$ to either $\mathbf{C u}$ or $\mathbf{C o}$.

Another explored route was that shown in Scheme 31. This involves in situ generation of the ligand where it immediately coordinates to the metal. Potassium hydroxide is dissolved in MeOH to make a 1.5 molar solution. Once dissolved the intermediate species is added, at room temperature, to the basic mixture. After fully dissolved, the metal salt is added to the stirring solution as a solid. After approximately 10 minutes, a colour change can be observed from the starting dark red colour to a lighter orange (cobalt) or dark green (copper) with a notable amount of precipitate. Once the reaction is done, all volatile components were removed. The blackish sludge is diluted with DCM and washed with a 1.0 M solution of NaCl in water. In the cobalt complexation reaction, 3 layers are obtained in the separatory funnel; the clear aqueous layer, the bright red organic layer, and a third black layer (not observed in the copper complexation reaction). This black layer likely contained some $\mathrm{Co}(\mathrm{OH})_{2}$, insoluble in most organic solvents (and water to an extent). The organic phased is dried $\left(\mathrm{MgSO}_{4}\right)$, filtered and all volatile components are removed. In the case of both reaction pathways, the precipitates are recrystallized by slow evaporation of a solution of $1: 1 \mathrm{DCM} / \mathrm{MeOH}$. This method is effective for all ligands tested as detailed below.


Scheme 31: An alternate route to $\mathrm{Cu} / \mathrm{Co}$ complexes from $\mathbf{3}$ or 5 .

### 2.5.1 Copper Complexes (7a-l)

One alkyl and eight aryl derivatives of the copper complexes were made in moderate to excellent yields (Scheme 32) and synthesized in one of two methods previously described. The colour of the reaction solutions was initially clear or pale yellow (depending on the colour of the pure ligand) and turned a dark green-brown when the sky-blue metal salt was added. All copper complexes were characterized by cyclic voltammetry (CV), elemental analysis (EA), their melting point (mp), IR spectroscopy, Ultraviolet-visible spectroscopy (UV-Vis), and in some cases, single crystal x-ray diffraction.


Scheme 32: Towards copper complexes with the ligand series 4.

Since these complexes have a presumed metal electron configuration of $d^{9}$, they are paramagnetic in nature, meaning they have one unpaired electron. This unpaired electron makes analyzing by NMR spectroscopy less conclusive. In the ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectrum, the closer a proton is to the paramagnetic center the broader the resonance signal will be for that proton (Figure 16). ${ }^{68}$ Due to this behaviour, other methods of characterization had to be used such as IR, X-ray, and UV-Vis.

Infrared spectroscopy shows the interaction of the ligand with the metal by observing a shift in the absorbance frequency when comparing to the free ligand. The stretching frequency assigned to either the $\mathrm{C}=\mathrm{C}$ or $\mathrm{C}=\mathrm{N}$ bond(s) resonate within a range of $1514-1548 \mathrm{~cm}^{-1}$, which is far lower than the reported values of the bare ligands $\left(1615-1635 \mathrm{~cm}^{-1}\right){ }^{35}$ The Cu center is presumably drawing electron density away from the bound ligand.


Figure 16: ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectrum of $\mathbf{7 a}$ (paramagnetic).


Figure 17: An example of a UV-Vis spectrum of copper complexes (7e).

The UV-Vis spectra bore assigned d-d transitions in the visible region and metal-to-ligand charge transfer (MLCT) bands in the ultraviolet region (Figure 17). The lower energy absorptions, in the ranges of 423-457 nm, are representative of a d-d transition. These transitions are seen due to the dark green-orange colour of the copper complexes (in solution). This higher energy absorptions in the range of 243-276 nm, have been assigned to the $\pi-\pi^{*}$ transition localized about either the aromatic ring $(\mathrm{C}=\mathrm{C})$ or the imine $(\mathrm{C}=\mathrm{N})$ within the oxazoline ring. This is likely the case as MLCT transition bands are primarily observed in low oxidation state metals whereas LMCT bands are more often observed in higher oxidation state transition metal complexes. The spectroscopic data obtained had confirmed the electronic properties of the complexes, such as aiding in differing the electron withdrawing complexes, 7b, from the electron donating complexes, 7d. The complexes bearing electron withdrawing ligands, 7b/e-f, experience a red shift (to lower frequencies).

To elucidate the exact structure of the copper complexes, we turned to single-crystal x-ray diffraction (x-ray crystallography). The structures were collected by Dr. Alan J. Lough at the University of Toronto at 150 K . Single crystals were obtained after slow evaporation of a $1: 1$ solution of $\mathrm{DCM} / \mathrm{MeOH}$. The crystals were washed with cold MeOH and dried over vacuum. This revealed the crystals as dark green-brown needles for $\mathbf{7 a} / \mathbf{c} \mathbf{- i}$, as well as a mixture of green plates and brown needles for 7b. X-ray crystallography was only performed on $\mathbf{7 g}$-h to help confirm the relative structure of the other derivatives. Structures of $\mathbf{7 a}$ and $\mathbf{7 i}$ have already been solved by our group. ${ }^{20,66}$ Figure 18 shows the ORTEP drawings of $\mathbf{7 g}$ and $\mathbf{7 h}$ obtain via x-ray crystallography.


Figure 18: ORTEP drawings of the unit cell of $\mathbf{7 g}$ and 7 h (x-ray crystallographic representation)

Of these two compounds, $7 \mathbf{g}$ exhibits a square planar geometry around the metal center while $\mathbf{7 h}$ (along with other Cu complexes analyzed by our group) exhibit a distorted square planar geometry. The geometry can be properly determined by calculating the $\tau^{4}$ value (geometry index). ${ }^{69,70}$ When the calculated geometry index is 0 the complex is said to be square planar, whereas then the index is calculated to be 1 the complex holds a tetrahedral geometry. Pictured below in Equation 2 are the calculations for their $\tau^{4}$ values. Where $\theta$ is the ideal bond angle for a tetrahedral compound $\left(109.5^{\circ}\right)$, and where $\alpha$ and $\beta$ are the two largest angles amongst the coordination center. The calculated values for $\mathbf{7 g}$ and $\mathbf{7 h}$ as well as other similar copper complexes by our group are in agreeance with those in the literature as $\mathrm{d}^{9}$ copper complexes normally adopt
a more square planar geometry. A reason as to why $\mathbf{7 g}$ adopts the perfect square planar geometry, where $\mathbf{7 h}$ does not, may be due to the steric effects of the ligand. The ligand $(\mathbf{4 g})$ when bonded to the copper center presumably imposes an axis of chirality, there the napthyl rings prohibit free rotation about the Cu center. The methyl groups on the oxazoline as well as the napthyl group appended on the opposite end of the ligand make it so that it can lock the orientation of the complex, making it unable to twist in such a way that $\mathbf{7 h}$ has. This phenomenon has been observed previously by our group where the oxazoline has been modified to a bulky chiral derivative. The chiral ligand locks the rotation of itself, against the other ligand, pinning it in place. ${ }^{20,66}$ As per their unit cell parameters, both compounds crystallized in the triclinic crystal system and both adopt the P-1 space group. Relevant bond lengths and angles are displayed in

Table 1 and Table 2. The angles are used to calculate the $\tau^{4}$ values, which give the corresponding value concluding their distorted square planar geometry. $\mathbf{7 h}$, giving a $\tau^{4}$ value of 0.49 confirms the distorted geometry, adopting a more seesaw geometry about the Cu center, whereas $7 \mathbf{g}$ adopts a perfect square planar geometry. The average length for a $\mathrm{Cu}-\mathrm{O}$ bond is 1.982 $\AA$ and for a $\mathrm{Cu}-\mathrm{N}$ bond is $2.036 \AA$. The experimental bond lengths and angles for $\mathbf{7 g}$ and $\mathbf{7 h}$ are consistent with other N,O-donor ligand complexes in the literature. ${ }^{20,47}$

Equation 2: Calculating the geometry index of $\mathbf{7 g}$ and $\mathbf{7 h}$.

| 7 g | $\tau^{4}=\frac{360^{\circ}-(\alpha+\beta)}{360^{\circ}-2 \theta}$ | 7 h | $\tau^{4}=\frac{360^{\circ}-(\alpha+\beta)}{360^{\circ}-2 \theta}$ |
| :--- | :--- | :--- | :--- |
|  | $\tau^{4}=\frac{360^{\circ}-(180+180)}{360^{\circ}-2(109.5)}$ |  | $\tau^{4}=\frac{360^{\circ}-(144.37+146.69)}{360^{\circ}-2(109.5)}$ |
|  | $\tau^{4}=0.00$ |  | $\tau^{4}=0.489$ |

Table 1: Relevant bond angles $\left({ }^{\circ}\right)$ and bond lengths $(\AA)$ for $\mathbf{7 g}$

| Bond Lengths (£) |  | Bond Angles ( ${ }^{\circ}$ ) |  |
| :---: | :---: | :---: | :---: |
| $\mathrm{Cu}(1)-\mathrm{O}(1) \# 1$ | $1.9122(10)$ | $\mathrm{O}(1) \# 1-\mathrm{Cu}(1)-\mathrm{O}(1)$ | 180 |


| $\mathrm{Cu}(1)-\mathrm{O}(1)$ | $1.9122(10)$ | $\mathrm{O}(1) \# 1-\mathrm{Cu}(1)-\mathrm{N}(1)$ | $88.54(5)$ |
| :---: | :---: | :---: | :---: |
| $\mathrm{Cu}(1)-\mathrm{N}(1)$ | $2.0007(11)$ | $\mathrm{O}(1)-\mathrm{Cu}(1)-\mathrm{N}(1)$ | $91.46(5)$ |
| $\mathrm{Cu}(1)-\mathrm{N}(1) \# 1$ | $2.0007(11)$ | $\mathrm{O}(1) \# 1-\mathrm{Cu}(1)-\mathrm{N}(1) \# 1$ | $91.46(5)$ |
|  |  | $\mathrm{O}(1) \# 1-\mathrm{Cu}(1)-\mathrm{N}(1) \# 1$ | $88.54(5)$ |
|  | $\mathrm{N}(1)-\mathrm{Cu}(1)-\mathrm{N}(1) \# 1$ | 180 |  |
|  |  |  |  |

Table 2: Select bond angles $\left({ }^{\circ}\right)$ and bond lengths $(\AA)$ for $\mathbf{7 h}$.

| Bond Lengths (Å) |  | Bond Angles ( ${ }^{\circ}$ ) |  |
| :--- | :---: | :--- | :---: |
| $\mathrm{Cu}(1 \mathrm{~B})-\mathrm{O}(1 \mathrm{~B})$ | $1.923(2)$ | $\mathrm{O}(1 \mathrm{~B})-\mathrm{Cu}(1 \mathrm{~B})-\mathrm{O}(3 \mathrm{~B})$ | $144.32(9)$ |
| $\mathrm{Cu}(1 \mathrm{~B})-\mathrm{O}(3 \mathrm{~B})$ | $1.928(2)$ | $\mathrm{O}(1 \mathrm{~B})-\mathrm{Cu}(1 \mathrm{~B})-\mathrm{N}(2 \mathrm{~B})$ | $97.60(10)$ |
| $\mathrm{Cu}(1 \mathrm{~B})-\mathrm{N}(2 \mathrm{~B})$ | $1.933(2)$ | $\mathrm{O}(3 \mathrm{~B})-\mathrm{Cu}(1 \mathrm{~B})-\mathrm{N}(2 \mathrm{~B})$ | $92.58(9)$ |
| $\mathrm{Cu}(1 \mathrm{~B})-\mathrm{N}(1 \mathrm{~B})$ | $1.942(2)$ | $\mathrm{O}(1 \mathrm{~B})-\mathrm{Cu}(1 \mathrm{~B})-\mathrm{N}(1 \mathrm{~B})$ | $92.50(9)$ |
|  |  |  |  |
|  | $\mathrm{O}(3 \mathrm{~B})-\mathrm{Cu}(1 \mathrm{~B})-\mathrm{N}(1 \mathrm{~B})$ | $98.69(9)$ |  |
|  | $\mathrm{N}(2 \mathrm{~B})-\mathrm{Cu}(1 \mathrm{~B})-\mathrm{N}(1 \mathrm{~B})$ | $144.66(10)$ |  |
|  |  |  |  |

For compound $\mathbf{7 b}$, two different forms of crystals were obtained. From a reaction where the Cu metal salt was $\mathrm{CuBr}_{2}$ the crystals took the form of brown needles. Whereas when the metal salt was $\mathrm{Cu}\left(\mathrm{NO}_{3}\right)_{2} \cdot 2.5 \mathrm{H}_{2} \mathrm{O}$, the crystals took the form of green plates (Figure 19). This strange type of behaviour was first noted when the metal salt was first added to the stirring ligand solution where the copper(II)bromide solution was notably dark brown in colour, and the copper(II)nitrate solution was a lighter brown-green colour. Once the precipitates were collected the colour difference was more noticeable, where the nitrate derived complex appeared as a dark green powder and the bromine derived complex appeared as a dark brown powder. Upon crystallization and analysis by IR spectroscopy, an obvious variance between them was revealed. The brown needles gave the $\mathrm{C}=\mathrm{N} / \mathrm{C}=\mathrm{C}$ bond stretch at $1455 \mathrm{~cm}^{-1}$, whereas the green plates gave, presumably, the same IR bond stretch at the much higher value of $1531 \mathrm{~cm}^{-1}$.


Figure 19: Possible polymorphic behaviour in 7a/b.

When sent for crystallographic analysis the green plates were determined to be the same material that was previously published by Gossage et al. ${ }^{20}$ The brown needles have yet to be analyzed by x-ray crystallography but are assumed to be a polymorph of 7a, perhaps differing by packing within the unit cell. This behaviour has been assumed for complex $\mathbf{7 b}$ as it also displayed similar characteristics. 7b precipitates out of solution as a brown or green powder (copper(II)bromine and copper(II)nitrate respectively) but when crystallized, both take the same crystal form (Figure 20).


Figure 20: Both brown and green powders crystalline forms for $\mathbf{7 b}$.

To work catalytically, many Cu and Co systems function by reversible redox events taking place within the metal complex, whether it's a reversible oxidation or reduction or both. This can be explained by cyclic voltammetry (CV). Thus, CV was performed by taking a blank sample of only the electrolyte, dissolving $\sim 193 \mathrm{mg}$ of $\left[\mathrm{N}(n-\mathrm{Bu})_{4}{ }^{+}\right]\left[\mathrm{PF}_{6}{ }^{-}\right]$in sparged $\mathrm{DCM}(0.1 \mathrm{M})$ then dissolving $\sim 20 \mathrm{mg}$ of 7. After blank and sample analysis, ferrocene $(0.1 \mathrm{mg})$ was added to the solution to serve as an internal standard. All scans, unless otherwise stated, started with the oxidative sweep then switched to the reductive sweep at the indicated potential. The scan rate was held constant at $100 \mathrm{mV} / \mathrm{s}$ for all scans unless otherwise stated. When tested for their redox capabilities, none of the synthesized Cu complexes displayed favourable redox reversibility.


Figure 21: Voltammogram of $\mathbf{7 h} / \mathbf{i}$ displaying irreversibility and ligand reduction.

Instead, they either exhibited irreversible oxidation presumably from Cu (II) to Cu (III), poor reversibility ( $\mathbf{7 h}$ ) or in the case of $\mathbf{7 i}$, likely reduction of the $p-\mathrm{NO}_{2}$ group within the ligand. This was the case regardless of the scan rate used, step in potential or direction of initial potential (starting with the reductive sweep instead of an oxidative sweep). In each case (alkyl and aryl), these undesirable properties were observed (Figure 21). In the interest of making new catalysts, these copper complexes would likely not be active in redox mediated chemistry and therefore we have halted their study in this area at this time.

### 2.5.2 Other Copper Complexes (8a-c)

One aryl derivative was successfully synthesized ( $\mathbf{8 a}, 70 \%$ yield) and two other aryl derivatives were attempted ( $\mathbf{8 b}$ and $\mathbf{8 c}$ ). Their synthetic scheme followed one of two methods previously described (Scheme 33). All copper complexes were characterized by cyclic voltammetry (CV), their melting point (mp), IR spectroscopy, ultraviolet-visible spectroscopy (UV-Vis), and mass spectrometry (MS).


Scheme 33: Synthesis of $\mathbf{C u}$ complexes with 6.

As in the preceding section, these complexes have a formal metal based electron configuration of $d^{9}$ meaning they are paramagnetic in nature. This coupled with their limited solubility in any organic solvent made them very difficult to characterize. Unfortunately, due to this solubility issue (insoluble even in DMSO and DMF), the compounds were unable to be recrystallized for x-ray crystallography purposes.

Unfortunately, 8a did not give a molecular ion (M+) when analyzed by mass spectrometry. Due to the poor results of MS, $\mathbf{8 a}$ and $\mathbf{8 b}$ were sent for elemental analysis (EA) [done by Atlantic Microlabs]. The analysis for 8a came back positive, giving elemental percentages within experimental error. In contrast, 8b negative results came back, stating that correct compound was
not present or highly contaminated. 8a could be dissolved enough to preform UV-Vis spectroscopy (as a suspension in solution). Using the EA data, the molar extinction coefficient ( $\varepsilon$ ) was estimated (Figure 22). 8a exhibited a similar UV-vis profile to those copper complexes known in the literature where there are three distinct absorption maxima present in the ultraviolet region ( $\sim 324$, $\sim 285, \sim 240 \mathrm{~nm})[\mathrm{MLCT}] .{ }^{71}$ In the IR spectra, 8a showcases similar profiles to complexes $\mathbf{7 a} \mathbf{a}$ i with two main strong signals at frequencies of 1540 and $750 \mathrm{~cm}^{-1}$.


Figure 22: UV-Vis profiles for 8a showing three main absorption maxima.

The attempted synthesis of compound $\mathbf{8 c}$ was carried out by adding $\mathrm{Cu}\left(\mathrm{NO}_{3}\right)_{2}$ to a 1.5 M methanolic potassium hydroxide solution after $\mathbf{5 d}$ had dissolved. The reaction was stirred at room temperature for 22 hours in open air. After the reaction was completed, the volatile components were removed and the sludge was diluted with DCM. The organic phase was washed twice, once with a 1.0 M solution of NaCl and a second time with a 0.1 M solution of $\mathrm{Na}_{2} \mathrm{CO}_{3}$. The organic phased was dried $\left(\mathrm{MgSO}_{4}\right)$, filtered and volatile components were removed. The resulting brown sludge was attempted to be recrystallized by two methods; the first was a layering of a mixture of

1:1 $\mathrm{DCM} / \mathrm{MeOH}$ and the second being a vapor diffusion of diethyl ether into a solution of DCM and the complex. Unfortunately, none of these two pathways yielded any pure materials.

### 2.5.3 Cobalt Complexes (9a-l)

Four alkyl and eight aryl derivatives of the cobalt complexes were synthesized in moderate to excellent yields (50-99 \%) in one of two methods previously described (Scheme 34). The colour of the reaction solutions was initially clear or pale yellow (depending on the colour of the pure ligand) and turned a dark orange-red when the magenta-coloured metal salt was added. All cobalt complexes were characterized by cyclic voltammetry (CV), elemental analysis (EA), their melting point (mp), IR spectroscopy, ultraviolet-visible spectroscopy (UV-Vis), and in some cases, single crystal x-ray diffraction.



Scheme 34: Towards cobalt complexes with the ligand series 4.

This series of cobalt complexes adopt the presumed $\mathrm{d}^{7}$ electron configuration, making the paramagnetic analogous to the aformentioned copper complexes. This nature makes characterizing
by NMR spectroscopy difficult as most resonance signals appear as broad sinlgets (Figure 23). The signals that are more deeply broadened are closer to the Co center whereas the shaper signals are further away. Using this, we can approximate the structure although this approximation would be a rough guess, at best. Similarly to the Cu complexes, as the Co complexes display this paramagnetic behaviour they were analyzed by IR, UV-Vis, EA, their mp, MS, and in most cases by x-ray crystallography.


Figure 23: ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectrum of $\mathbf{9 a}$ (paramagnetic).

Infrared spectroscopy showed the interaction of the ligand with the metal by displaying a shift in the absorbance frequency when compared to the ligand. The stretching frequency assigned to either $\mathrm{C}=\mathrm{C}$ or $\mathrm{C}=\mathrm{N}$ stretching resonated within a range of $1498-1525 \mathrm{~cm}^{-1}$, which is far lower than the reported values of the bare ligands within the range of $1615-1635 \mathrm{~cm}^{-1} .{ }^{35}$ The C-O stretching frequencies were seen at frequencies of $753-767 \mathrm{~cm}^{-1}$, indicative of a change from the
free ligand. ${ }^{35}$ Due to the drastic shift in stretching frequencies in the IR spectra, we hypothesize that the Co center is drawing electron density away from the bound ligand.

The UV-Vis spectra displayed weak d-d transitions in the visible region and metal-toligand charge transfer (MLCT) bands in the ultraviolet region (Figure 24). Lower energy absorptions, in the ranges of 534-550 nm, are representative of d-d transitions. These transitions are observed due to dark red/pink colour of the solution. This higher energy absorptions in the range of 296-321 nm, have been assigned to the $\pi-\pi^{*}$ transition localized to either the aromatic ring $(\mathrm{C}=\mathrm{C})$ or the imine group $(\mathrm{C}=\mathrm{N})$. As is the case for the copper complexes, MLCT transition bands are primarily observed in low oxidation state metals, such as $\mathrm{Co}^{2+}$. Complexes bearing electron withdrawing ligands, $\mathbf{9 b} / \mathbf{e}-\mathbf{f}$, as well as conjugation extending functional groups $\left(-\mathrm{NO}_{2}\right.$ etc.) will experience a bathochromic shift (to a higher wavelength).


Figure 24: UV-Vis trace of $\mathbf{6 e}$.




Figure 25: ORTEP representations of $\mathbf{9 j} \mathbf{j}$ -

X-ray crystallography was employed to determine the exact structure for several of the Co complexes. These were sent to the University of Toronto, where Dr. A. J Lough analyzed and solved each of their structures. Only three structures and their respective data sets were collected ( $\mathbf{9 j} \mathbf{j} \mathbf{I}$ ), Figure 25, as our group has previously structurally characterized complexes $\mathbf{9 a - c}$ and $\mathbf{9 g}$ i. ${ }^{66}$ X-ray quality crystals are grown with slow evaporation of a $1: 1$ solution of DCM and MeOH . Compounds $\mathbf{9 a - f} \mathbf{- i}$ crystallized as orange needles, $\mathbf{9 g}$ crystallizes as dark red cubic shapes, and complexes $\mathbf{9 h} / \mathbf{j}$-l crystallize as pink rectangular plates.

The calculated $\tau^{4}$ values for these compounds are displayed in Table 3 and suggest the complexes adopt a more tetrahedral geometry. This approximation is supported by the relevant bond angles in

Table 4, Table 5, and Table 6. Based on the unit cell parameters all three complexes crystallized in the orthorhombic crystal system with space groups $\mathrm{Pca} 2{ }_{1}, \mathrm{Pbca}$, and $\mathrm{Pna} 2{ }_{1}$, for $\mathbf{9 j} \mathbf{- I}$ respectively. It is expected for the $\mathrm{Co}-\mathrm{N}$ bond to be longer than the $\mathrm{Co}-\mathrm{O}$ bond as the former is a coordination bond, meaning it is not a true bond but a mutual sharing of electrons between the two atoms. The average length for a Co-O bond is $1.932 \AA$ and for a Co-N bond is $2.035 \AA$. The
experimental bond lengths and angles for $\mathbf{9 j} \mathbf{- l}$ are consistent with other $\mathrm{N}, \mathrm{O}$-donor ligand complexes in the literature. ${ }^{66,72}$

Table 3: Calculated $\tau^{4}$ values for all Co complexes

| Complex | $\tau^{4}$ | Complex | $\tau^{4}$ |
| :---: | :---: | :---: | :---: |
| $\mathbf{9 i} \mathbf{w} / \mathbf{D C M}$ | 0.82 | $\mathbf{9 b} \mathbf{w /} \mathbf{D C M}$ | 0.82 |
| $\mathbf{9 a}$ | 0.83 | $\mathbf{9 g}$ | 0.82 |
| $\mathbf{9 h}$ | 0.81 | $\mathbf{9 j}$ | 0.84 |
| $\mathbf{9 i} \mathbf{~ w / ~ C H C l}$ |  |  |  |
| $\mathbf{3}$ | 0.82 | $\mathbf{9 k}$ | 0.83 |
| $\mathbf{9 c}$ | 0.78 | $\mathbf{9 l}$ | 0.80 |

Table 4: Selected bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for $\mathbf{9 j}$

| Bond Lengths (£) |  | Bond Angles ( ${ }^{\circ}$ ) |  |
| :---: | :---: | :---: | :---: |
| $\mathrm{Co}(1)-\mathrm{O}(3)$ | $1.935(3)$ | $\mathrm{O}(3)-\mathrm{Co}(1)-\mathrm{O}(1)$ | $118.64(13)$ |
| $\mathrm{Co}(1)-\mathrm{O}(1)$ | $1.944(3)$ | $\mathrm{O}(3)-\mathrm{Co}(1)-\mathrm{N}(2)$ | $95.42(13)$ |
| $\mathrm{Co}(1)-\mathrm{N}(2)$ | $1.957(3)$ | $\mathrm{O}(1)-\mathrm{Co}(1)-\mathrm{N}(2)$ | $112.90(11)$ |
| $\mathrm{Co}(1)-\mathrm{N}(1)$ | $1.958(3)$ | $\mathrm{O}(3)-\mathrm{Co}(1)-\mathrm{N}(1)$ | $113.84(12)$ |
|  |  | $\mathrm{O}(1)-\mathrm{Co}(1)-\mathrm{N}(1)$ | $95.03(13)$ |
|  | $\mathrm{N}(2)-\mathrm{Co}(1)-\mathrm{N}(1)$ | $122.89(16)$ |  |
|  |  |  |  |

Table 5: Selected bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for $9 \mathbf{k}$.

| Bond Lengths (£) |  | Bond Angles ( ${ }^{\circ}$ ) |  |
| :---: | :---: | :---: | :---: |
| $\mathrm{Co}(1)-\mathrm{O}(3)$ | $1.9315(19)$ | $\mathrm{O}(1)-\mathrm{Co}(1)-\mathrm{O}(3)$ | $116.69(8)$ |
| $\mathrm{Co}(1)-\mathrm{O}(1)$ | $1.9449(19)$ | $\mathrm{O}(1)-\mathrm{Co}(1)-\mathrm{N}(1)$ | $94.87(9)$ |
| $\mathrm{Co}(1)-\mathrm{N}(2)$ | $1.964(2)$ | $\mathrm{O}(3)-\mathrm{Co}(1)-\mathrm{N}(1)$ | $113.29(9)$ |
| $\mathrm{Co}(1)-\mathrm{N}(1)$ | $1.964(2)$ | $\mathrm{O}(1)-\mathrm{Co}(1)-\mathrm{N}(2)$ | $112.19(9)$ |
|  | $\mathrm{O}(3)-\mathrm{Co}(1)-\mathrm{N}(2)$ | $94.78(9)$ |  |
|  | $\mathrm{N}(1)-\mathrm{Co}(1)-\mathrm{N}(2)$ | $126.71(9)$ |  |
|  |  |  |  |

Table 6: Selected bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for 91.

| Bond Lengths (£) |  | Bond Angles ( ${ }^{\circ}$ ) |  |
| :---: | :---: | :---: | :---: |
| $\mathrm{Co}(1)-\mathrm{O}(3)$ | $1.936(3)$ | $\mathrm{O}(3)-\mathrm{Co}(1)-\mathrm{O}(1)$ | $117.13(15)$ |
| $\mathrm{Co}(1)-\mathrm{O}(1)$ | $1.949(3)$ | $\mathrm{O}(3)-\mathrm{Co}(1)-\mathrm{N}(2)$ | $111.12(15)$ |
| $\mathrm{Co}(1)-\mathrm{N}(2)$ | $1.963(4)$ | $\mathrm{O}(1)-\mathrm{Co}(1)-\mathrm{N}(2)$ | $94.21(14)$ |
| $\mathrm{Co}(1)-\mathrm{N}(1)$ | $1.968(4)$ | $\mathrm{O}(3)-\mathrm{Co}(1)-\mathrm{N}(1)$ | $94.42(15)$ |
|  | $\mathrm{O}(1)-\mathrm{Co}(1)-\mathrm{N}(1)$ | $111.09(15)$ |  |
|  | $\mathrm{N}(2)-\mathrm{Co}(1)-\mathrm{N}(1)$ | $130.67(17)$ |  |
|  |  |  |  |

As was for the copper complexes, cyclic voltammetry was employed to probe the redox properties of the cobalt complexes. All scans started with an oxidative sweep following by the reductive sweep with a forward scan rate of $100 \mathrm{mV} / \mathrm{s}$. The Co complexes were prepared in the same manner as the Cu complexes by first running a blank scan of a 0.1 M solution of $[\mathrm{N}(n-$ $\left.\mathrm{Bu})_{4}{ }^{+}\right]\left[\mathrm{PF}_{6}{ }^{-}\right]$followed by the sample $(\sim 20 \mathrm{mg})$. Ferrocene $(0.1 \mathrm{mg})$ was added afterwards to serve as an internal standard. All derivatives, 9a-l, were analyzed in this way. All complexes excluding 9h, showed irreversible oxidation. Previous students in the Gossage group attempted polymerization by ATRP with 9a and other derivatives but obtained no polymer material at the terminus of their reaction. ${ }^{66}$ Complex $9 \mathbf{h}$ was the only complex that displayed quasi-reversible oxidation from $\mathrm{Co}^{2+}$ to $\mathrm{Co}^{3+}$ at approximately +1.75 eV , making it a potential target for catalytic studies (vide infra).


Figure 26: Voltammograms for $\mathbf{9 e}$ and $9 \mathbf{h}$ in DCM.

### 2.5.3.1 Attempted Oxidation of a $\mathrm{Co}^{2+}$ Complex

Upon observing promising redox behaviour in the CV, we decided to attempt various reactions to purposely oxidize the Co center to a permanent $\mathrm{Co}(\mathrm{III})$ resting state. This type of reaction was tried four different ways with $\mathbf{9 a}$ and once with $\mathbf{9 h}$ (Table 7).

Table 7: Attempted oxidation of a $\mathrm{Co}^{2+}$ center.

| Trial | Complex | $\mathrm{X}_{2}$ | Time (hr) | $\mathbf{9 : \mathrm { X } _ { 2 }}$ | Notes | Product |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | $9 \mathbf{a}$ | Br | 0.5 | $1: 1$ | light | ${ }^{*} \mathrm{CoBr}_{2}$ |
| 2 | 9 a | Br | 0.25 | $2: 1$ | dark | ${ }^{*} \mathrm{CoBr}_{2}$ |
| 3 | 9 a | I | 1 | $1: 1$ | - | 9 a |
| 4 | 9 a | I | 1 | $1: 1$ | - | 9a |
| 5 | 9 h | Br | 1 | $1: 1.4$ | with ACN | ^green oil/orange <br> powder |

In trial 1,9a was dissolved in toluene and bromine $\left(\mathrm{Br}_{2}\right)$ was added dropwise in a 1:1 molar ratio. During addition of $\mathrm{Br}_{2}$, it was noted that the solution had started to phase separate leaving a dark red top layer and a blue oil on the bottom of the flask. The reaction was done uncovered in open air for 0.5 hours. Upon removal of the excess toluene and bromine, a fragile blue-green solid. The solids were insoluble in most organic solvents $\left(\mathrm{CDCl}_{3}, \mathrm{C}_{6} \mathrm{D}_{6}\right.$, toluene, $\left.\mathrm{CHCl}_{3}\right)$ but was soluble in acetone, MeOH and water. An NMR spectrum was taken in acetone $-\mathrm{d}_{6}$ and unfortunately from
this there were no distinct signals in either the proton or carbon spectra. A qualitative test was performed by adding both DCM and water to the flask and rapidly stirring for approximately 10 minutes. This resulted in the loss of the original green colour and appearance of a pink aqueous layer and cloudy organic layer (Figure 27, B-C). After NMR analysis, the sample was poured into a beaker where it was diluted further with acetone. Commercial grade $\mathrm{CoBr}_{2}$ was dissolved in both acetone and MeOH in two other beakers and the three compared (Figure 27, A). It seemed likely that $\mathrm{CoBr}_{2}$ was indeed the formed product and hence decomposition of $\mathbf{9 a}$ is likely the result of the above treatments.


Figure 27: A qualitative test of Trial $1\left(\mathbf{9 a}+\mathrm{Br}_{2}\right)$

For the second trial, the reaction was carried out in a similar fashion, this time stirring in the dark. After the reaction was done and excess components removed in vacuo a blue powder was left behind. The blue powder was recrystallized with a $1: 1$ mixture of $\mathrm{DCM} / \mathrm{MeOH}$ as was the case for $\mathbf{7}$ and 9 . Upon accidental contact with water the blue powder was instantly dissolved. There was a notable colour change from light blue to a pinky-purple colour. Commercial grade $\mathrm{CoBr}_{2}$
was likewise dissolved in EtOH and revealed similar behaviour. After more research, the blue powder was concluded to be anhydrous $\mathrm{CoBr}_{2}$.

Trials 3 and 4 gave the same result of recovery of starting material. The iodine, in both polar aprotic and nonpolar solvents, remained unreacted in each case. This was later confirmed by NMR spectroscopy where the same broad signals associated with 9a (Figure 23) were observed.


Scheme 35: Attempted bromination of $\mathbf{9 h}$.

Trial 5 was done with $\mathbf{9 h}$, the catalytic candidate (Scheme 35). 9h was initially dissolved in ACN where the solution instantly changed from a light pink to a dark purple. This colour change is assumed to be coordination of either one of two ACN molecules to the cobalt center, although this has yet to be confirmed. This complex would still be paramagnetic and therefore would not be observable by NMR spectroscopy. Continuing with the reaction once fully dissolved, bromine was added dropwise and the solution took a noticeable colour change to a dark green. Once all volatile components were removed a green resin was left behind. This resin was soluble in $\mathrm{CHCl}_{3}$ and acetone although did not turn the bright teal-blue colour once dissolved in acetone, possibly being the target complex.

Performing NMR spectroscopy on the green resin in $\mathrm{CDCl}_{3}$ gave a paramagnetic-like spectrum with broad signals spanning many ppm units (Figure 28). The green oil was dissolved in MeOH , where the solution was a bright pink colour. Once the MeOH is removed, the compound becomes a resin, again green in colour. We hypothesize this may be signaling the release and re-
coordination of a ligand ( $\mathrm{Br}^{-}$or ACN ) giving back $\mathbf{9 h}$. These mixtures did not yield a pure oxidized product of $\mathbf{9 h}$. More studies in this area needs to be conducted for an exact conclusion to be drawn.


Figure 28: ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectrum of proposed $\mathbf{9 h} \mathbf{- 1}$.

### 2.5.4 Cobalt Complexes (10a-d and 11a/11c)

Cobalt complexes with ligand series $\mathbf{6}$ were also synthesized. In this series, three aryl derivatives were successfully synthesized (Scheme 36).



Scheme 36: Synthesis of complexes 10a-d.

The synthesis was carried out in a method like those described above where to a stirring solution of the ligand with 2.5 equivalents of $\mathrm{NEt}_{3}$ dissolved in EtOH , 1 equivalent of a metal salt is added (also dissolved in EtOH ). Upon addition of the Co metal salt to the ligand solution, an evident colour change from dark red/clear to a pastel orange is observed (Figure 29, B).


Figure 29: $\underline{\text { A- 10a }}$ and 10 c as a powder. $\underline{B}$ - RIGHT: 10c (orange) during synthesis.

After which, the orange/tan precipitates are collected via vacuum filtration and are recrystallized with a layering of 1:1 DCM/MeOH (Figure 29, A). These compounds, where applicable, were characterized by IR, UV-Vis, their mp, EA and in some cases, x-ray crystallography. Co complex 10d was unable to be synthesized regardless of the route taken.

Infrared spectroscopy of $\mathbf{1 0 a} \mathbf{- c}$ indicated an interaction between the ligand and the metal by displaying a shift in the absorbance frequency when contrasted against the bare ligand. The stretching frequency assigned to either $\mathrm{C}=\mathrm{C}$ or $\mathrm{C}=\mathrm{N}$ stretching resonated within a range of 1527$1531 \mathrm{~cm}^{-1}$. The C-O stretching frequencies were seen at frequencies of $746-770 \mathrm{~cm}^{-1}$, indicative of a change from the free ligand which bears no C-O bond but a carbonyl stretch. ${ }^{9,38,39}$ Due to the drastic shift in stretching frequencies in the IR spectra we conclude that the Co center is drawing electron density away from the bound ligand.

The UV-Vis spectra displayed weak d-d transitions in the visible region and MLCT bands in the ultraviolet region (Figure 30). Lower energy absorptions, in the ranges of 528-548 nm, are characteristic of d-d transitions. The orange/tan colour of the solutions are dependent on these d-d transitions as the transmit the complementary colour. The higher energy absorptions in the range of 235-242 nm and $310-321 \mathrm{~nm}$, have been assigned to the $\pi-\pi^{*}$ transition localized to either the aromatic ring $(\mathrm{C}=\mathrm{C})$ or the imine group $(\mathrm{C}=\mathrm{N})$.


Figure 30: UV-Vis trace for 10b.

Crystals of compound 10a were gown from vapor diffusion of diethyl ether into a solution of warm DCM. These crystals were sent to the University of Toronto for structural analysis. Complex 10a crystallizes as dark red cubes. The calculated $\tau^{4}$ value for this complex is 0.83 , giving it a more tetrahedral-like geometry. 10a crystallizes in the monoclinic crystal system with an assigned space group of $\mathrm{P}_{1} / \mathrm{n}$, supporting its geometry. Relevant bond lengths and angles are shown in Table 8, which are comparable to other Co $\mathrm{N}, \mathrm{O}$ bidentate complexes. ${ }^{66}$

Table 8: Selected bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for $\mathbf{1 0 a}$.

| Bond Lengths (£) |  | Bond Angles ( ${ }^{\circ}$ ) |  |
| :---: | :---: | :---: | :---: |
| $\mathrm{Co}(1)-\mathrm{O}(3)$ | $1.9348(12)$ | $\mathrm{O}(1)-\mathrm{Co}(1)-\mathrm{O}(3)$ | $108.80(5)$ |
| $\mathrm{Co}(1)-\mathrm{O}(1)$ | $1.9360(12)$ | $\mathrm{O}(1)-\mathrm{Co}(1)-\mathrm{N}(2)$ | $116.97(6)$ |
| $\mathrm{Co}(1)-\mathrm{N}(2)$ | $1.9588(14)$ | $\mathrm{O}(3)-\mathrm{Co}(1)-\mathrm{N}(2)$ | $94.75(5)$ |
| $\mathrm{Co}(1)-\mathrm{N}(1)$ | $1.9621(14)$ | $\mathrm{O}(1)-\mathrm{Co}(1)-\mathrm{N}(1)$ | $95.14(6)$ |
|  | $\mathrm{O}(3)-\mathrm{Co}(1)-\mathrm{N}(1)$ | $115.29(6)$ |  |
|  | $\mathrm{N}(2)-\mathrm{Co}(1)-\mathrm{N}(1)$ | $126.20(6)$ |  |
|  |  |  |  |

Cyclic voltammetry was carried out to probe the redox properties of the $\mathbf{1 0 a} \mathbf{- c}$ complexes. All scans were conducted first the oxidative sweep following by the reductive sweep, scanning with a forward scan rate of $1.0 \mathrm{mV} / \mathrm{s}$. The Co complexes were prepared in the same manner as the previous complexes by first running a blank scan of a 0.1 M solution of $\left[\mathrm{N}(n-\mathrm{Bu})_{4}{ }^{+}\right]\left[\mathrm{PF}_{6}{ }^{-}\right]$followed by the sample ( $\sim 20 \mathrm{mg}$ ). Afterwards, ferrocene $(0.1 \mathrm{mg})$ was added to serve as an internal standard. All derivatives, 10a-c, were analyzed in this way. All complexes showed irreversible oxidation (Figure 31).


Figure 31: Cyclic voltammetry for 10a and 10c

### 2.5.4.1 Usual Oxidation from $\mathrm{Co}^{2+}$ to $\mathrm{Co}^{3+}$ Complexes (11a/c)

Interestingly, darkening of the crystallization solution of both $\mathbf{1 0 a}$ and $\mathbf{1 0 c}$ were observed. When 10a was initially recrystallized with a $1: 1$ mixture of $\mathrm{DCM} / \mathrm{MeOH}$ after approximately 24 hours, black crystals were apparent at the bottom of the vial (Figure 32, E). When sent for crystallographic determination, a novel complex, compound 11a was identified (Figure 32, F). This phenomenon was tracked over the course of three days by dissolving 10a in only DCM and observing changes each day. In each instance, 11a was obtained.


Figure 32: Solution darkening and oxidation of $\mathrm{Co}^{2+}$ to $\mathrm{Co}^{3+}$ (10a to 11a)

Experiments were done to try to synthesize 11a from just the ligand and cobalt metal salt. This was done by dissolving 3 equivalents of $\mathbf{6 a}$ in MeOH and adding 1 equivalent of the Co metal salt also dissolved in MeOH . Upon addition, the ligand solution turned a dark brown-red. The reaction was stirred at room temperature for 24 hours. The same reaction was tried a second time, although refluxing (with identical conditions) for 5 hours. In both cases, 10a was the only product isolated. In another reaction, 1 equivalent of $\mathbf{1 0 a}$ was added to 1 equivalent of $\mathbf{6 a}$, attempting to coordination another ligand, in MeOH . This was left to stir at room temperature. Upon completion,
again the only collected product was 10a. In another test, 34 mg of 10a was dissolved in 2 ml of DCM. This mixture could sit till all the solvents had evaporated. The resulting complex, 11a, was separated and weighted out. 11a was present, an approximate $50 \%$ conversion from 10a to 11a. No other pure materials could be isolated from this mixture.

Similarly, 10c also exhibits this behaviour, formally oxidizing the metal from a $\mathrm{Co}^{2+}$ to $\mathrm{Co}^{3+}$. The reaction is carried out in a similar way to $\mathbf{1 0 a}$ where 2 equivalents of $\mathbf{6 c}$ and 3 equivalents of $\mathrm{NEt}_{3}$ are dissolved in EtOH . To this solution, 1 equivalent of $\mathrm{Co}\left(\mathrm{NO}_{3}\right)_{2} \cdot 6 \mathrm{H}_{2} \mathrm{O}$ dissolved in EtOH was added dropwise. After 1.5 hrs, the precipitates were collected (85 \%) and recrystallized. Two recrystallization vials were set up; one with layering of DCM and $\mathrm{MeOH}(1: 1)$ and the second a vapour diffusion if diethyl ether into warm DCM. These two methods revealed red cubic crystals and short black needles (respectively, 10c and 11c)

On both compounds (11a/c) IR, CV, UV-Vis, EA, their mp, and where applicable x-ray crystallography were carried out. In the IR spectra, a noticeable shift to lower frequencies is observed. In comparison to $\mathbf{1 0 a}\left(1537,746 \mathrm{~cm}^{-1}\right)$ a shift to 1526 and $746 \mathrm{~cm}^{-1}$ is observed in the $\mathrm{C}=\mathrm{N} / \mathrm{C}=\mathrm{C}$ and $\mathrm{C}-\mathrm{O}$ stretching. The same is observed to 11c, a shift from 1498, $770 \mathrm{~cm}^{-1}$ to 1495 and $756 \mathrm{~cm}^{-1}$ for the $\mathrm{C}=\mathrm{N} / \mathrm{C}=\mathrm{C}$ and $\mathrm{C}-\mathrm{O}$ stretching respectively.

In UV-Vis spectra slight red-shifting of the absorption maxima in both the d-d transitions and MLCT bands are observed. Lower energy absorptions, in the ranges of $528-549 \mathrm{~nm}$ for $\mathbf{1 0 a} / \mathbf{c}$ are shifted to approximately 567 nm with the appearance of a new weak absorption of around 445 nm . The black/green colour of the solutions is dependent on these d -d transitions. The $\pi-\pi^{*}$ transitions, localized to either the aromatic ring $(\mathrm{C}=\mathrm{C})$ or the imine group $(\mathrm{C}=\mathrm{N})$, in the range of 235-240 nm and 312-318 nm, have also been red-shift slightly to now 244-245 nm and 346-347 nm respectively. Both complexes (11a and 11c) were analyzed by EA. The results came back
within experimental error of their calculated elemental compositions, with the expectation of 11a which held also half a molecule of DCM within the elemental lattice. With DCM considered, both analyses were considered accurate (within $3 \%$ error).

Both 11a and 11c were sent for crystallographic analysis and returned with positive results (Figure 33). As per the unit cell parameters, 11a crystallizes in a triclinic crystal system within the $\mathrm{P}-1$ space group and 11c crystallizes in a monoclinic crystal system within the $\mathrm{P} 2_{1} / \mathrm{c}$ space group. Both complexes have octahedral geometry and are both mer isomers (all nitrogen/oxygen atoms found along the same meridian). Of the three ligands attached to the Co metal center, in both the case of 11a and 11c, there is one ligand with elongated bonds (both $\mathrm{Co}-\mathrm{O}$ and $\mathrm{Co}-\mathrm{N}$ ) to the center (Table 9, Table 10).


Figure 33: ORTEP representations of 11a and 11c

Table 9: Select bond angles $\left({ }^{\circ}\right)$ and lengths ( $\AA$ ) for 11a

| Bond Lengths ( $\AA$ ) |  | Bond Angles ( ${ }^{\circ}$ ) |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{Co}(1)-\mathrm{O}(5)$ | 1.8983(16) | $\mathrm{O}(5)-\mathrm{Co}(1)-\mathrm{O}(1)$ | 88.61(7) | $\mathrm{O}(3)-\mathrm{Co}(1)-\mathrm{N}(2)$ | 92.96(8) |
| $\mathrm{Co}(1)-\mathrm{O}(1)$ | 1.8993(16) | $\mathrm{O}(5)-\mathrm{Co}(1)-\mathrm{O}(3)$ | 174.68(7) | $\mathrm{N}(3)-\mathrm{Co}(1)-\mathrm{N}(2)$ | 91.15(8) |
| $\mathrm{Co}(1)-\mathrm{O}(3)$ | 1.9072(16) | $\mathrm{O}(1)-\mathrm{Co}(1)-\mathrm{O}(3)$ | 89.04(7) | $\mathrm{O}(5)-\mathrm{Co}(1)-\mathrm{N}(1)$ | 88.15(7) |
| $\mathrm{Co}(1)-\mathrm{N}(3)$ | 1.9144(19) | $\mathrm{O}(5)-\mathrm{Co}(1)-\mathrm{N}(3)$ | 94.33(7) | $\mathrm{O}(1)-\mathrm{Co}(1)-\mathrm{N}(1)$ | 92.11(7) |
| $\mathrm{Co}(1)-\mathrm{N}(2)$ | 1.915(2) | $\mathrm{O}(1)-\mathrm{Co}(1)-\mathrm{N}(3)$ | 84.09(8) | $\mathrm{O}(3)-\mathrm{Co}(1)-\mathrm{N}(1)$ | 87.16(7) |
| $\mathrm{Co}(1)-\mathrm{N}(1)$ | 1.9219(19) | $\mathrm{O}(3)-\mathrm{Co}(1)-\mathrm{N}(3)$ | 90.18(8) | $\mathrm{N}(3)-\mathrm{Co}(1)-\mathrm{N}(1)$ | 175.40(8) |
|  |  | $\mathrm{O}(5)-\mathrm{Co}(1)-\mathrm{N}(2)$ | 89.78(8) | $\mathrm{N}(2)-\mathrm{Co}(1)-\mathrm{N}(1)$ | 92.73(8) |
|  |  | $\mathrm{O}(1)-\mathrm{Co}(1)-\mathrm{N}(2)$ | 174.84(7) |  |  |

Table 10: Select bond angles $\left({ }^{\circ}\right)$ and lengths $(\AA)$ for 11c

| Bond Lengths ( $\AA$ ) |  | Bond Angles ( ${ }^{\circ}$ ) |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{Co}(1)-\mathrm{N}(3)$ | 1.892(4) | $\mathrm{N}(3)-\mathrm{Co}(1)-\mathrm{O}(4)$ | 91.27(16) | $\mathrm{N}(2)-\mathrm{Co}(1)-\mathrm{O}(1)$ | 87.30(16) |
| $\mathrm{Co}(1)-\mathrm{O}(4)$ | 1.896(3) | $\mathrm{N}(3)-\mathrm{Co}(1)-\mathrm{O}(7)$ | 93.73(16) | $\mathrm{N}(3)-\mathrm{Co}(1)-\mathrm{N}(1)$ | 90.92(17) |
| $\mathrm{Co}(1)-\mathrm{O}(7)$ | 1.902(3) | $\mathrm{O}(4)-\mathrm{Co}(1)-\mathrm{O}(7)$ | 173.77(14) | $\mathrm{O}(4)-\mathrm{Co}(1)-\mathrm{N}(1)$ | 87.06(16) |
| $\mathrm{Co}(1)-\mathrm{N}(2)$ | 1.906(4) | $\mathrm{N}(3)-\mathrm{Co}(1)-\mathrm{N}(2)$ | 89.22(17) | $\mathrm{O}(7)-\mathrm{Co}(1)-\mathrm{N}(1)$ | 89.14(16) |
| $\mathrm{Co}(1)-\mathrm{O}(1)$ | 1.912(3) | $\mathrm{O}(4)-\mathrm{Co}(1)-\mathrm{N}(2)$ | 93.58(16) | $\mathrm{N}(2)-\mathrm{Co}(1)-\mathrm{N}(1)$ | 179.35(18) |
| $\mathrm{Co}(1)-\mathrm{N}(1)$ | 1.913(4) | $\mathrm{O}(7)-\mathrm{Co}(1)-\mathrm{N}(2)$ | 90.21(16) | $\mathrm{O}(1)-\mathrm{Co}(1)-\mathrm{N}(1)$ | 92.88(16) |
|  |  | $\mathrm{N}(3)-\mathrm{Co}(1)-\mathrm{O}(1)$ | 176.07(16) | $\mathrm{O}(7)-\mathrm{Co}(1)-\mathrm{O}(1)$ | 88.11(14) |
|  |  | $\mathrm{O}(4)-\mathrm{Co}(1)-\mathrm{O}(1)$ | 87.13(15) |  |  |

Complexes 11a and 11c have been also tested for their redox behaviour using previously described methods. Unfortunately, only irreversible behaviour was observed, regardless of scan rate and starting potential, for both complexes (Figure 34).


Figure 34: Voltammogram of 11a and 11c in DCM.

### 2.6 Polymerization Studies with a $\mathrm{Co}^{2+}$ Catalyst

The successful observation of the redox properties of $\mathbf{9 h}$ lead to testing of its abilities as a catalyst in polymerization. Thus, this reversible oxidation metal catalyst was tested in atom transfer radical polymerization (ATRP).


Scheme 37: General route to polymerization of MMA.

Each reaction trial was set up in the same way where all glassware was flame-dried and purged of air. The catalyst, monomer and initiator were dissolved in 3 ml of the dry solvent specified in Table 11. For all polymerizations, tosyl chloride (TsCl) was selected as the initiator due to it being readily available. ${ }^{60,73}$ This mixture was left to heat at the temperature specified in a sealed round-bottom flask for an allotted amount of time (Table 11). After completion, the solvent was concentrated to about 1 ml . This mixture was slowly dropped into cold, rapidly stirring MeOH $\left(-30^{\circ} \mathrm{C}\right)$ to reveal the polymer as a white threadlike substance. The complex, $\mathbf{9 h}$, is soluble in

MeOH . During the precipitation process the MeOH , is filtered and the solvent removed via rotary evaporator. In each case, complete recovery of the catalyst can be made. This gives way to be reused in another trial (Table 11, entry 8) modest conversion of the monomer to the polymer was observed, giving percent conversions between 14-42, but mostly around $40 \%$. Polymerization was tried twice without an initiator, as proof of principal. Without the initiator present, no polymer was formed. This further supports the ATRP-like catalytic nature of $\mathbf{9 h}$.

Table 11: Trials and data for the polymerization of MMA

| Trial | 9h <br> Mol\% | Solvent | Time | Temperature <br> $\left({ }^{\circ} \mathrm{C}\right)$ | Initiator : <br> $\mathrm{mol} \%$ | Mw (Da) : <br> PDI | Conversion <br> $(\%)$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 2 | THF | 24 | 60 | N/A | N/A | 0 |
| 2 | 2 | Tol. | 24 | 90 | N/A | N/A | 0 |
| 3 | 2 | THF | 72 | 60 | $\mathrm{TsCl}: 0.3$ | $60 \mathrm{~K}: 1.38$ | 38 |
| 4 | 2 | THF | 24 | 60 | $\mathrm{TsCl}: 0.3$ | $50 \mathrm{~K}: 1.19$ | 42 |
| 5 | 2 | THF | 4 | 60 | $\mathrm{TsCl}: 0.3$ | $53 \mathrm{~K}: 1.17$ | 23 |
| 6 | 5 | THF | 4 | 60 | $\mathrm{TsCl}: 0.3$ | $39 \mathrm{~K}: 1.21$ | 14 |
| 7 | 10 | THF | 4 | 60 | $\mathrm{TsCl}: 0.3$ | $32 \mathrm{~K}: 1.20$ | 40 |
| 8 | 2 | THF | 12 | 60 | $\mathrm{TsCl}: 0.3$ | $45 \mathrm{~K}: 1.18$ | 38 |



Scheme 38: Formation of PMMA, based on best trial from Table 11.

Gel permeation chromatography (GPC) data revealed a generally well controlled polymerization of MMA showing respectable PDI's ranging from 1.17-1.38 with high molecular weights (3260,000 Da).

Based on the data in Table 11 and other literature protocols ${ }^{60,74}$, we propose a mechanism for the polymerization of MMA with $\mathbf{9 h}$ (Scheme 39). Upon heating the solution, the initiator $(\mathrm{TsCl})$ radicalizes. A radical finds the catalyst and bonds to the cobalt metal which can accommodate the extra bonded halogen. In this step, the cobalt becomes oxidized to an oxidation state of 3+. The tosyl radical anion interacts with the monomer species by attacking the terminal olefin and creating a bond. This change in electronic structure sends the electron propagating along the rest of the monomer till another monomer near is hit by the radical monomer. Propagation along the main chain continues till there are no monomer units left or till all the radical species have been terminated. During this process, the tosyl group can unbind from the growing polymer chain to stop the polymerization process as the $9 h^{3+}-\mathrm{Cl}$ will always be close by the growing chain. When all monomer units have been used up, the chlorine bonded to the metal catalyst will be released and bound to the end of the polymer chain (Scheme 38).


Propogation


Scheme 39: Proposed mechanism for the formation of PMMA via $\mathbf{9 h}$.

Ongoing experiments are being performed to further optimize not only the reaction yield but also the PDI's of the resulting polymer. Once optimized, $\mathbf{9 h}$ with be tested in the polymerization of other monomers such as styrene.

### 2.7 Synthesis and Characterization Other Group 9 complexes

Below Cobalt in Group 9 lies both Rhodium and Iridium. In recent years, there have been various studies surrounding their redox properties as well as their candidacy as catalysts. This lead to their increasingly popularity in the field of catalytic-coordination chemistry. Two of the best complexes for studying hydrogen transfer, as well as other general oxidative addition reactions, are Vaska's complex, $\operatorname{IrCl}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2}$, and Wilkinson's catalyst. For these reasons, we propose a modification to these complexes to hopefully enrich their redox potential.

### 2.7.1 Attempted Synthesis and Characterization of Rh Complexes

Initial investigations of other group 9 complexes involved reactions of $\mathbf{4 a}$ with Wilkinson's catalyst. Some groups have been able to oxidatively add neutral and other hydride species to Wilkinson's catalyst. These types of Rh-compounds tend to be used as hydrogenation catalysts. ${ }^{75,76}$ There have been other groups interested in the catalytic properties of nanoparticles, coating and grafting a tether to a particle. Once grafted, they can coordinate Wilkinson's catalyst to it. This makes for a highly effective and selective hydrogenation agent. ${ }^{77}$

Our exploration of this was first done by dissolving Wilkinson's catalyst and $\mathbf{4 a}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$ while in the glove box. Once out of the glove box, the solution was heated at $50^{\circ} \mathrm{C}$ and monitored by its ${ }^{31} \mathrm{P}-\mathrm{NMR}$ spectrum (Figure 35).


Scheme 40: Attempted substitution of Wilkinson's Catalyst with 4a.

By analyzing the NMR spectra obtained over the 24 -hour period, it was concluded that Wilkinson's catalyst was decomposing in solution, releasing $\mathrm{PPh}_{3}$ which was oxidized almost entirely to $\mathrm{O}=\mathrm{PPh}_{3}$. This reaction was tried again, this time refluxing in $\mathrm{CDCl}_{3}$ for only 6 hours (Scheme 40). Analysis by NMR spectroscopy revealed one signal at $+29 \mathrm{ppm}\left(\mathrm{O}=\mathrm{PPh}_{3}\right)$. Precipitation of Rh metal was also recovered from the reaction, further supporting decomposition of the catalyst. Further reactions with this material were not continued.


Figure 35: ${ }^{31} \mathrm{P}-\mathrm{NMR}$ spectra of reaction between Wilkinson's catalyst and 4a.

### 2.7.2 Attempted Synthesis and Characterization of Vaska-type Complexes

Another typical candidate to study oxidative addition is Vaska's complex and its Rh analogue. Other groups have been able to take advantage of the oxidative properties of $\mathrm{Ir}^{+}$. In this regard, various silane species as well as small carbon-tin based spheres have been shown to oxidatively add to the Ir center. ${ }^{78,79}$


Figure 36: Target group 9 complexes for substitution.

Various attempts were made to substitute ligands on 12 and 13 (Figure 36) with 4a. An NMR tube was charged with 1 equivalent of $\mathbf{1 2} / \mathbf{1 3}$ and 1 equivalent of $\mathbf{4 a}$ dissolved in $\mathrm{CDCl}_{3}$, heated at $50{ }^{\circ} \mathrm{C}$ and monitored by its ${ }^{31} \mathrm{P}-\mathrm{NMR}$ spectrum over 2 days (Figure 37). In the reaction with 12, the disappearance of the main signal in the NMR spectrum at 28.8 ppm as well as the appearance of two new signals, at 29.2 and 20.6 ppm , are observed. The signal at 29.2 ppm corresponds to the formation of triphenylphosphine oxide $\left(\mathrm{O}=\mathrm{PPh}_{3}\right)$. For it to have been oxidized, $\mathrm{PPh}_{3}$ must have been released from the complex. The appearance of a new signal at 20.6 ppm could be indicative of a new iridium complex being formed between $\mathbf{1 2}$ and $\mathbf{4 a}$ although in all attempts to isolate the new signal from the mixture only $\mathbf{1 2}$ was obtained.

In the reaction with 13, the disappearance of the starting material was observed (29.0 ppm) and the appearance of a new doublet was observed at 43.4 ppm , as well as $\mathrm{O}=\mathrm{PPh}_{3}$ at 29.2 ppm . This new signal at 43 ppm confirmed the formation of a new rhodium complex. Rhodium has a spin of $1 / 2$, the same as phosphorus, therefore they will couple together to appear as a doublet instead of a singlet. Unfortunately, attempted isolation of this new complex only gave the starting material (13) back as crystalline yellow needles.


Figure 37: Substitution of 4a to either 12 (left) or $\mathbf{1 3}$ (right).

Substitution of $\mathbf{1 2} / \mathbf{1 3}$ with $\mathbf{4 a}$ was tried again, this time on a slightly larger scale with using toluene as a solvent. These mixtures were refluxed 24 hours before being cooled to room temperature where $(20 \mathrm{ml}) n$-hexanes was added dropwise. The Rh and Ir containing flasks were set aside in a $-30^{\circ} \mathrm{C}$ freezer for recrystallization. After cooled, the two were subjected to vacuum filtration where in the case of Rh, a brown powder was revealed and washed with cold $n$-hexanes and diethyl ether. After dry, a ${ }^{31} \mathrm{P}-\mathrm{NMR}$ had shown only one signal at $+29 \mathrm{ppm}\left(\mathrm{O}=\mathrm{PPh}_{3}\right)$. In the case of Ir, a yellow powder was revealed and washed with cold $n$-hexanes and diethyl ether. After dry, ${ }^{31}$ P-NMR disclosed 2 signals at +25 and +5 ppm (starting material). In each case, none of the complexes had either reacted (12-Ir) with $\mathbf{4 a}$ or only decomposed (13-Rh).

The reaction was attempted again, although this time with a synthetic approach more like that of the formation of $\mathrm{Cu} / \mathrm{Co}$ complexes [see $\mathbf{S e c} \mathbf{2 . 5}$ ]. This was done by adding 1 equivalent of $\mathbf{1 2}$ and $\mathbf{4 a}$, dissolving them in toluene and then added 3.4 equivalents of $\mathrm{NEt}_{3}$. It was hoped that the base would make the ligand more nucleophilic towards the Ir center. The solution was refluxed for 14 hours. Upon completion, the reaction was cooled to room temperature were $n$-hexanes was layered on top and put into the $-30^{\circ} \mathrm{C}$ fridge. Once filtered, washed and dried the precipitates were
checked by NMR spectroscopy. Checking by ${ }^{31} \mathrm{P}-\mathrm{NMR}$ spectroscopy, however, revealed only starting material (12).

### 2.7.3 Synthesis and Characterization of Ir Complexes (14 and 15)

Since group 9 carbonyl/phosphine complexes could not be readily substituted with $\mathbf{4 a}$ another route was taken to explore the reactivity of 4a. Instead, a structurally strained Ir dimer was made $\left([\operatorname{Ir}(\mathrm{COD}) \mathrm{Cl}]_{2}(\mathbf{1 4})\right)$. The dimer is known to react with N,O-donor, and other pro-chelate ligands, as it readily splits to form a new chelated $\mathrm{Ir}^{+}$complex. ${ }^{80-82}$

Examples of this reactivity can be found in preparations by Carlton. ${ }^{54,80}$ They've showcased the oxidative properties of their iridium-COD complex by adding $\mathrm{HSiPh}_{3}, \mathrm{HSnPh}_{3}$ and $\mathrm{SC}_{5} \mathrm{~F}_{6}$ to the iridium center, changing its formal oxidation number to +1 to +3 . Using a simple twostep method (formation of an iridium-COD dimer then coordination of their ligand) then by the addition of the nucleophilic species, the Carlton group has been able to synthesise an array of H -Ir-R complexes. This reactions series showcases the redox ability of the iridium centered complex as it oxidizes from an $\operatorname{Ir}(\mathrm{I})$ to $\operatorname{Ir}(\mathrm{III})$.

Thus, 1 equivalent of $\mathbf{1 4}$ was added together with 2.1 equivalents of $\mathbf{4 a}$ in a flask. This flask was purged and backfilled with nitrogen. The two solids were dissolved in dry DCM and 3.1 equivalents of $\mathrm{NEt}_{3}$ was also added. This solution was left to stir at room temperature for 3 hours under a constant stream of nitrogen gas. At the terminus of the reaction, excess volatile components were removed in vacuo and TLC was preformed to observed conversion, if any. After development in $30 \% \mathrm{EtOAc} / n$-hexanes, two spots will distinguishable $\mathrm{R}_{f}$ values were obtained (one at 0.26 and the other at 0.56 ). Column chromatography was performed the material the following day eluting with $25 \% \mathrm{EtOAc} / n$-hexanes. Although, after developing TLC plates containing fractions from the
column only revealed a compound with an $\mathrm{R}_{f}$ of 0.26 . Re-running the crude sample from the previous days TLC showed also only the one spot. Regardless after analyzing by ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}-\mathrm{NMR}$ spectra, the compound which eluted from the column was determined to be 15 (Figure 38).


Figure 38: ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectrum of $\mathbf{1 5}$

The structural identity of $\mathbf{1 5}$ was probed by a variety of NMR spectroscopic techniques (both 1D and 2D) and via x-ray crystallography. In the ${ }^{1} \mathrm{H}$-NMR spectrum (Figure 38), each of the signals belonging to the parent ligand experience a slight upfield shift of about 0.2 ppm and a notable disappearance of the NH signal (resonates at $\sim 9.95 \mathrm{ppm}$ in $\mathbf{4 a}$ ). This, along with the appearance of the six sets of complex multiplets indicating asymmetry in the 'COD' ring, give evidence that a new complex with 'COD' encorporated was formed. The ${ }^{13} \mathrm{C}$-NMR shows a significant downfield shift of the enolic proton from $\sim 58 \mathrm{ppm}$ in $\mathbf{4 a}$ to $\sim 81 \mathrm{ppm}$ in $\mathbf{1 5}$. Assignments to $\mathbf{1 5}$ were made with a combination of the assignments of $\mathbf{4 a}$ (made by COSY/HSQC NMR) as well as crude
assignments of the 'COD' ring were done with HSQC and COSY NMR. The olefinic protons/carbons are shifted more downfield, making them distinguishable from the alkyl signals.

The reaction was done a second time, although this time preforming preparative TLC (eluting with $25 \% \mathrm{EtOAc} / n$-hexanes) of the product mixture the same day to isolate both $\mathrm{R}_{f}$ spots on the TLC plate. When both spots were analyzed by NMR what looked like the same compound being scanned twice appeared. The only different between the two compounds were a fairly large downfield shift of the olefin protons/carbons of the 'COD' ring (Figure 39, Figure 40). We propose that less polar of the two spots may be an intermediate complex such as an Ir-COD-4a dimer which over time breaks apart into the thermodynamic product, 15.


Figure 39: ${ }^{1} \mathrm{H}-\mathrm{NMR}$ stacked of both $\mathrm{R}_{f}$ spots on the TLC plate of $\mathbf{1 5}$.


Figure 40: ${ }^{1} \mathrm{H}-\mathrm{NMR}$ stacked of both $\mathrm{R}_{f}$ spots on the TLC plate of $\mathbf{1 5}$.

The synthetic route that gave the best yield of $\mathbf{1 5}$ is as described above except instead of 3 hours, the reaction is only stirred for an hour and instead of column chromatography, a rinse with cold MeOH and then decanting off the liquor is used to purify the complex (Scheme 41). This method gave the target compound, 15, in high yields ( $90 \%$ ). 15 exhibits C-O stretching at a frequency of $776 \mathrm{~cm}^{-1}$ and the $\mathrm{C}=\mathrm{N} / \mathrm{C}=\mathrm{C}$ stretches at $1534 \mathrm{~cm}^{-1}$, in contrast to the free ligand, $\mathbf{4 a}$, which shows $\mathrm{aC}=\mathrm{N} / \mathrm{C}=\mathrm{C}$ stretching frequency at $1620 \mathrm{~cm}^{-1} .{ }^{35}$


Scheme 41: Synthetic route to make 15

The identity of complex $\mathbf{1 5}$ was unequivocally assigned once after it was crystallized and examined by x-ray crystallography. $\mathbf{1 5}$ crystallized as yellow cubic structures, grown by slow evaporation of neat $\mathrm{CDCl}_{3}$ over a period of 30 minutes. As per the unit cell parameters, $\mathbf{1 5}$ crystallized in the monoclinic crystal system with the crystal space group $\mathrm{P} 2_{1} / \mathrm{n}$. The average length for a Ir-O bond is $2.106 \AA$ and for a Ir-N bond is $2.081 \AA$. The Ir-O bond lengths in $\mathbf{1 5}$ are slightly shorter than those reported in the literature (Table 12) although, other experimental bond lengths and angles for $\mathbf{1 5}$ are consistent with other $\mathrm{Ir}^{+}-\mathrm{COD}$ complexes in the literature. ${ }^{55,80,83,84}$

Table 12: Relevant bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for $\mathbf{1 5}$.

| Bond Lengths ( $\AA$ ) |  | Bond Angles ( ${ }^{\circ}$ ) |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\operatorname{Ir}(1)-\mathrm{O}(1)$ | 2.039(2) | $\mathrm{O}(1)-\operatorname{Ir}(1)-\mathrm{N}(1)$ | 89.87(10) | $\mathrm{C}(5)-\operatorname{Ir}(1)-\mathrm{C}(1)$ | 97.48(15) |
| $\operatorname{Ir}(1)-\mathrm{N}(1)$ | 2.087(3) | $\mathrm{O}(1)-\operatorname{Ir}(1)-\mathrm{C}(5)$ | 158.12(13) | $\mathrm{C}(2)-\operatorname{Ir}(1)-\mathrm{C}(1)$ | 39.24(13) |
| $\operatorname{Ir}(1)-\mathrm{C}(5)$ | 2.101(4) | $\mathrm{N}(1)-\operatorname{Ir}(1)-\mathrm{C}(5)$ | 96.61(13) | $\mathrm{O}(1)-\operatorname{Ir}(1)-\mathrm{C}(6)$ | 159.02(12) |
| $\operatorname{Ir}(1)-\mathrm{C}(2)$ | 2.108(3) | $\mathrm{O}(1)-\operatorname{Ir}(1)-\mathrm{C}(2)$ | 85.69(12) | $\mathrm{N}(1)-\operatorname{Ir}(1)-\mathrm{C}(6)$ | 100.44(13) |
| $\operatorname{Ir}(1)-\mathrm{C}(1)$ | 2.117(3) | $\mathrm{N}(1)-\operatorname{Ir}(1)-\mathrm{C}(2)$ | 161.21(13) | $\mathrm{C}(5)-\operatorname{Ir}(1)-\mathrm{C}(6)$ | 39.06(13) |
| $\operatorname{Ir}(1)-\mathrm{C}(6)$ | 2.126(4) | $\mathrm{C}(5)-\operatorname{Ir}(1)-\mathrm{C}(2)$ | 81.46(14) | $\mathrm{C}(2)-\operatorname{Ir}(1)-\mathrm{C}(6)$ | 89.85(14) |
|  |  | $\mathrm{O}(1)-\operatorname{Ir}(1)-\mathrm{C}(1)$ | 83.31(12) | $\mathrm{C}(1)-\operatorname{Ir}(1)-\mathrm{C}(6)$ | 80.32(14) |
|  |  | $\mathrm{N}(1)-\operatorname{Ir}(1)-\mathrm{C}(1)$ | 157.88(14) |  |  |



Figure 41: ORTEP representation of $\mathbf{1 5}$ (left) and cubic crystals of $\mathbf{1 5}$ (right)

### 2.7.3.1 Oxidation Addition of various substrates to $\mathbf{1 5}$ (16-18)

Iridium (I) complexes are known in the literature to perform oxidation addition reactions with relative ease with a variety of substrates. ${ }^{54,80}$ Complex 15 was tested for oxidation addition reactions with MeI, $\mathrm{HSiCl}_{3}$, and $\mathrm{HSnPh}_{3}$. The first addition to 15 was with MeI. This was done by purging a two-necked flask containing 15 and back-filling will nitrogen gas three times. After assurance of an air free atmosphere, toluene was added to dissolve 15. Once completely dissolved, a 5-fold excess of MeI was added to the flask. This mixture was left to stir under nitrogen at room temperature for 24 hours (Scheme 42). As the reaction proceeded a notable colour change occurred from bright yellow to dark red. A TLC was performed to monitor reaction progress, which showed completion conversion to a less polar substrate and disappearance of starting material. Upon completion of the reaction, the solvent and excess volatile components were removed by a rotary evaporator. When taken off the rotary evaporator, the resulting oil solidified. The brown solids were dissolved in a minimal amount of toluene and precipitated into rapidly stirring cold $n$ hexanes. The tan coloured precipitate was filtered and dried over vacuum, which was ultimately recrystallized with neat $\mathrm{C}_{6} \mathrm{D}_{6}$.


Scheme 42: Oxidative addition of MeI to 15 to give 16.

Complex 16 gives a slightly shifted IR spectrum so that the C-O stretch is at $697 \mathrm{~cm}^{-1}$ and the $\mathrm{C}=\mathrm{N} / \mathrm{C}=\mathrm{C}$ stretching band is now at $1434 \mathrm{~cm}^{-1}$. This is expected seeing as now $\mathbf{1 6}$ has a lot more electron withdrawing character about the $\mathbf{I r}$ center when compared to $\mathbf{1 5}$.

This behaviour is also observed in the ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ spectra. Upon oxidative addition of MeI, the complex becomes asymmetrical, giving each proton and carbon their own unique chemical environment. This is observed in the ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectrum where all protons on the oxazoline are diastereotopic, now splitting protons on the same carbon. In Figure 42 there is a clear splitting of the protons labeled 1 giving rise to two singlets (an apparent doublet) and at the protons labeled 2 giving rise to an ABq splitting pattern. This signal is found at $\delta_{\mathrm{H}}=3.89 \mathrm{ppm}$. This methodology can be ascertained by viewing the ${ }^{13} \mathrm{C}-\mathrm{NMR}$, where all carbons assigned to the ' COD ' ring are dissimilar giving rise to a unique resonance signal for each. All other assignments to $\mathbf{1 6}$ were made by analysis by 2D NMR spectroscopy (HSQC, COSY, nOesy). One assignment of note is the one of the proton labeled 15 in Figure 42. This assignment was not only important from a completion stand-point but also important in detailing the exact geometry of the complex.

In an oxidative addition reaction, there are three main mechanisms of how the small molecule adds to the complex; by a concerted mechanism (where bond breaking and bond forming happen simultaneously), by a non-concerted mechanism (where bond breaking and bond forming happen one after another) or by radical insertion (where the small molecule radicalizes and adds in a non-concerted manner). In the case of 16, we proposed a non-concerted reaction where either the iodide anion or the methyl ion first add to $\mathbf{1 5}$ in which the other follows. This hypothesis gives the trans addition product. This being the case as first either the iodide or methyl group will attack on face of the complex, leaving only the opposite face with room for attack, coming in separately. This is viewed also in the nOesy NMR spectrum where there is a subtle interaction between a few
of the 'COD' protons as well as the methyl's on the oxazoline (1/1a) with the methyl group (15) directly bonded to the iridium center, proving 15 lays in between both ligands (Figure 43, marked).


Figure 42: ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectrum of $\mathbf{1 6 .}$

The absolute geometry was confirmed by growing x-ray crystallography quality crystals by slow evaporation in neat $\mathrm{C}_{6} \mathrm{D}_{6}$ (Figure $\mathbf{4 4}$ ). 16 crystallized as brown needles in the monoclinic crystal system within in the $\mathrm{P} 2_{1} / \mathrm{n}$ space group. This is ascertained by the unit cell parameters. Bond angles and Ir-O, Ir-N and Ir-C bond lengths are comparable to other $\mathrm{Ir}^{+3}-\mathrm{COD}$ complexes (

Table 13). ${ }^{55,80,83,84}$


Figure 43: ${ }^{1} \mathrm{H}-{ }^{-1} \mathrm{H}$ nOesy NMR spectrum of $\mathbf{1 6}$. Marked is the $\mathrm{CH}_{3}(15)$ interactions with the oxazoline protons (1/1a).


Figure 44: ORTEP representation of 16.

Table 13: Select bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for 16.

| Bond Lengths (A) |  | Bond Angles ( ${ }^{\circ}$ ) |  | Bond Angles ( ${ }^{\circ}$ ) |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\operatorname{Ir}(1)-\mathrm{O}(1)$ | 2.0426(19) | $\mathrm{O}(1)-\operatorname{Ir}(1)-\mathrm{N}(1)$ | 91.57(8) | $\mathrm{C}(14)-\operatorname{Ir}(1)-\mathrm{C}(18)$ | 94.65(12) |
| $\operatorname{Ir}(1)-\mathrm{N}(1)$ | 2.108(2) | $\mathrm{O}(1)-\operatorname{Ir}(1)-\mathrm{C}(22)$ | 82.21(10) | $\mathrm{O}(1)-\operatorname{-r}(1)-\mathrm{C}(21)$ | 157.73(9) |
| $\operatorname{Ir}(1)-\mathrm{C}(22)$ | 2.184(3) | $\mathrm{N}(1)-\operatorname{Ir}(1)-\mathrm{C}(22)$ | 79.87(10) | $\mathrm{N}(1)-\operatorname{Ir}(1)-\mathrm{C}(21)$ | 103.83(10) |
| $\operatorname{Ir}(1)-\mathrm{C}(17)$ | 2.187(3) | $\mathrm{O}(1)-\operatorname{Ir}(1)-\mathrm{C}(17)$ | 83.47(10) | $\mathrm{C}(22)-\operatorname{Ir}(1)-\mathrm{C}(21)$ | 115.93(11) |
| $\operatorname{Ir}(1)-\mathrm{C}(14)$ | 2.191(3) | $\mathrm{N}(1)-\operatorname{Ir}(1)-\mathrm{C}(17)$ | 158.96(11) | $\mathrm{C}(17)-\operatorname{Ir}(1)-\mathrm{C}(21)$ | 87.35(11) |
| $\operatorname{Ir}(1)-\mathrm{C}(18)$ | 2.204(3) | $\mathrm{C}(22)-\operatorname{Ir}(1)-\mathrm{C}(17)$ | 79.20(12) | $\mathrm{C}(14)-\mathrm{Ir}(1)-\mathrm{C}(21)$ | 37.10(11) |
| $\operatorname{Ir}(1)-\mathrm{C}(21)$ | 2.211(3) | $\mathrm{O}(1)-\operatorname{Ir}(1)-\mathrm{C}(14)$ | 156.93(10) | $\mathrm{C}(18)-\mathrm{Ir}(1)-\mathrm{C}(21)$ | 78.67(11) |
| $\operatorname{Ir}(1)-\mathrm{I}(1)$ | 2.8598(2) | $\mathrm{N}(1)-\operatorname{Ir}(1)-\mathrm{C}(14)$ | 97.87(10) | $\mathrm{O}(1)-\mathrm{Ir}(1)-\mathrm{I}(1)$ | 85.50(6) |
|  |  | $\mathrm{C}(22)-\operatorname{Ir}(1)-\mathrm{C}(14)$ | 78.83(11) | $\mathrm{N}(1)-\operatorname{Ir}(1)-\mathrm{I}(1)$ | 81.65(6) |
|  |  | $\mathrm{C}(17)-\operatorname{Ir}(1)-\mathrm{C}(14)$ | 80.19(11) | $\mathrm{C}(22)-\operatorname{Ir}(1)-\mathrm{I}(1)$ | 157.45(8) |
|  |  | $\mathrm{O}(1)-\operatorname{Ir}(1)-\mathrm{C}(18)$ | 81.78(10) | C(17)-Ir(1)-I(1) | 118.12(9) |
|  |  | $\mathrm{N}(1)-\operatorname{lr}(1)-\mathrm{C}(18)$ | 161.82(11) | $\mathrm{C}(14)-\mathrm{Ir}(1)-\mathrm{I}(1)$ | 116.60(8) |
|  |  | $\mathrm{C}(22)-\operatorname{Ir}(1)-\mathrm{C}(18)$ | 115.62(11) | $\mathrm{C}(18)-\operatorname{Ir}(1)-\mathrm{I}(1)$ | 80.98(8) |
|  |  | $\mathrm{C}(17)-\operatorname{Ir}(1)-\mathrm{C}(18)$ | 37.21(12) | $\mathrm{C}(21)-\mathrm{Ir}(1)-\mathrm{I}(1)$ | 81.03(8) |
|  |  | $\mathrm{O}(1)-\mathrm{Ir}(1)-\mathrm{N}(1)$ | 91.57(8) | $\mathrm{C}(14)-\operatorname{Ir}(1)-\mathrm{C}(18)$ | 94.65(12) |

The second oxidation addition reaction tried upon 15 was that with $\mathrm{HSiCl}_{3}$. This reaction was carried out in a similar manner to that of $\mathbf{1 6}$. In a small round bottom flask, $\mathbf{1 5}$ was purged and back filled with nitrogen gas. To the flask, toluene was added to dissolve 15. Once fully dissolved, a 10 -fold excess of $\mathrm{HSiCl}_{3}$ was added to the reaction mixture. Upon addition of the silane species, the solution changed colour from a bright yellow to a dull beige colour as well as the appearance of an oily substance at the bottom of the reaction flask. This was stirred at room temperature for

24 hours under a constant stream of nitrogen gas (Scheme 43). It was noted that after the reaction was finished the mixture had a distinct odour, like that of COD. After completion, excess volatile components were removed in vacuo. Without further purification, the complex was dissolved in a deuterated solvent to check its progress. The beige powder which was left behind had extreme limited solubility in both $\mathrm{CDCl}_{3}$ and $\mathrm{C}_{6} \mathrm{D}_{6}$ making analysis by NMR spectroscopy tough. An overnight ${ }^{29} \mathrm{Si}$-NMR experiment was performed (14 hours) which revealed no silicon signals in the sample. Due to time constraints, further reactions of $\mathbf{1 5}$ with H -Si reagents were abandoned.


Scheme 43: Attempted oxidative addition to 15 to make 17.

The final oxidative addition reaction attempted was the addition of $\mathrm{HSnPh}_{3}$ to $\mathbf{1 5}$. Triphenylstannane, a white material $\left({ }^{119} \mathrm{Sn} \delta=-163 \mathrm{ppm}\right)$ was mixed with $\mathbf{1 5}$ and $1.0 \mathrm{ml}_{6} \mathrm{D}_{6}$ in the glovebox in a small flask. The flask, brought out of the glovebox, was filled with nitrogen gas and left undisturbed (stirring) for 24 hours under the $\mathrm{N}_{2(\mathrm{~g})}$ atmosphere. Upon completion of the reaction the solution was concentrated further under vacuum. To this, dry $n$-hexanes was added which lead to immediate precipitation of a bright yellow powder. The power was filtered, washed with cold $\mathrm{Et}_{2} \mathrm{O}$ and dried (Scheme 44). The compound was analyzed by ${ }^{119} \mathrm{Sn}$-NMR spectroscopy to confirm purity. The ${ }^{119} \mathrm{Sn}$-NMR spectrum displayed one tin resonance signal at $\delta_{\mathrm{Sn}}=-178 \mathrm{ppm}$ (Figure 45). This value is comparable to other Sn-Ir-H complexes. ${ }^{54,80}$


Scheme 44: Synthesis and oxidative addition of $\mathrm{HSnPh}_{3}$ to $\mathbf{1 5}$ to make 18.


Figure 45: $\underline{A}-{ }^{119} \mathrm{Sn}-\mathrm{NMR}$ spectrum of $\mathbf{1 8}, \underline{B}-{ }^{1} \mathrm{H}-\mathrm{NMR}$ spectrum of $\mathbf{1 8}$

In the IR spectrum, there is a notable shift in the frequency of $\mathrm{C}-\mathrm{O}\left(693 \mathrm{~cm}^{-1}\right)$ and less drastic shift in the $\mathrm{C}=\mathrm{N} / \mathrm{C}=\mathrm{C}\left(1537 \mathrm{~cm}^{-1}\right)$ stretching frequency. This is expected as $\mathbf{1 8}$ now has more electron withdrawing character around the center, making the resting state of the overall compound more neutral.

Assignments of $\mathbf{1 8}$ were made by a combination of 1 D and 2 D NMR experiments $\left({ }^{1} \mathrm{H},{ }^{13} \mathrm{C}\right.$, ${ }^{119}$ Sn, COSY, HSQC, nOesy). By looking at the 1D NMR spectra information like coupling can be deduced, not only ${ }^{1} \mathrm{H}-{ }^{1} \mathrm{H}$ coupling but also ${ }^{1} \mathrm{H}-{ }^{-119} \mathrm{Sn}$ and ${ }^{13} \mathrm{C}-{ }^{119} \mathrm{Sn}$. As was in the case of 16, 18
also experiences desymmetrization upon addition of $\mathrm{HSnPh}_{3}$, seeing the protons of the oxazoline ring being split in the same fashion (doublet for methyl groups, and an ABq for the methylene protons) as well as each 'COD' proton and carbon now giving their own resonance signal in each 1D NMR spectrum. Perhaps more interesting is the appearance of the lone hydride signal, resonating at ${ }^{1} \mathrm{H} \delta-17.40 \mathrm{ppm}$. To this signal are distinct ${ }^{1} \mathrm{H}^{-119} \mathrm{Sn}$ coupling satellites giving a coupling constant of ${ }^{2} J_{\text {cis }}=23.0 \mathrm{~Hz}$, indicating they are no longer bonded together but are instead being separated by another atom (presumably Ir). ${ }^{80}$ This behaviour is also observed in the ${ }^{13} \mathrm{C}$ NMR spectrum, in which all the ortho carbons in the $-\mathrm{SnPh}_{3}$ group can be seen coupling with a coupling constant of ${ }^{2} J_{S n-C}=17.0 \mathrm{~Hz}$. The interactions of the hydride can be monitored by nOesy NMR. The nOesy of $\mathbf{1 8}$ shows interactions of the hydride with both the methyl/methylene groups on the oxazoline and the rest of $-\mathrm{SnPh}_{3}$. Geometry proposed for $\mathbf{1 8}$ is where the hydride and Sn atoms are cis to one another, supported by nOesy-NMR spectroscopy (Figure 46). This notion was later confirmed by x-ray crystallography, indefinitely proving a cis-addition of triphenylstannane to $\mathbf{1 5}$ (Figure 47). X-ray crystallography quality crystals were grown by slow diffusion of dry n-hexanes into THF at $-30^{\circ} \mathrm{C}$ for 8 days. $\mathbf{1 8}$ crystallized as yellow cubes in the monoclinic crystal system within in the $\mathrm{P} 2_{1} / \mathrm{n}$ space group. This is ascertained by the unit cell parameters. Bond angles and Ir-O and Ir-N bond lengths as well as Ir-H and Ir-Sn bond lengths are comparable to other $\mathrm{Ir}^{+3}$ - COD complexes (Table 14)..$^{55,79,80,83-86}$


Figure 46: nOesy NMR spectrum of $\mathbf{1 8}$ (red box highlights NOE interactions)


Figure 47: ORTEP representation of 18.

Table 14: Select bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for 18.

| Bond Lengths ( $\AA$ ) |  | Bond Angles ( ${ }^{\circ}$ ) |  | Bond Angles ( ${ }^{\circ}$ ) |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\operatorname{Ir}(1)-\mathrm{N}(1)$ | 2.095(2) | $\mathrm{N}(1)-\operatorname{Ir}(1)-\mathrm{O}(1)$ | 87.95(8) | $\mathrm{N}(1)-\operatorname{Ir}(1)-\operatorname{Sn}(1)$ | 93.55(6) |
| $\operatorname{Ir}(1)-\mathrm{O}(1)$ | 2.1592(19) | $\mathrm{N}(1)-\operatorname{Ir}(1)-\mathrm{C}(18)$ | 165.61(10) | $\mathrm{O}(1)-\operatorname{Ir}(1)-\operatorname{Sn}(1)$ | 86.42(5) |
| $\operatorname{Ir}(1)-\mathrm{C}(18)$ | 2.166(2) | $\mathrm{O}(1)-\operatorname{Ir}(1)-\mathrm{C}(18)$ | 78.79(9) | $\mathrm{C}(18)-\operatorname{Ir}(1)-\operatorname{Sn}(1)$ | 91.19(7) |
| $\operatorname{Ir}(1)-\mathrm{C}(19)$ | 2.180(3) | $\mathrm{N}(1)-\operatorname{Ir}(1)-\mathrm{C}(19)$ | 155.50(10) | $\mathrm{C}(19)-\operatorname{Ir}(1)-\operatorname{Sn}(1)$ | 92.31(7) |
| $\operatorname{Ir}(1)-\mathrm{C}(14)$ | 2.294(3) | $\mathrm{O}(1)-\operatorname{Ir}(1)-\mathrm{C}(19)$ | 116.16(9) | $\mathrm{C}(14)-\operatorname{Ir}(1)-\operatorname{Sn}(1)$ | 159.20(8) |
| $\operatorname{Ir}(1)-\mathrm{C}(15)$ | 2.310(3) | $\mathrm{C}(18)-\operatorname{Ir}(1)-\mathrm{C}(19)$ | 37.39(10) | $\mathrm{C}(15)-\operatorname{Ir}(1)-\operatorname{Sn}(1)$ | 165.09(8) |
| $\operatorname{Ir}(1)-\operatorname{Sn}(1)$ | 2.6137(2) | $\mathrm{N}(1)-\operatorname{Ir}(1)-\mathrm{C}(14)$ | 86.95(9) | $\mathrm{N}(1)-\mathrm{Ir}(1)-\mathrm{H}(1 \mathrm{IR})$ | 84.6(13) |
| $\operatorname{Ir}(1)-\mathrm{H}(1 \mathrm{IR})$ | 1.37(3) | $\mathrm{O}(1)-\operatorname{Ir}(1)-\mathrm{C}(14)$ | 114.38(9) | $\mathrm{O}(1)-\mathrm{Ir}(1)-\mathrm{H}(1 \mathrm{IR})$ | 165.3(13) |
|  |  | $\mathrm{C}(18)-\operatorname{Ir}(1)-\mathrm{C}(14)$ | 93.41(10) | $\mathrm{C}(18)-\mathrm{Ir}(1)-\mathrm{H}(1 \mathrm{IR})$ | 109.6(13) |
|  |  | $\mathrm{C}(19)-\operatorname{Ir}(1)-\mathrm{C}(14)$ | 79.33(10) | $\mathrm{C}(19)-\mathrm{Ir}(1)-\mathrm{H}(1 \mathrm{IR})$ | 72.8(13) |
|  |  | $\mathrm{N}(1)-\operatorname{Ir}(1)-\mathrm{C}(15)$ | 92.83(9) | $\mathrm{C}(14)-\mathrm{Ir}(1)-\mathrm{H}(1 \mathrm{IR})$ | 78.0(13) |
|  |  | $\mathrm{O}(1)-\operatorname{lr}(1)-\mathrm{C}(15)$ | 80.36(10) | $\mathrm{C}(15)-\mathrm{Ir}(1)-\mathrm{H}(1 \mathrm{IR})$ | 112.6(13) |
|  |  | $\mathrm{C}(18)-\operatorname{Ir}(1)-\mathrm{C}(15)$ | 79.56(10) | $\mathrm{Sn}(1)-\mathrm{Ir}(1)-\mathrm{H}(1 \mathrm{IR})$ | 81.4(13) |
|  |  | $\mathrm{C}(19)-\operatorname{Ir}(1)-\mathrm{C}(15)$ | 87.41(11) | $\mathrm{O}(1)-\operatorname{Ir}(1)-\mathrm{N}(1)$ | 91.57(8) |

### 2.7.3.2 Attempted displacement of the COD ring of complex 15 (19a-e)

Attempts were also made to displace the 'COD' ligand of $\mathbf{1 5}$ with another either mono- or di-chelating nitrogen or phosphorus based nucleophiles. A series of displacement reactions were carried out on $\mathbf{1 5}$ in attempt to yield a series of novel Ir catalysts. Displacement of the 'COD' ring with TMEDA, pyridine, dppf, $\mathrm{PPh}_{3}$, and $\mathrm{P}(\mathrm{OEt})_{3}$ were attempted (Scheme 45). Unfortunately, each case gave either quantitative recovery of starting materials or an inseparable mixture of byproducts.


Scheme 45: Various attempted displacement reactions with P/N nucleophiles with 15.

### 3.0 Conclusions and Future directions:

A series of $1,5-\mathrm{N}, \mathrm{O}$-bidentate ligands (4a-1/6a-c) and their respective copper (11 compounds, 7/8) and cobalt (19 compounds, 9-11) complexes have been successfully synthesized. With regards to heavier group 9 complexes, the synthesis of three novel iridium compounds were synthesized with ligand $\mathbf{4 a}$. The explored synthetic pathways showcased the ease of tuning both the electronic and structural properties of the oxazoline-based ligand. Recrystallization from simple organic solvents gave relatively modest yields ranging from 23-99 \% for the ligands (4/6), 32-99 \% for the copper and cobalt series (7-11), and yields of 42-75 \% for the iridium containing compounds (15-18). All organic compounds were characterized by ${ }^{1} \mathrm{H}-,{ }^{13} \mathrm{C}-\mathrm{NMR}$, their melting point and EA (where applicable). All transition metal containing complexes were characterized by IR, UV-Vis, EA, MS, CV, their melting point, and x-ray crystallography where appropriate. With the characterization obtained, mainly the reversible nature of its oxidation displayed in the cyclic voltammetry, only 9 h was deemed a viable candidate for catalysis and thus was trial in the ATRP of MMA. 9h gave PMMA in $42 \%$ conversion with a PDI of 1.19 and molecular weight of $\sim 50,000$ Da. Preliminary coordination studies have been carried out with Ir and Rh centers giving compound 15 in a decent yield ( $75 \%$ ). 15 underwent oxidation addition reactions with MeI and $\mathrm{HSnPh}_{3}$. Displacement reactions were undertaken of $\mathbf{1 5}$ in attempt to replace the 'COD' ring with another ligand although all attempts were unsuccessful.

Future directions for this project would be to perfect the ARTP of MMA by changing aspects such as initiator, time, temperature and solvent. Once optimized, different monomers (such as styrene) could be polymerized. With regards to heavy group 9 complexes, the continued attempted synthesis of 'COD' displaced compounds should be tried with other nucleophiles
ligands. To complex 15, a good continuation of its oxidative properties could be the addition of $\mathrm{HSiPh}_{3}$, which has been proved to work more effectively over $\mathrm{HSiCl}_{3}$ in these types of reactions.

### 4.0 Experimental

### 4.1 General Considerations

All reagents, solvents and deuterated solvents were obtained from commercially available sources. Dry solvents were dispensed from an Mbraun solvent purification system immediately before use. Thin layer chromatography (TLC) was performed on aluminum backed sheets pre-coated with silica F254 ( 0.25 nm thick; Silicycle, Quebec, Canada) adsorbent eluting with the specified solvent system used. All preparative thin layer chromatography was performed on silica plated glassbacked plates. All TLC results were observed by either UV irradiation or iodine vapour staining. Column chromatography was carried out on 250-400 mesh size silica gel, eluting with the specified solvent system for each listed compound. Nuclear magnetic resonance spectroscopy $\left({ }^{1} \mathrm{H}\right.$ NMR $=$ $400 \mathrm{MHz},{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}=101 \mathrm{MHz},{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}-\mathrm{NMR}=161 \mathrm{MHz},{ }^{29} \operatorname{Si}\left\{{ }^{1} \mathrm{H}\right\}-\mathrm{NMR}=79 \mathrm{MHz}$, $\left.{ }^{119} \mathrm{Sn}\left\{{ }^{1} \mathrm{H}\right\}-\mathrm{NMR}=149 \mathrm{MHz}\right)$ was completed on Bruker Avance II AC-400 MHz spectrometer at 300 K in the specified deuterated solvent for each compound. Signals were picked and processed based on solvent residual ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ peaks. Proton and carbon assignments were made using a variety of 2D-NMR experiments (COSY, HSQC, HMBC, nOesy). Abbreviations used to indicate multiplicity are as followed: $\mathrm{s}=$ singlet, $\mathrm{d}=$ doublet, $\mathrm{t}=$ triplet, $\mathrm{m}=$ multiplet, $\mathrm{dd}=$ doublet of doublets, $\mathrm{td}=$ triplet of doublets, $\mathrm{ABq}=\mathrm{AB}$ quartet. Infrared spectroscopy was performed on an Agilent Cary 630 -FTIR Spectrometer in open air and have been left uncorrected. Cyclic voltammetry data was collected using a MetrOhm $\mu$-Autolab Type III potentiostat/galvanostat. All solvents (DCM) were degassed prior to analysis by cyclic voltammetry. UV-Vis absorption profiles were collected using an Agilent Cary 5000 UV-vis-NIR spectrophotometer with a cuvette with a path length of 1 cm was used. Molar extinction coefficients were calculated using the BeerLambert law. Melting points were determined in open air and in triplicate and have been left
uncorrected. The purity of all the products was confirmed by a combination of melting point, Xray and NMR spectroscopies. The growth of all metal complex single crystals was carried out in either a $1: 1$ mixture of $\mathrm{DCM} / \mathrm{MeOH}$ or by slow diffusion of $\mathrm{Et}_{2} \mathrm{O}$ into $\mathrm{CHCl}_{3}$, whereas crystal growth of all organic compounds was carried out by slow evaporation of neat acetone. A BrukerNonius Kappa-CCD diffractometer was used to collect the X-ray information crystal. This machine is equipped with monochromated $\mathrm{Mo}-\mathrm{K} \alpha$ radiation source. All x-ray crystallographic data sets were obtained and solved by Dr. Alan J. Lough and the University of Toronto. Molecular weights of polymers were determined by triple detection gel permeation chromatography (TDGPC) equipped with a Refractive Index Detector (RI), a four-capillary differential viscometer (VISC), a right-angle laser light scattering detector and a low angle laser light scattering detector. GPC columns were calibrated against polystyrene standards. HPLC grade THF was used as the mobile phase with a constant flow rate of $1 \mathrm{~mL} / \mathrm{min}$. GPC samples were made at a concentration of $5 \mathrm{mg} / \mathrm{mL}$ and diluted as per the GPC experimental method. Elemental Analysis was performed by Atlantic Microlabs in Norcross, Georgia. Toluene was used in lieu of benzene for the purposes of re-crystallization for all organic compounds (intermediates [3/5] and ligands [4/6]). The analyses of synthesized compounds which have been previously reported in the literature are comparable to their referenced literature sources. For these compounds only new data is reported (IR/NMR spectral data not included), or have information reported for comparison with data gathered in this thesis.

### 4.2 Synthesis and Characterization of Intermediates species (3a-h)


4.2.1 Synthesis of ( $E$ )-2-(3-benzoyl-4,4-dimethyloxazolidin-2-ylidene)-1-phenylethan-1-one (3a)

At room temperature 1a ( $5.0 \mathrm{~mL}, 39.2 \mathrm{mmol}$ ), $\mathrm{NEt}_{3}(14.2 \mathrm{~mL}, 101.9 \mathrm{mmol})$ and $\mathrm{ACN}(50 \mathrm{~mL})$ was added to a $250-\mathrm{mL}$ round-bottom flask. After letting the solution cool to $0^{\circ} \mathrm{C}$, benzoyl chloride $(10.0 \mathrm{~mL}, 86.2 \mathrm{mmol})$ was added dropwise via an addition funnel. The suspension was refluxed for 3 hours. Upon completion of the reaction rotary evaporator was employed to remove the solvent. The solids were diluted with $\mathrm{dH}_{2} \mathrm{O}(50 \mathrm{~mL})$ and washed with $\mathrm{DCM}(2 \times 50 \mathrm{~mL})$. The organic layer was subjected to a second wash with a $10 \%$ solution of $\mathrm{Na}_{2} \mathrm{CO}_{3(\text { aq) }}(3 \times 100 \mathrm{~mL})$. Excess solvents were removed by rotary evaporator leaving behind a sludgy orange mixture. This mixture was then recrystallized with a $2: 1$ hexane-toluene blend to reveal the product as a pale yellow solid ( $10.61 \mathrm{~g}, 84 \%$ yield). Analysis agrees with the literature data for this compound. ${ }^{20,35}$

Melting Point Range: $115-118{ }^{\circ} \mathrm{C}$ (lit: $119-120^{\circ} \mathrm{C}$ )
TLC: $45 \% \mathrm{EtOAc} / n$-hexanes, $\mathrm{R}_{\mathrm{f}}=0.13$

4.2.2 Synthesis of (Z)-2-(3-(3,4-dichlorobenzoyl)-4,4-dimethyloxazolidin-2-ylidene)-1-(3,4-dichlorophenyl)ethan-1-one (3b)

A flask was charged with $\mathbf{1 a}(3.00 \mathrm{~mL}, 23.5 \mathrm{mmol})$, THF ( 50 mL ), and $\mathrm{NEt}_{3}(10.0 \mathrm{~mL}, 71.7 \mathrm{mmol})$. After allowing the solution to cool to $0^{\circ} \mathrm{C}, 3,4$-dichlorobenzoyl chloride ( $10.9 \mathrm{~g}, 52.1 \mathrm{mmol}$ ) in THF ( 25 mL ) was added via addition funnel. The mixture was set to reflux for 3 hours. The solution was cooled to room temperature and filtered to remove the integrated salt. Following filtration, the volatile components were removed via rotary evaporator. To the resulting pale yellow solid, $\mathrm{dH}_{2} \mathrm{O}$ ( 75 mL ) was added then the solution was washed with $\mathrm{CHCl}_{3}(75 \mathrm{~mL})$. The organic components were washed one last time with a $10 \%$ solution of $\mathrm{Na}_{2} \mathrm{CO}_{3(\mathrm{aq})}(1 \times 100 \mathrm{~mL})$. Sodium sulphate was added, filtered and the volatile constituents were removed via rotary evaporator. The resulting white powder was recrystallized with a 1:2 mixture of toluene-hexane. Filtration revealed a pale yellow fluffy solid ( $6.7 \mathrm{~g}, 63 \%$ yield).

Melting Point Range: $79-82^{\circ} \mathrm{C}$
TLC: $20 \% \mathrm{EtOAc} / n$-hexanes, $\mathrm{R}_{\mathrm{f}}=0.16$
${ }^{1} \mathrm{H}-\mathrm{NMR}:\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 1.66(\mathrm{~s}, 6 \mathrm{H}, 1), 4.38(\mathrm{~s}, 2 \mathrm{H}, 3), 4.93(\mathrm{~s}, 1 \mathrm{H}, 5), 7.21-7.23(\mathrm{~m}, 1 \mathrm{H}$, $\operatorname{Ar}-\underline{\mathbf{H}})$, 7.36-7.38 (m, 1H, Ar- $\underline{\mathbf{H}}), \mathbf{7 . 5 4 - 7 . 6 5}(\mathrm{m}, 3 \mathrm{H}, \mathrm{Ar}-\underline{\mathrm{H}}), 7.85(\mathrm{~m}, 1 \mathrm{H}, \mathrm{Ar}-\underline{\mathbf{H}})$
${ }^{13}$ C-NMR: (101 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 22.8$ (1); 63.4 (2); 79.9 (5); 85.2 (3); 126.2 (Ar-H); 128.1 (ArH); 129.2 (Ar-H); 130.3 (Ar-H); 130.9 (Ar-H); 131.1 (Ar-H); 132.6 (Ar-X); 133.8 (Ar-X); 133.9 (Ar-X); 135.8 (Ar-X); 137.8 (Ar-X); 139.6 (Ar-X); 161.5 (6'); 166.2 (4); 184.1 (6)

4.2.3 (E)-2-(3-(4-methoxybenzoyl)-4,4-dimethyloxazolidin-2-ylidene)-1-(4-methoxyphenyl)ethan-1-one (3c)

A $150-\mathrm{mL}$ flask was charged with $p$-methoxybenzoic acid ( $3.10 \mathrm{~g}, 20.4 \mathrm{mmol}$ ) and $\mathrm{SOCl}_{2}(50.0$ $\mathrm{mL}, 0.689 \mathrm{~mol})$ and was refluxed $\left(90^{\circ} \mathrm{C}\right)$ for 2 hours. Volatile components were removed in vacuo. The acid chloride ( $3.48 \mathrm{~g}, 20.4 \mathrm{mmol}$ ) was not isolated and immediately used. After cooling to 0 ${ }^{\circ} \mathrm{C}, \mathbf{1 a}(1.18 \mathrm{~mL}, 9.27 \mathrm{mmol}), \mathrm{NEt}_{3}(3.88 \mathrm{~mL}, 27.81 \mathrm{mmol})$ and THF $(50 \mathrm{~mL})$ were added to the flask. The mixture was refluxed for 3 hours. Upon completion, the resultant salt was filtered off and the volatiles were removed via rotary evaporator. DCM ( 50 mL ) was added and the solution was washed with $\mathrm{dH}_{2} \mathrm{O}(50 \mathrm{~mL} \times 1)$. The organics were washed one final time with a solution of $10 \% \mathrm{Na}_{2} \mathrm{CO}_{3(\mathrm{aq})}(30 \mathrm{~mL})$ and brine $(50 \mathrm{~mL})$. Sodium sulphate was added, filtered out, and the volatile components removed via rotary evaporator. The resulting orange sludge was obtained, although not isolated. Recrystallization was carried out with a mixture of 1:2 toluene-hexane, giving a yellow powder ( $1.258 \mathrm{~g}, 35 \%$ yield). Analyses are consistent with those in the literature. ${ }^{20,87}$

Melting Point Range: $174-176{ }^{\circ} \mathrm{C}$ (lit: $175-176^{\circ} \mathrm{C}$ )
TLC: $70 \%$ EtOAc/Hexanes $\mathrm{R}_{\mathrm{f}}=0.09$

4.2.4 Synthesis of (Z)-2-(3-(3,4-dimethylbenzoyl)-4,4-dimethyloxazolidin-2-ylidene)-1-(3,4-dimethylphenyl)ethan-1-one (3d)

A $150-\mathrm{mL}$ flask was charged with 3,4-dimethylbenzoic acid (3.10 g, 20.4 mmol ), DMF ( 0.10 mL , $99 \mathrm{mg}, 1.4 \mathrm{mmol}), \mathrm{SOCl}_{2}(50.0 \mathrm{~mL}, 82.0 \mathrm{~g}, 0.689 \mathrm{~mol})$ and was refluxed for 2 hours. Volatile components were removed in vacuo. The acid chloride ( $3.48 \mathrm{~g}, 20.4 \mathrm{mmol}$ ) was not isolated and immediately used. After cooling to $0^{\circ} \mathrm{C}, \mathbf{1 a}(1.18 \mathrm{~mL}, 1.05 \mathrm{~g}, 9.27 \mathrm{mmol}), \mathrm{NEt}_{3}(3.88 \mathrm{~mL}, 2.82 \mathrm{~g}$, 27.8 mmol ) and THF ( 50 mL ) were added to the flask. The mixture was refluxed for 3 hours. Upon completion, the resultant salt was filtered off and the volatiles were removed via a rotary evaporator. The solids were diluted with $\mathrm{DCM}(50 \mathrm{~mL})$ and washed with $\mathrm{dH}_{2} \mathrm{O}(50 \mathrm{~mL} \times 1)$. Organics were washed one final time with a solution of $10 \% \mathrm{Na}_{2} \mathrm{CO}_{3(\mathrm{aq})}(30 \mathrm{~mL})$ and brine ( 50 $\mathrm{mL})$. The organic phase was dried $\left(\mathrm{Na}_{2} \mathrm{SO}_{4}\right)$, filtered, and volatile components removed via a rotary evaporator. The orange oil was recrystallized with a mixture of $1: 2$ toluene $/ n$-hexanes, giving a yellow powder ( $1.3 \mathrm{~g}, 35 \%$ yield $)$.

Melting Point Range: $122-124^{\circ} \mathrm{C}$
TLC: $20 \% \mathrm{EtOAc} / n$-hexanes, $\mathrm{R}_{\mathrm{f}}=0.11$
${ }^{\mathbf{1}} \mathbf{H}-\mathbf{N M R}:\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta \mathbf{1 . 6 8}(\mathrm{s}, 6 \mathrm{H}, \mathbf{1}), \mathbf{2 . 1 7}\left(\mathrm{s}, 3 \mathrm{H}, \mathrm{Ar}-\mathrm{CH}_{3}\right), \mathbf{2 . 2 4}\left(\mathrm{s}, 3 \mathrm{H}, \mathrm{Ar}-\mathrm{CH}_{3}\right), \mathbf{2 . 3 4}$ ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{Ar}-\mathrm{CH}_{3}$ ), 2.38 ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{Ar}-\mathrm{CH}_{3}$ ), 4.37 (s, 2H, 3), 5.12 ( $\mathrm{s}, 1 \mathrm{H}, \mathbf{5}$ ), 7.00-7.02 (m, 2H, Ar), 7.11 (dd, $J=1.5,4.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Ar}), 7.29$ (d, $J=8.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Ar})$, 7.49-7.53 (m, 2H, Ar).
${ }^{13}$ C-NMR: (101 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 19.7$ (Ar-Me); 19.7 (Ar-Me); 19.8 (Ar-Me); 20.1 (Ar-Me); 22.8 (1); 62.6 (2); 79.7 (5); 85.7 (3); 124.9 (Ar); 126.8 (Ar); 128.5 (Ar); 129.3 (Ar); 130.1 (Ar); 130.1 (Ar); 132.4 (Ar); 136.0 (Ar); 137.4 (Ar); 138.1 (Ar); 140.3 (Ar); 142.1 (Ar); 161.2 (6'); 169.1 (4); 186.8 (6)

EA: (\%): calc'd. (found) for $\mathrm{C}_{24} \mathrm{H}_{27} \mathrm{NO}_{3}$ : C 73.73 (73.93); H 7.33 (7.33); N 3.58 (3.61).

4.2.5 Synthesis of (Z)-2-(3-(4-chloro-3-methylbenzoyl)-4,4-dimethyloxazolidin-2-ylidene)-1-(4-chloro-3-methylphenyl)ethan-1-one (3e)

A flask was charged with 4-chloro-3-methylbenzoic acid (5.01 g, 29.4 mmol$)$, DMF ( $0.10 \mathrm{~mL}, 99$ $\mathrm{mg}, 1.4 \mathrm{mmol})$ and $\mathrm{SOCl}_{2}(10.0 \mathrm{~mL}, 16.4 \mathrm{~g}, 0.138 \mathrm{~mol})$ and was refluxed for 1 hour. Volatile components were removed in vacuo. 1a ( $1.70 \mathrm{~mL}, 1.51 \mathrm{~g}, 13.3 \mathrm{mmol}$ ) and THF ( 20 mL ) were added and cooled to $0^{\circ} \mathrm{C}$. The acid chloride (in THF, 20 mL ) was added dropwise to 1a-containing flask. $\mathrm{NEt}_{3}(5.90 \mathrm{~mL}, 4.38 \mathrm{~g}, 42.3 \mathrm{mmol})$ was added to the flask. The mixture was refluxed for 3 hours. The resultant salt was filtered off and the volatiles were removed via rotary evaporator. The solids were diluted with $\mathrm{DCM}(50 \mathrm{~mL})$ and washed with $\mathrm{dH}_{2} \mathrm{O}(50 \mathrm{~mL} \times 2)$. The organics were washed with a solution of $10 \% \mathrm{Na}_{2} \mathrm{CO}_{3(\text { aq })}(1 \times 70 \mathrm{~mL})$. Organics were dried $\left(\mathrm{MgSO}_{4}\right)$, filtered and the volatile constituents were removed via a rotary evaporator. The target product was recrystallized with a $1: 1$ mixture of toluene and $n$-hexanes and was isolated as an off-yellowcoloured powder ( $4.8 \mathrm{~g}, 86 \%$ yield).

Melting Point Range: $154-156^{\circ} \mathrm{C}$
TLC: $45 \% \mathrm{EtOAc} / n$-hexanes, $\mathrm{R}_{\mathrm{f}}=0.19$
${ }^{1}$ H-NMR: ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta \mathbf{1 . 6 2}(\mathrm{s}, 6 \mathrm{H}, \mathbf{1}), \mathbf{2 . 3 0}(\mathrm{s}, 3 \mathrm{H}, 13), \mathbf{2 . 4 6}\left(\mathrm{s}, 3 \mathrm{H}, 13^{\prime}\right), \mathbf{4 . 3 3}(\mathrm{s}, 2 \mathrm{H}, \mathbf{3})$, 4.95 (s, 1H, 5), $7.04\left(\mathrm{~d}, J=1.1 \mathrm{~Hz}, 1 \mathrm{H}, 8^{\prime}\right) 7.09\left(\mathrm{~d}, J=7.9 \mathrm{~Hz}, 1 \mathrm{H}, 12^{\prime}\right), 7.23(\mathrm{dd}, J=8.0,1.1 \mathrm{~Hz}$, $1 \mathrm{H}, 11$ '), 7.36 (d, $J=7.8 \mathrm{~Hz}, 1 \mathrm{H}, 8$ ), 7.49 (dd, $J=7.8,1.1 \mathrm{~Hz}, 1 \mathrm{H}, 12$ ), $7.70(\mathrm{~d}, J=1.1 \mathrm{~Hz}, 1 \mathrm{H}$, 11)
${ }^{13}$ C-NMR: (101 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 20.1$ (13); 20.5 (13'); 22.8 (1); 63.0 (2); 79.8 (5); 85.4 (3); 125.5 (11'); 127.2 (11); 127.8 (8'); 129.6 (8); 130.7 (12'); 131.4 (12); 133.5 (Ar); 134.0 (Ar); 135.2 (Ar); 139.4 (Ar); 139.6 (Ar); 141.8 (Ar); 161.4 (6'); 167.3 (4); 185.1 (6)

EA: (\%): calc'd. (found) for $\mathrm{C}_{22} \mathrm{H}_{21} \mathrm{Cl}_{2} \mathrm{NO}_{3}$ : C 61.19 (61.47); H 5.25 (5.34); N 3.24 (3.42).

4.2.6 Synthesis of (Z)-2-(3-(3-chloro-4-methylbenzoyl)-4,4-dimethyloxazolidin-2-ylidene)-1-(3-chloro-4-methylphenyl)ethan-1-one ( $\mathbf{3 f}$ )

A flask was charged with 3-chloro-4-methylbenzoic acid (5.078 g, 29.8 mmol$)$, DMF ( 0.10 mL , $99 \mathrm{mg}, 1.4 \mathrm{mmol})$ and $\mathrm{SOCl}_{2}(10.0 \mathrm{~mL}, 16.4 \mathrm{~g}, 0.138 \mathrm{~mol})$ and was refluxed for 1 hour. Volatile components were removed in vacuo. 1a ( $1.70 \mathrm{~mL}, 1.51 \mathrm{~g}, 13.3 \mathrm{mmol}$ ) and THF ( 20 mL ) were added and was cooled to $0^{\circ} \mathrm{C}$. The acid chloride ( $5.63 \mathrm{~g}, 29.8 \mathrm{mmol}$ ) was dissolved in THF (20 $\mathrm{mL})$ and added dropwise 1a-containing flask. $\mathrm{NEt}_{3}(5.90 \mathrm{~mL}, 4.50 \mathrm{~g}, 42.3 \mathrm{mmol})$ was added to the flask. The mixture was refluxed at for 3 hours. The resultant salt was filtered off and the volatiles were removed via a rotary evaporator. The solids were diluted with DCM ( 50 mL ) and washed with $\mathrm{dH}_{2} \mathrm{O}(50 \mathrm{~mL} \times 2)$. The organics were washed with a solution of $10 \% \mathrm{Na}_{2} \mathrm{CO}_{3(\mathrm{aq})}(1 \times 70$ $\mathrm{mL})$. The solution was dried $\left(\mathrm{MgSO}_{4}\right)$, filtered and the volatile constituents were removed via a rotary evaporator. The target product was recrystallized with a $1: 1$ mixture of toluene and $n$ hexanes then was isolated as a pale-yellow-coloured powder ( $3.8 \mathrm{~g}, 68 \%$ yield).

Melting Point Range: $142-145^{\circ} \mathrm{C}$
TLC: $20 \% \mathrm{EtOAc} / n$-hexanes, $\mathrm{R}_{\mathrm{f}}=0.53$
${ }^{1}$ H-NMR: ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 1.65$ (s, 6H, 1), 2.28 (s, 3H, 13), 2.43 (s, 3H, 13'), 4.35 (s, 2H, 3), 4.97 (s, 1H, 5), 7.03 (d, $\left.J=1.5 \mathrm{~Hz}, 8^{\prime}\right), 7.09$ (dd, $\left.J=8.2,1.5 \mathrm{~Hz}, \mathbf{1 2}^{`}\right), 7.22$ (d, $\left.J=8.2 \mathrm{~Hz}, 11^{\prime}\right)$, 7.47-7.52 (m, 2H, 8,12), 7.60 (s, 1H, 11)
${ }^{13}$ C-NMR: (101 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 20.0$ (13); 20.0 (13'); 22.8 (1); 79.8 (2); 85.6 (5); 126.1 (Ar-H); 127.2 (Ar-H); 127.9 (Ar-H); 129.0 (Ar-H); 129.7 (Ar-H); 129.8 (Ar-H); 131.4 (Ar); 135.9 (Ar); 137.4 (Ar); 138.7 (Ar); 139.4 (Ar); 141.6 (Ar); 161.3 (6'); 167.8 (4); 185.7 (6')

EA: (\%): calc'd. (found) for $\mathrm{C}_{22} \mathrm{H}_{21} \mathrm{Cl}_{2} \mathrm{NO}_{3}$ : C 61.19 (61.24); H 5.25 (5.46); N 3.24 (3.32).

4.2.7 (Z)-(2-(2-hydroxy-2-(naphthalen-1-yl)vinyl)-4,4-dimethyl-4,5-dihydro-314-oxazol-3$\mathrm{yl})($ naphthalen-1-yl)methanone (3g)

A flask was charged with $\mathbf{1 a}(5.0 \mathrm{~mL}, 39.19 \mathrm{mmol})$ and THF $(25 \mathrm{~mL})$. After allowing the solution to cool to $0^{\circ} \mathrm{C}$, 1-napthoyl chloride $(13.00 \mathrm{~g}, 86.22 \mathrm{mmol})$ as added to the mixture. Once added, the solution was warmed to room temperature where $\mathrm{NEt}_{3}(16.39 \mathrm{~mL}, 117.58 \mathrm{mmol})$ was then added. The mixture was set to reflux for 3 hours. Upon completed of the allotted time, the solution was cooled to room temperature and filtered to remove the integrated salt. Following filtration, the volatile components were removed via rotary evaporator. To the resulting pale yellow solid, $\mathrm{dH}_{2} \mathrm{O}$ $(50 \mathrm{~mL})$ was added then the solution was washed with $\mathrm{DCM}(50 \mathrm{~mL})$. The organic components were washed one last time with a $10 \%$ solution of $\mathrm{Na}_{2} \mathrm{CO}_{3(\mathrm{aq)}}(1 \times 60 \mathrm{~mL})$. Sodium sulphate was added, filtered and the volatile constituents were removed via rotary evaporator. The resulting yellow powder was recrystallized with a 1:1 mixture of toluene-hexane. Filtration revealed a pale yellow fluffy solid $(12.611 \mathrm{~g}, 76$ \% yield $)$. EA of this compound is pending.

Melting Point Range: $140-143^{\circ} \mathrm{C}$
TLC: $20 \% \mathrm{EtOAc} / n$-hexanes, $\mathrm{R}_{\mathrm{f}}=0.34$

4.2.8 (E)-1-(4,4-dimethyl-3-pivaloyloxazolidin-2-ylidene)-3,3-dimethylbutan-2-one. (3h) ${ }^{20,35}$

A flask was charged with $\mathbf{1 a}(2.00 \mathrm{~mL}, 15.7 \mathrm{mmol}), \mathrm{NEt}_{3}(7.00 \mathrm{~mL}, 50.2 \mathrm{mmol})$ and $\mathrm{ACN}(15$ $\mathrm{mL})$. Trimethylacetyl chloride ( $4.20 \mathrm{~mL}, 34.1 \mathrm{mmol}$ ) as added to the mixture. The mixture was set to reflux for 3 hours. Upon completed of the allotted time, the solution was cooled to room temperature and the volatile components were removed via rotary evaporator. To the resulting pale yellow solids, $\mathrm{dH}_{2} \mathrm{O}(50 \mathrm{~mL})$ was added then the solution was washed with $\mathrm{CHCl}_{3}(50 \mathrm{~mL})$. The organic components were washed one last time with a $10 \%$ solution of $\mathrm{Na}_{2} \mathrm{CO}_{3(\mathrm{aq})}(1 \times 70 \mathrm{~mL})$. Magnesium sulphate was added, filtered and the volatile constituents were removed via rotary evaporator. The resulting yellow oil was used crude and determined pure via NMR (3.849g, $87 \%$ yield). Analyses of this compound are consistent with those in the literature. ${ }^{20,35}$

Melting Point Range: $75-77{ }^{\circ} \mathrm{C}$ (lit: 75-75.5 ${ }^{\circ} \mathrm{C}$ )
TLC: $35 \% \mathrm{EtOAc} /$ Hexanes $\mathrm{R}_{\mathrm{f}}=0.28$
 2H, 3), 5.76 (s, 1H, 5)
${ }^{13}$ C-NMR: (101 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 27.2$ (8'); 27.6 (8); 28.2 (1); 37.4 (7`); 39.2 (7); 66.3 (2); 78.5 (5); 102.1 (3); 159.7 (6'); 164. 1 (4); 174.8 (6)

### 4.3 Synthesis and Characterization for the Ligand Series made with 1a


4.3.1 Synthesis of (Z)-2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-1-phenylethen-1-ol (4a)

In a $250-\mathrm{mL}$ round-bottom flask, $\mathrm{KOH}(4.233 \mathrm{~g}, 75.5 \mathrm{mmol}, 1.5 \mathrm{M})$ was dissolved in $\mathrm{MeOH}(50$ $\mathrm{mL})$ at room temperature. After fully dissolved, compound $\mathbf{3 a}(5.04 \mathrm{~g}, 15.6 \mathrm{mmol})$ was added to the mixture and was stirred for 6 hours at room temperature. Any solids were filtered off the solution. The filtrate was washed twice with DCM $(2 \times 25 \mathrm{~mL})$. The organic layer was washed again with $\mathrm{dH}_{2} \mathrm{O}(3 \times 25 \mathrm{~mL})$ and once with a solution of brine $(20 \mathrm{~mL})$. Removal of solvents was done by rotary evaporator after the addition of $\mathrm{MgSO}_{4}$ and filtration. Evaporation of excess solvents yielded a pale-yellow powder $(4.22 \mathrm{~g}, 64 \%$ yield $)$. Analyses of this compound are consistent with those in the literature..$^{20,35}$

Melting Point Range: $99-101^{\circ} \mathrm{C}$ (lit: $100.5-101^{\circ} \mathrm{C}$ )
TLC: 45 \% EtOAc/ $n$-hexanes $\mathrm{R}_{\mathrm{f}}=0.47$

4.3.2 (E)-1-(3,4-dichlorophenyl)-2-(4,4-dimethyloxazolidin-2-ylidene)ethan-1-one (4b)

In a $50-\mathrm{mL}$ round-bottom flask, $\mathrm{KOH}(2.14 \mathrm{~g}, 37.5 \mathrm{mmol}, 1.5 \mathrm{M})$ was dissolved in $\mathrm{MeOH}(25 \mathrm{~mL})$ at room temperature. After fully dissolved, compound $\mathbf{3 b}(1.04 \mathrm{~g}, 2.19 \mathrm{mmol})$ was added to the mixture and was stirred for 19 hours at room temperature. Volatile components were removed by rotary evaporator. The resulting white solid was diluted with $\mathrm{dH}_{2} \mathrm{O}(25 \mathrm{~mL})$ and washed with DCM $(1 \times 25 \mathrm{~mL})$. Organic constituents were washed once more with $\mathrm{dH}_{2} \mathrm{O}(50 \mathrm{~mL})$. Sodium sulphate was added, filtered and any volatiles removed via rotary evaporator. The target product was collected as a white, needle-like solid ( $532 \mathrm{mg}, 84 \%$ yield).

Melting Point Range: $119-121^{\circ} \mathrm{C}$
TLC: $20 \% \mathrm{EtOAc} / n$-hexanes, $\mathrm{R}_{\mathrm{f}}=0.14$
${ }^{\mathbf{1}} \mathrm{H}-\mathrm{NMR}:\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 1.43$ ( $\mathrm{s}, 6 \mathrm{H}, \mathbf{1}$ ), 4.16 ( $\mathrm{s}, 2 \mathrm{H}, 3$ ), 5.46 ( $\mathrm{s}, 1 \mathrm{H}, \mathbf{6}$ ), 7.44 (d, $J=8.25$ Hz, 1H, 12), $7.65(\mathrm{dd}, J=1.75,8.25 \mathrm{~Hz}, 1 \mathrm{H}, 13), 7.92(\mathrm{~d}, J=1.75 \mathrm{~Hz}, 1 \mathrm{H}, 9), 9.91(\mathrm{~s}, 1 \mathrm{H}, 4)$
${ }^{13}$ C-NMR: (101MHz, $\mathrm{CDCl}_{3}$ ) $\delta 27.1$ (1); 58.7 (2); 73.9 (6); 79.1 (3); 126.0 (13); 128.9 (9); 130.1 (12); 132.4 (10); 134.4 (8); 139.9 (11); 169.8 (5); 184.5 (7)

EA: (\%): calc'd. (found) for $\mathrm{C}_{13} \mathrm{H}_{13} \mathrm{Cl}_{2} \mathrm{NO}_{2}$ : C 54.57 (54.50); H 4.58 (4.51); N 4.89 (4.85).
MS: $(\mathrm{m} / \mathrm{z})$ : calc'd (found): $\left[\mathrm{M}^{+}\right]=286.12$ (286.1)

4.3.3 Synthesis of (E)-2-(4,4-dimethyloxazolidin-2-ylidene)-1-(4-methoxyphenyl)ethan-1-one (4c)

In a $100-\mathrm{mL}$ round-bottom flask, $\mathrm{KOH}(4.25 \mathrm{~g}, 75.7 \mathrm{mmol}, 1.51 \mathrm{M})$ was dissolved in $\mathrm{MeOH}(50$ mL ) at room temperature. After fully dissolved, compound $\mathbf{3 c}(1.26 \mathrm{~g}, 3.30 \mathrm{mmol})$ was added to the mixture and was stirred for 9 hours at room temperature. Any solids were filtered off the solution. Volatile components were removed by rotary evaporator. The resulting white solid was diluted with $\mathrm{dH}_{2} \mathrm{O}(50 \mathrm{~mL})$ and washed with $\mathrm{DCM}(1 \times 50 \mathrm{~mL})$. Organic constituents were washed once more with brine ( 50 mL ). Magnesium sulphate was added, filtered and any volatiles removed via rotary evaporator. The target product was collected as an orange-yellow solid ( $401 \mathrm{mg}, 49 \%$ yield). Analyses of this compound are consistent with those in the literature. ${ }^{20,88}$

Melting Point Range: $104-106^{\circ} \mathrm{C}$ (lit: $105-106{ }^{\circ} \mathrm{C}$ )
TLC: $45 \% \mathrm{EtOAc} / n$-hexanes, $\mathrm{R}_{\mathrm{f}}=0.19$

4.3.4 Synthesis of (E)-2-(4,4-dimethyloxazolidin-2-ylidene)-1-(3,4-dimethylphenyl)ethan-1-one (4d)

In a $100-\mathrm{mL}$ round-bottom flask, $\mathrm{KOH}(2.15 \mathrm{~g}, 38.3 \mathrm{mmol}, 1.53 \mathrm{M})$ was dissolved in $\mathrm{MeOH}(25.0$ mL ) at room temperature. After fully dissolved, compound $\mathbf{3 d}(0.843 \mathrm{~g}, 2.23 \mathrm{mmol})$ was added to the mixture and was stirred for 20 hours at room temperature. Any solids were filtered off the solution. Volatile components were removed by a rotary evaporator. The resulting solids were diluted with $\mathrm{dH}_{2} \mathrm{O}(50 \mathrm{~mL})$ and washed with $\mathrm{CHCl}_{3}(1 \times 50 \mathrm{~mL})$. Organic constituents were washed once more with $\mathrm{dH}_{2} \mathrm{O}(1 \times 50 \mathrm{~mL})$. The organic phase was dried $\left(\mathrm{MgSO}_{4}\right)$ filtered and volatiles removed via a rotary evaporator. The target product was collected as a pale yellow solid ( $0.300 \mathrm{~g}, 56 \%$ yield).

Melting Point Range: $149-151^{\circ} \mathrm{C}$
TLC: $35 \%$ EtOAc/Hexanes $\mathrm{R}_{\mathrm{f}}=0.18$
${ }^{1} \mathbf{H}-$ NMR: $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta \mathbf{1 . 4 2}(\mathrm{s}, 6 \mathrm{H}, \mathbf{1}), \mathbf{2 . 2 8}(\mathrm{d}, J=5.8 \mathrm{~Hz}, 6 \mathrm{H}, \mathbf{1 4 - 1 5}), 4.12(\mathrm{~s}, 2 \mathrm{H}, \mathbf{3})$, $5.56(\mathrm{~s}, 1 \mathrm{H}, 6), 7.14(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}, 12), 7.59(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}, 13), 7.64(\mathrm{~s}, 1 \mathrm{H}, 9), 9.91(\mathrm{~s}$, 1H, 4)
${ }^{13} \mathbf{C}$-NMR: (101MHz, $\mathrm{CDCl}_{3}$ ) $\delta 19.8$ (14); 19.9 (15); 27.1 (1); 58.5 (2); 73.8 (6); 73.9 (3); 124.4 (13); 128.1 (9); 129.4 (12); 136.2; 137.6; 139.5; 169.5 (5); 187.7 (7)

EA: (\%): calc'd. (found) for $\mathrm{C}_{15} \mathrm{H}_{19} \mathrm{NO}_{2}$ : C 73.44 (71.99); H 7.81 (7.64); N 5.71 (5.39).

- 0.5 Acetone was found in the lattice in elemental analysis

MS: $(\mathrm{m} / \mathrm{z})$ : calc'd (found): $\left[\mathrm{M}^{+}+\mathrm{H}\right]=245.3$ (246.4)

4.3.5 Synthesis of ( $E$ )-1-(4-chloro-3-methylphenyl)-2-(4,4-dimethyloxazolidin-2-ylidene)ethan-1-one (4e)

In a $150-\mathrm{mL}$ beaker, $\mathrm{KOH}(2.20 \mathrm{~g}, 39.2 \mathrm{mmol}, 1.57 \mathrm{M})$ was dissolved in $\mathrm{MeOH}(25.0 \mathrm{~mL})$ at room temperature. The $\mathrm{KOH} / \mathrm{MeOH}$ mixture was added to a $250-\mathrm{mL}$ flask containing $\mathbf{3 e}$ ( $1.51 \mathrm{~g}, 3.60$ mmol ) was added to the mixture and was stirred for 6 hours at room temperature. Volatile components were removed by a rotary evaporator. The resulting solids were diluted with dH 2 O $(50 \mathrm{~mL})$ and washed with $\mathrm{DCM}(1 \times 50 \mathrm{~mL})$. Organic constituents were washed once more with $\mathrm{dH}_{2} \mathrm{O}(1 \times 100 \mathrm{~mL})$. Magnesium sulphate was added to dry the solution. The mixture was then filtered and the volatile constituents were removed via a rotary evaporator. The orange oil was recrystallized with a mixture containing 1:4 toluene/ $n$-hexanes. The target product was collected as a pale yellow-coloured solid $(0.588 \mathrm{~g}, 69$ \% yield $)$.

Melting Point Range: $127-129^{\circ} \mathrm{C}$
TLC: $45 \% \mathrm{EtOAc} / n$-hexanes, $\mathrm{R}_{\mathrm{f}}=0.30$
${ }^{1}$ H-NMR: ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 1.42$ ( $\mathrm{s}, 6 \mathrm{H}, \mathbf{1}$ ), 2.37 ( $\mathrm{s}, 3 \mathrm{H}, 14$ ), 4.14 ( $\mathrm{s}, 2 \mathrm{H}, 3$ ), 5.49 ( $\mathrm{s}, 1 \mathrm{H}, \mathbf{6}$ ), 7.22 (d, $J=7.9 \mathrm{~Hz}, 1 \mathrm{H}, 12), 7.61(\mathrm{dd}, J=7.9,1.7 \mathrm{~Hz}, 1 \mathrm{H}, 13), 7.81(\mathrm{~d}, J=1.7 \mathrm{~Hz}, 1 \mathrm{H}, 9), 9.79$ (s, 1H, 4)
${ }^{13}$ C-NMR: 20.2 (14); 27.2 (1); 58.7 (2); 73.9 (6); 79.1 (3); 125.1 (9); 127.7 (13); 130.8 (12); 134.4 (10); 138.6 (8), 139.4 (11); 169.8 (5); 185.9 (7)

EA: (\%): calc'd. (found) for $\mathrm{C}_{14} \mathrm{H}_{16} \mathrm{ClNO}_{2}$ : C 63.28 (63.47); H 6.07 (5.97); N 5.27 (5.17).
MS: $(\mathrm{m} / \mathrm{z})$ : calc'd (found): $\left[\mathrm{M}^{+}+\mathrm{H}\right]=265.7$ (266.1)

4.3.6 Synthesis of ( $E$ )-1-(3-chloro-4-methylphenyl)-2-(4,4-dimethyloxazolidin-2-ylidene)ethan-1-one (4f)

In a $100-\mathrm{mL}$ round-bottom flask, $\mathrm{KOH}(4.53 \mathrm{~g}, 80.5 \mathrm{mmol}, 1.61 \mathrm{M})$ was dissolved in $\mathrm{MeOH}(50.0$ $\mathrm{mL})$ at room temperature. $3 \mathrm{Hf}(2.01 \mathrm{~g}, 4.80 \mathrm{mmol})$ was added to the mixture and was stirred for 16 hours at room temperature. Volatile components were removed by a rotary evaporator. The solid was diluted with $\mathrm{dH} 2 \mathrm{O}(50 \mathrm{~mL})$ and washed with DCM $(2 \times 50 \mathrm{~mL})$. Organic constituents were washed once more with dH2O $(1 \times 100 \mathrm{~mL})$. Magnesium sulphate was added to dry the solution. The mixture was then filtered and the volatile constituents were removed via a rotary evaporator. The target product was collected as a pinkish-coloured solid ( $0.62 \mathrm{~g}, 49 \%$ yield).

Melting Point Range: $143-145^{\circ} \mathrm{C}$
TLC: $45 \% \mathrm{EtOAc} / n$-hexanes, $\mathrm{R}_{\mathrm{f}}=0.28$
${ }^{1}$ H-NMR: ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 1.41$ ( $\mathrm{s}, 6 \mathrm{H}, \mathbf{1}$ ), $2.39(\mathrm{~s}, 3 \mathrm{H}, 14), 4.13(\mathrm{~s}, 2 \mathrm{H}, 3), 5.50(\mathrm{~s}, 1 \mathrm{H}, 6)$, $7.33(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}, 9), 7.59(\mathrm{dd}, J=8.3,1,8 \mathrm{~Hz}, 1 \mathrm{H}, 13) 7.71(\mathrm{~d}, J=1.8 \mathrm{~Hz}, 1 \mathrm{H}, 12), 9.93(\mathrm{~s}$, 1H, 4)
${ }^{13}$ C-NMR: (101MHz, $\mathrm{CDCl}_{3}$ ) $\delta 20.2$ (14); 27.1 (1); 58.6 (2); 73.9 (6); 79.0 (3); 125.6 (13); 128.8 (9); 129.4 (12); 135.7 (10); 136.7 (8); 138.5 (11); 169.6 (5); 186.4 (7)

EA: (\%): calc'd. (found) for $\mathrm{C}_{14} \mathrm{H}_{16} \mathrm{ClNO}_{2}$ : C 63.28 (63.17); H 6.07 (5.97); N 5.27 (5.19).
MS: $(\mathrm{m} / \mathrm{z})$ : calc'd (found): $\left[\mathrm{M}^{+}\right]=265.7$ (265.8)

4.3.7 Synthesis of (E)-2-(4,4-dimethyloxazolidin-2-ylidene)-1-(naphthalen-1-yl)ethan-1-one ( $\mathbf{4 g}$ )

In a $150-\mathrm{mL}$ beaker, $\mathrm{KOH}(4.52 \mathrm{~g}, 80.7 \mathrm{mmol}, 1.46 \mathrm{M})$ was dissolved in $\mathrm{MeOH}(55 \mathrm{~mL})$ at room temperature. The $\mathrm{KOH} / \mathrm{MeOH}$ mixture was added to a $100-\mathrm{mL}$ flask containing $\mathbf{3 g}(10.18 \mathrm{~g}, 24.08$ mmol ) was added to the mixture and was stirred for 16 hours at room temperature. Volatile components were removed by rotary evaporator. The resulting solids were diluted with $\mathrm{dH}_{2} \mathrm{O}$ ( 50 $\mathrm{mL})$ and washed with $\mathrm{DCM}(2 \times 50 \mathrm{~mL})$. Organic constituents were washed once more with $\mathrm{dH}_{2} \mathrm{O}$ $(1 \times 100 \mathrm{~mL})$. Magnesium sulphate was added, filtered and any volatiles removed via rotary evaporator. The orange gel was purified via flash column chromatography with a solvent mixture containing 1:1 ethyl acetate/hexanes. The target product was collected as either a pale yellow solid or white solid ( $1.5 \mathrm{~g}, 23 \%$ yield).

Melting Point Range: $129-132^{\circ} \mathrm{C}$
TLC: $50 \% \mathrm{EtOAc} / n$-Hexanes, $\mathrm{R}_{\mathrm{f}}=0.29$
${ }^{1} \mathrm{H}-\mathrm{NMR}:\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 1.46(\mathrm{~s}, 6 \mathrm{H}, 1), 4.14(\mathrm{~s}, 2 \mathrm{H}, 3), 5.36(\mathrm{~s}, 1 \mathrm{H}, \mathbf{6}), \mathbf{7 . 4 3 - 7 . 5 7}(\mathrm{m}, 3 \mathrm{H}$, $11,13,16), 7.63(\mathrm{~d}, J=7.0 \mathrm{~Hz}, 1 \mathrm{H}, 12) 7.85(\mathrm{~d}, J=7.7 \mathrm{~Hz}, 2 \mathrm{H}, 15,17), 8.48(\mathrm{~d}, J=8.20,1 \mathrm{H}, 10)$ 9.93 (s, 1H, 4)
${ }^{13}$ C-NMR: 27.2 (1); 58.6 (2); 78.8 (6); 79.0 (3); 124.9 (Ar); 125.1 (12); 125.8 (Ar); 126.3 (Ar) 126.3 (10); 128.1 (15/17); 129.5 (15/17); 130.3 (14); 133.8 (9); 140.6 (8); 169.1 (5); 191.6 (7)

EA: (\%): calc'd. (found) for $\mathrm{C}_{17} \mathrm{H}_{17} \mathrm{NO}_{2}$ : C 76.38 (76.29); H 6.41 (6.35); N 5.24 (5.11).
MS: $(\mathrm{m} / \mathrm{z})$ : calc'd (found): $\left[\mathrm{M}^{+}\right]=258.1$ (258.0)

4.3.8 Synthesis of (E)-1-(4,4-dimethyloxazolidin-2-ylidene)-3,3-dimethylbutan-2-one (4h)

In a $150-\mathrm{mL}$ beaker, $\mathrm{KOH}(8.537 \mathrm{~g}, 152.0 \mathrm{mmol}, 1.20 \mathrm{M})$ was dissolved in $\mathrm{MeOH}(100 \mathrm{~mL})$ at room temperature. The $\mathrm{KOH} / \mathrm{MeOH}$ mixture was added to a $100-\mathrm{mL}$ flask containing $\mathbf{3 h}$ (10.99 $\mathrm{g}, 39.05 \mathrm{mmol}$ ) was added to the mixture and stirred for 18 hours at room temperature. Volatile components were removed via rotary evaporator. The resulting solid mass was diluted with $\mathrm{dH}_{2} \mathrm{O}$ ( 60 mL ) and washed with $\mathrm{CHCl}_{3}(2 \times 60 \mathrm{~mL})$. Organic constituents were washed once more with $\mathrm{dH}_{2} \mathrm{O}(1 \times 120 \mathrm{~mL})$. Magnesium sulphate was added, filtered and any volatiles removed via rotary evaporator. The crude off-white powder was recrystallized with a mixture of 1:4 toluene/hexanes to afford white needle-like crystals. $(7.3 \mathrm{~g}, 94 \%$ yield). Analyses of this compound are consistent with those in the literature. ${ }^{20,35}$

Melting Point Range: $94-95^{\circ} \mathrm{C}$ (lit: $94.5-95{ }^{\circ} \mathrm{C}$ )
TLC: 45 \% EtOAc/Hexanes $\mathrm{R}_{\mathrm{f}}=0.49$

4.3.9 Synthesis of ( $E$ )-1-(4,4-dimethyloxazolidin-2-ylidene)propan-2-one ( $\mathbf{4} \mathbf{j}$ )

A Schlenk flask was charged with dry THF ( 50.0 mL ) and $\mathbf{1 a}(10.0 \mathrm{~mL}, 8.87 \mathrm{~g}, 78.4 \mathrm{mmol})$ and cooled to $-84{ }^{\circ} \mathrm{C}$. Once cooled, $n$ - $\mathrm{BuLi}(1.0 \mathrm{M}$ in $n$-hexanes, $60.0 \mathrm{~mL}, 90.0 \mathrm{mmol})$ was added dropwise over 45 minutes. As the solution stirred overnight ( $\sim 18$ hours), the colour turned from a pale yellow to a vibrant, deep yellow. The solution was cooled back down to $-84^{\circ} \mathrm{C}$, after which EtOAc ( $15.0 \mathrm{~mL}, 13.5 \mathrm{~g}, 153 \mathrm{mmol}$ ) in THF ( 10 mL ) was added dropwise to the stirring solution. The mixture was stirred for 2 hours where it gradually warmed to room temperature, where it turned a dark orange colour, before quenching with degassed $\mathrm{dH}_{2} \mathrm{O}$. It was washed with $\mathrm{Et}_{2} \mathrm{O}$ (100 $\mathrm{mL} \times 2$ ). Magnesium sulphate was added to dry the solution. The mixture was then filtered and the volatile constituents were removed via a rotary evaporator. This left behind crude mixture of $4 \mathbf{j}$ and the dimer (above). The mixture was stirred at $60^{\circ} \mathrm{C}$ in $\mathrm{dH}_{2} \mathrm{O}$ for 4 hours. After cooling to room temperature, the mixture was washed with $\mathrm{Et}_{2} \mathrm{O}(60 \mathrm{~mL} \times 2)$. Magnesium sulphate was added to dry the solution. The mixture was then filtered and the volatile constituents were removed via a rotary evaporator. The solids were rinsed with cold $n$-heptanes and separated to reveal $\mathbf{4} \mathbf{j}(2.5 \mathrm{~g}$, $20 \%$ yield). Analyses of this compound are consistent with those in the literature. ${ }^{34,36}$

Melting Point Range: $123-126^{\circ} \mathrm{C}$ (lit: $125-127^{\circ} \mathrm{C}$ )
 3.39 (s, 2H, $3^{\prime}$ ), 3.98 ( $\mathrm{s}, 2 \mathrm{H}, 6^{\prime}$ ), 4.07 ( $\mathrm{s}, 2 \mathrm{H}, 3$ ), 4.87 ( $\mathrm{s}, 1 \mathrm{H}, 6$ ), 9.47 ( $\mathrm{s}, 1 \mathrm{H}, 4$ )
${ }^{13} \mathbf{C}-\mathbf{N M R}:\left(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 27.0$ (1); 28.2 (1'); 28.7 (8); 29.5 (8'); 43.6 (6'); 58.3 (2); 67.4 (2'); 76.9 (6); 78.7 (3'); 79.5 (3); 159.9 (5'); 168.3 (5) 194.2 (7); 201.5 (7$)$

4.3.10 Synthesis of ( $E$ )-3-(4,4-dimethyloxazolidin-2-ylidene)-1,1,1-trifluoropropan-2-one ( $\mathbf{4 k}$ )

A round-bottom flask was charged with $\mathbf{1 a}(2.00 \mathrm{~mL}, 1.77 \mathrm{~g}, 15.7 \mathrm{mmol})$, py $(7.60 \mathrm{~mL}, 7.46 \mathrm{~g}$, $94.4 \mathrm{mmol})$ and $\mathrm{ACN}(10.0 \mathrm{~mL})$ and cooled to $0^{\circ} \mathrm{C}$. In a separate round-bottom flask, TFAA (4.80 $\mathrm{mL}, 7.15 \mathrm{~g}, 34.1 \mathrm{mmol})$ and $\mathrm{ACN}(10.0 \mathrm{~mL})$ were cooled to $0^{\circ} \mathrm{C}$. Once cooled, the anhydride was transferred to the oxazoline containing flask via dropwise addition over a period of 10 minutes. The reaction was stirred at $0{ }^{\circ} \mathrm{C}$ for a period of 6 hours, periodically replacing the cold bath. Upon completion, excess volatile components were removed via a rotary evaporator. The resulting sludge was dissolved in brine $(30 \mathrm{~mL})$ and washed with $\mathrm{DCM}(2 \times 30 \mathrm{~mL})$ and additionally once with brine ( 60 mL ). Magnesium sulphate was added to dry the solution. The mixture was then filtered and the volatile constituents were removed via a rotary evaporator. The mixture was dissolved in a minimal amount of hot $n$-hexanes. Once cooled, the target product was revealed as a fluffy white powder ( $2.1 \mathrm{~g}, 64 \%$ yield $)$. Analyses of this compound are consistent with those in the literature. ${ }^{8}$

Melting Point Range: $140-142^{\circ} \mathrm{C}$ (lit: $141-142{ }^{\circ} \mathrm{C}$ )
${ }^{\mathbf{1}} \mathrm{H}-\mathrm{NMR}:\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta \mathbf{1 . 4 3}(\mathrm{s}, 6 \mathrm{H}, \mathbf{1}), 4.19(\mathrm{~s}, 2 \mathrm{H}, 3), 5.16(\mathrm{~s}, 1 \mathrm{H}, \mathbf{6}), 9.86(\mathrm{~s}, 1 \mathrm{H}, 4)$
${ }^{19}$ F-NMR: $\left(376 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta-76.4(9,3 \mathrm{~F})$
${ }^{13}$ C-NMR: (101 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta 26.6$ (1); 59.7 (2); 72.6 (6); 79.8 (3); $117.9\left(\mathbf{q}, J_{F-C}=288.5 \mathrm{~Hz}\right.$, 8); 170.3 (5); $175.3\left(\mathbf{q}, J_{F-C}=33.0 \mathrm{~Hz}, 7\right)$

4.3.11 Synthesis of (E)-1,1,1-trichloro-3-(4,4-dimethyloxazolidin-2-ylidene)propan-2-one (4I)

A round-bottom flask was charged with $\mathbf{1 a}(2.00 \mathrm{~mL}, 1.77 \mathrm{~g}, 15.7 \mathrm{mmol})$, pyridine ( $2.80 \mathrm{~mL}, 2.75$ $\mathrm{g}, 34.8 \mathrm{mmol})$ and $\mathrm{ACN}(10.0 \mathrm{~mL})$ and cooled to $0^{\circ} \mathrm{C}$. In a separate round-bottom flask, TCAC ( $3.80 \mathrm{~mL}, 6.16 \mathrm{~g}, 33.9 \mathrm{mmol}$ ) and $\mathrm{ACN}(10.0 \mathrm{~mL})$ were cooled to $0^{\circ} \mathrm{C}$. Once cooled, the acid chloride was transferred to the oxazoline containing flask via dropwise addition over a period of 10 minutes. The reaction was stirred at $0^{\circ} \mathrm{C}$ for a period of 6 hours, periodically replacing the cold bath. Upon completion, excess volatile components were removed in vacuo. The resulting sludge was dissolved in $\mathrm{dH}_{2} \mathrm{O}(40 \mathrm{~mL})$ and washed with $\mathrm{DCM}(2 \times 40 \mathrm{~mL})$. Magnesium sulphate was added to dry the solution. The mixture was then filtered and the volatile constituents were removed via a rotary evaporator. The mixture was washed with hot $n$-hexanes. Once cooled, the target product was revealed as a fluffy white powder $(1.1 \mathrm{~g}, 25 \%$ yield $)$. Analyses of this compound are consistent with those in the literature. ${ }^{8}$

Melting Point Range: $140-142^{\circ} \mathrm{C}$ (lit: $142-144{ }^{\circ} \mathrm{C}$ )
${ }^{\mathbf{1}} \mathrm{H}-\mathrm{NMR}:\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta \mathbf{1 . 4 5}(\mathrm{s}, 6 \mathrm{H}, \mathbf{1}), 4.23(\mathrm{~s}, 2 \mathrm{H}, 3), 5.55(\mathrm{~s}, 1 \mathrm{H}, \mathbf{6}), 9.35(\mathrm{~s}, 1 \mathrm{H}, 4)$
${ }^{13}$ C-NMR: (101 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 27.2$ (1); 59.1 (2); 69.8 (6); 79.8 (3); 97.2 (8); 170.9 (5); 181.1 (7)

### 4.4 Synthesis of the ligand series with 1b


4.4.1 Synthesis of ( $E$ )-2-(oxazolidin-2-ylidene)-1-phenylethan-1-one (5a to 6a);

A flask was charged with $\mathbf{1 b}(5.06 \mathrm{~mL}, 5.03 \mathrm{~g}, 59.1 \mathrm{mmol})$, THF ( 20 mL ) and $\mathrm{NEt}_{3}(20.6 \mathrm{~mL}, 14.9$
$\mathrm{g}, 148 \mathrm{mmol})$. The solution was cooled to $0^{\circ} \mathrm{C}$, benzoyl chloride ( $15.1 \mathrm{~mL}, 18.3 \mathrm{~g}, 130 \mathrm{mmol}$ ) was added. The mixture was refluxed for 3 hours. The solution was cooled to room temperature, the salt was filtered and the volatile components were removed via a rotary evaporator. $\mathrm{dH}_{2} \mathrm{O}(50$ $\mathrm{mL})$ was added, and the solution was washed with $\mathrm{CHCl}_{3}(2 \times 50 \mathrm{~mL})$. The organics were washed with a $10 \%$ solution of $\mathrm{Na}_{2} \mathrm{CO}_{3(\mathrm{aq})}(1 \times 100 \mathrm{~mL})$. The organic phase was dried $\left(\mathrm{Na}_{2} \mathrm{SO}_{4}\right)$, filtered and the volatile constituents removed via a rotary evaporator. $\mathrm{KOH}(7.31 \mathrm{~g}, 130 \mathrm{mmol}, 2.17 \mathrm{M})$ was dissolved in $\mathrm{MeOH}(60 \mathrm{~mL})$ and added to $\mathbf{5 a}(0.20 \mathrm{~g}, 0.44 \mathrm{mmol})$. The contents were stirred for 16 hours at room temperature. Volatile components were removed via a rotary evaporator. $\mathrm{dH}_{2} \mathrm{O}(50 \mathrm{~mL})$ was added and washed with $\mathrm{DCM}(2 \times 50 \mathrm{~mL})$ and washed with $\mathrm{dH}_{2} \mathrm{O}(1 \times 100$ $\mathrm{mL})$. The solution was dried $\left(\mathrm{Na}_{2} \mathrm{SO}_{4}\right)$, filtered and the volatile constituents removed via a rotary evaporator. The gel was purified with column chromatography eluting with $2: 1$ acetone $/ n$-hexanes. The target product was collected as pinkish-white solids ( $3.66 \mathrm{~g}, 33.0 \%$ yield). Analyses of this compound are consistent with those in the literature. ${ }^{9,40}$

Melting Point Range: $105-107{ }^{\circ} \mathrm{C}$ (lit: $105-106^{\circ} \mathrm{C}$ )
TLC: $40 \%$ acetone $/ n$-hexanes, $\mathrm{R}_{\mathrm{f}}=0.30$
${ }^{1} \mathbf{H}-$ NMR: $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta \mathbf{3 . 8 2}(\mathrm{t}, J=8.5 \mathrm{~Hz}, 2 \mathrm{H}, \mathbf{1}), \mathbf{4 . 4 9}(\mathrm{t}, J=8.5 \mathrm{~Hz}, 2 \mathrm{H}, \mathbf{2}), \mathbf{5 . 6 4}(\mathrm{s}, 1 \mathrm{H}$, 5), 7.39-7.41 (m, 3H, 9-10), 7.87 (dd, $J=7.5,1.0 \mathrm{~Hz}, 2 \mathrm{H}, 8), \mathbf{1 0 . 0 0}(\mathrm{s}, 1 \mathrm{H}, 3)$
${ }^{13}$ C-NMR: (101MHz, $\mathrm{CDCl}_{3}$ ) $\delta 43.2$ (1); 67.5 (2), 74.3 (5); 127.0 (8); 128.3 (9); 130.7 (10); 140.1 (7); 170.9 (4); 187.8 (6)

4.4.2 Synthesis of ( $E$ )-1-(3,4-dichlorophenyl)-2-(oxazolidin-2-ylidene)ethan-1-one ( $\mathbf{5 b}$ to $\mathbf{6 b}$ ) A flask was charged with $\mathbf{1 b}(2.00 \mathrm{~mL}, 2.01 \mathrm{~g}, 23.4 \mathrm{mmol})$ and THF ( 45 mL ). The solution was cooled to $0^{\circ} \mathrm{C}$, 3,4-dichlorobenzoyl chloride ( $10.63 \mathrm{~g}, 50.73 \mathrm{mmol}$ ) was added. $\mathrm{NEt}_{3}(10.00 \mathrm{~mL}$, $7.260 \mathrm{~g}, 71.75 \mathrm{mmol}$ ) was added and was refluxed for 3 hours. The solution was cooled to room temperature, the salt filtered and the volatile components were removed via a rotary evaporator. $\mathrm{dH}_{2} \mathrm{O}(50 \mathrm{~mL})$ was added, and the solution was washed with $\mathrm{CHCl}_{3}(2 \times 50 \mathrm{~mL})$. The organics were washed with a $10 \%$ solution of $\mathrm{Na}_{2} \mathrm{CO}_{3(\mathrm{aq})}(1 \times 100 \mathrm{~mL})$. The solution was dried $\left(\mathrm{Na}_{2} \mathrm{SO}_{4}\right)$, filtered and volatile constituents were removed via a rotary evaporator (10.13 g). KOH ( 2.30 g , $40.9 \mathrm{mmol}, 1.64 \mathrm{M})$ was dissolved in $\mathrm{MeOH}(25 \mathrm{~mL})$ and added to $\mathbf{5 b}(0.20 \mathrm{~g}, 0.44 \mathrm{mmol})$. The contents were stirred for 3 hours at room temperature. The solids were diluted with $\mathrm{dH}_{2} \mathrm{O}(50 \mathrm{~mL})$ and washed with $\mathrm{DCM}(2 \times 50 \mathrm{~mL})$. Organics were washed with $\mathrm{dH}_{2} \mathrm{O}(1 \times 100 \mathrm{~mL})$. The solution was dried $\left(\mathrm{Na}_{2} \mathrm{SO}_{4}\right)$, filtered and volatile constituents were removed via a rotary evaporator. The gel was recrystallized with a mixture of 1:4 toluene/ $n$-hexanes to collect a pale yellow solid (110 mg, 92 \% yield).

TLC: 45 \% EtOAc $/ n$-hexanes $\mathrm{R}_{\mathrm{f}}=0.07$
${ }^{1} \mathbf{H}-\mathrm{NMR}:\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta \mathbf{3 . 8 3}(\mathrm{t}, J=8.5 \mathrm{~Hz}, 2 \mathrm{H}, \mathbf{1}), 4.52(\mathrm{t}, J=8.5 \mathrm{~Hz}, 2 \mathrm{H}, 2), 5.53(\mathrm{~s}, 1 \mathrm{H}$, 5), 7.44 (d, $J=8.5 \mathrm{~Hz}, 1 \mathrm{H}, 11), 7.65(\mathrm{dd}, J=2.0,8.5 \mathrm{~Hz}, 1 \mathrm{H}, 12), 7.92(\mathrm{~d}, J=2.0 \mathrm{~Hz}, \mathrm{H}, 8), 9.94$ (s, 1H, 4)
${ }^{13}$ C-NMR: 43.2 (1); 67.8 (2); 74.2 (5); 126.2 (12); 129.1 (8); 130.3 (11); 132.66 (Ar); 134.7 (Ar); 140.0 (7); 171.2 (3); 184.9 (6)

EA: (\%): calc'd. (found) for $\mathrm{C}_{11} \mathrm{H}_{9} \mathrm{Cl}_{2} \mathrm{NO}_{2}$ : C 51.19 (49.92); H 3.51 (3.39); N 5.43 (5.25). 0.5 water molecules found in the lattice in elemental analysis

4.4.3 Synthesis of (E)-1-(4-methoxyphenyl)-2-(oxazolidin-2-ylidene)ethan-1-one (5c to $\mathbf{6 c}$ )

A flask was charged with $\mathbf{1 b}(2.00 \mathrm{~mL}, 2.01 \mathrm{~g}, 23.4 \mathrm{mmol})$ and THF ( 40 mL ). The solution was to cooled to $0^{\circ} \mathrm{C}$, $p$-methoxybenzoyl chloride $(7.01 \mathrm{~g}, 51.9 \mathrm{mmol})$ was added. $\mathrm{NEt}_{3}(10.00 \mathrm{~mL}$, $7.260 \mathrm{~g}, 71.75 \mathrm{mmol}$ ) was added and was refluxed for 3 hours. The solution was cooled to room temperature, the salt filtered and volatile components were removed via a rotary evaporator. $\mathrm{dH}_{2} \mathrm{O}$ ( 50 mL ) was added and was washed with $\mathrm{CHCl}_{3}(2 \times 50 \mathrm{~mL})$. The organics were washed with a $10 \%$ solution of $\mathrm{Na}_{2} \mathrm{CO}_{3(\mathrm{aq})}(1 \times 100 \mathrm{~mL})$. The solution was dried $\left(\mathrm{Na}_{2} \mathrm{SO}_{4}\right)$, filtered and volatile constituents were removed via a rotary evaporator ( 8.34 g ). $\mathrm{KOH}(2.26 \mathrm{~g}, 40.2 \mathrm{mmol}, 1.61 \mathrm{M})$ was dissolved in $\mathrm{MeOH}(25 \mathrm{~mL})$ at room temperature and was added to a $100-\mathrm{mL}$ flask containing $\mathbf{5 c}$ ( $8.34 \mathrm{~g}, 23.4 \mathrm{mmol}$ ). The contents were stirred for 3 hours at room temperature. The solids were diluted with $\mathrm{dH}_{2} \mathrm{O}(50 \mathrm{~mL})$ and washed with $\mathrm{DCM}(2 \times 50 \mathrm{~mL})$. Organic constituents were washed once more with $\mathrm{dH}_{2} \mathrm{O}(1 \times 100 \mathrm{~mL})$. The organic phase was dried $\left(\mathrm{Na}_{2} \mathrm{SO}_{4}\right)$, filtered and the volatile constituents were removed via a rotary evaporator. The oil was purified via column chromatography eluting with $30 \% \mathrm{EtOAc} / n$-hexanes. The target was collected a pale yellow solid $\left(0.63 \mathrm{mg}, 12 \%\right.$ yield). Analyses of this compound are consistent with those in the literature. ${ }^{38,39}$

TLC: $45 \% \mathrm{EtOAc} / n$-hexanes $\mathrm{R}_{\mathrm{f}}=0.12$
${ }^{1} H-N M R:\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta \mathbf{3 . 8 0 - 3 . 8 8}(\mathrm{m}, 5 \mathrm{H}, \mathbf{1 , 1 3}), 4.50(\mathrm{t}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}, 2), \mathbf{5 . 6 0}(\mathrm{s}, 1 \mathrm{H}$, 5), $\mathbf{6 . 8 9}$ (dt, $J=3.0,9.0 \mathrm{~Hz}, 2 \mathrm{H}, \mathbf{9}, 11$ ), 7.83 (dt, $J=3.0,9.0 \mathrm{~Hz}, 1 \mathrm{H}, 8,12$ ), 9.94 (s, $1 \mathrm{H}, 4$ )
${ }^{13}$ C-NMR: (101 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 43.2$ (1); 55.5 (13); 67.5 (2); 73.7 (5); 113.5 (9,11); 128.8 (8,12); 132.8 (10); 161.9 (7); 170.7 (3); 187.2 (6)

4.4.4 Attempted Synthesis of ( $E$ )-1-(4-nitrophenyl)-2-(oxazolidin-2-ylidene)ethan-1-one ( $\mathbf{5 d} / \mathbf{6 d}$ ) A flask was charged with $\mathbf{1 b}(1.00 \mathrm{~mL}, 1.01 \mathrm{~g}, 11.8 \mathrm{mmol})$, $\mathrm{NEt}_{3}(5.00 \mathrm{~mL}, 3.63 \mathrm{~g}, 35.9 \mathrm{mmol})$ and dry THF ( 20 mL ). p-Nitrobenzoyl chloride ( $4.891 \mathrm{~g}, 26.36 \mathrm{mmol}$ ) was dissolved in dry THF $(30 \mathrm{~mL})$ and added dropwise to the stirring $\mathbf{1 b}$-mixture. The reaction was set to reflux for 3 hours. The solution was cooled to room temperature where the incorporated salt was removed by filtration and the volatile components were removed via a rotary evaporator. To the resulting brown sludge, $\mathrm{dH}_{2} \mathrm{O}(50 \mathrm{~mL})$ was added then the solution was washed with $\mathrm{DCM}(2 \times 50 \mathrm{~mL})$. The organic components were washed one last time with a $5 \%$ solution of $\mathrm{Na}_{2} \mathrm{CO}_{3(\mathrm{aq})}(1 \times 100 \mathrm{~mL})$. Magnesium sulphate was added to dry the solution. The mixture was then filtered and the volatile constituents were removed via a rotary evaporator. The resulting orange sludge was purified via column chromatography eluting with $2: 1$ acetone $/ n$-hexanes. The resulting white powder ( 434 mg , 1.13 mmol ) was dissolved in $\mathrm{MeOH}(55 \mathrm{~mL})$ and $\mathrm{KOH}(4.53 \mathrm{~g}, 80.6 \mathrm{mmol}, 1.46 \mathrm{M})$ was added. The contents were stirred at room temperature for 6 hours. Volatile components were removed via a rotary evaporator. The solids were diluted with $\mathrm{dH}_{2} \mathrm{O}(60 \mathrm{~mL})$ and washed with $\mathrm{DCM}(2 \times 60$ $\mathrm{mL})$. Organic constituents were washed once more with $\mathrm{dH}_{2} \mathrm{O}(1 \times 120 \mathrm{~mL})$. The solution was dried $\left(\mathrm{MgSO}_{4}\right)$ filtered and the volatile constituents were removed via a rotary evaporator. The crude wine-red powder was purified by column chromatography, eluting with $45 \% \mathrm{EtOAc} / n-$ hexanes. All attempts of this reaction were met with no success. All NMR spectra showed resonance signals indicative of the starting material (p-nitrobenzoyl chloride).

### 4.5 Synthesis and Characterization of Cu complexes made with 1a


4.5.1 Chelation of $\mathbf{4 a}$ to Copper metal to obtain 7a

A round-bottom flask was charged with $\mathbf{4 a}(0.502 \mathrm{~g}, 2.39 \mathrm{mmol}), \mathrm{NEt}_{3}(1.00 \mathrm{~mL}, 0.726 \mathrm{~g}, 7.17$ mmol ), and EtOH ( 5 mL ). After the yellow-coloured solids were completely dissolved, $\mathrm{Cu}\left(\mathrm{NO}_{3}\right)_{2} \cdot 2.5 \mathrm{H}_{2} \mathrm{O}(0.269 \mathrm{~g}, 1.16 \mathrm{mmol})$, a bright blue compound, was dissolved in $\mathrm{EtOH}(5 \mathrm{~mL})$ and added to the solution. Upon addition of the two, the solution turned colour from yellow to a deep green. The solution was stirred at room temperature for 1 hour. Following completion of the reaction, green precipitates were collected which was recrystallized from a mixture of $1: 1$ DCM/MeOH ( $474 \mathrm{mg}, 81 \%$ yield). Analyses of this compound are consistent with those in the literature. ${ }^{20}$

MP: Green plates: $164-156^{\circ} \mathrm{C}$ (lit: $165{ }^{\circ} \mathrm{C}$ decomp.)
IR: Green plates $\left(\mathrm{cm}^{-1}\right) 2892,1592,1572,1531,1487,1412,1351,1309,1173,1106,1032,994$, 944, 861, 837, 790, 751, 732, 659

MP: Brown needles: $158-160^{\circ} \mathrm{C}$
IR: Brown needles $\left(\mathrm{cm}^{-1}\right) 2882,1561,1527,1496,1455,1429,1349,1312,1250,1194,1140$, 1105, 1048, 1025, 993, 949, 873, 836, 832, 756, 735, 695

4.5.2 Chelation of $\mathbf{4 b}$ to Copper metal to obtain 7b

A round-bottom flask was charged with $\mathbf{4 b}(1.01 \mathrm{~g}, 3.49 \mathrm{mmol})$ and $\mathrm{EtOH}(10 \mathrm{~mL})$. After the yellow-coloured solids were completely dissolved, $\mathrm{Cu}\left(\mathrm{NO}_{3}\right)_{2} \cdot 2.5 \mathrm{H}_{2} \mathrm{O}(0.402 \mathrm{~g}, 1.75 \mathrm{mmol})$, a soft black compound, was dissolved in $\mathrm{EtOH}(10 \mathrm{~mL})$ and added to the solution. Upon addition of the two, the solution turned colour from yellow to a dark green. The solution was stirred at room temperature for 16 hours. Following completion of the reaction, dark green precipitates were collected which were recrystallized in a mixture of $1: 1 \mathrm{DCM} / \mathrm{MeOH}(0.628,57 \%$ yield $)$.

Melting Point Range: $208-210^{\circ} \mathrm{C}$
IR: $\left(\mathrm{cm}^{-1}\right) 2964,1750,1593,1527,1458,1353,1304,1179,1139,1101,1027,997,943,889,823$, 764, 727, 671

UV-Vis: (DCM: $\left.1.89 \times 10^{-5} \mathrm{M}\right) \lambda_{\max 1}=434 \mathrm{~nm}\left(\varepsilon=1.62 \times 10^{3} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 2}=335 \mathrm{~nm}(\varepsilon=$ $\left.3.39 \times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 3}=296 \mathrm{~nm}\left(\varepsilon=3.42 \times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 4}=246 \mathrm{~nm}(\varepsilon=4.21$ $\left.\times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right)$.

EA: (\%): calc'd. (found) for $\mathrm{C}_{26} \mathrm{H}_{24} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{Cl}_{4} \mathrm{Cu}$ : C 49.27 (49.13); H 3.82 (3.63); N 4.42 (4.45).
MS: $(\mathrm{m} / \mathrm{z})$ found $\left(\mathrm{calc}{ }^{\prime} \mathrm{d}\right)[\mathrm{M}+\mathrm{H}]^{+}=634.1$ (633.8)

4.5.3 Chelation of $\mathbf{4 c}$ to Copper metal to obtain 7c

A round-bottom flask was charged with $\mathbf{4 c}(0.10 \mathrm{~g}, 0.40 \mathrm{mmol})$ and $\mathrm{EtOH}(15 \mathrm{~mL}) . \mathrm{NEt}_{3}(0.1 \mathrm{~mL}$, 0.72 mmol ) was added to the solution. After the yellow-coloured solids were completely dissolved, $\mathrm{Cu}\left(\mathrm{NO}_{3}\right)_{2} \cdot 2.5 \mathrm{H}_{2} \mathrm{O}(0.045 \mathrm{~g}, 0.19 \mathrm{mmol})$, a blue-coloured compound, was dissolved in EtOH ( 5 mL ) and added to the solution. Upon addition of the two, the solution turned colour to a dark green. The solution was stirred at room temperature for 2 hours. Following completion of the reaction, dark green precipitates were collected which were recrystallized in a mixture of $1: 1 \mathrm{DCM} / \mathrm{MeOH}$ ( $103 \mathrm{mg}, 96 \%$ yield).

Melting Point Range: $203-205^{\circ} \mathrm{C}$
IR: $\left(\mathrm{cm}^{-1}\right) 2890,1896,1740,1589,1531,1496,1434,1355,1298,1254,1168,1114,1028,999$, 867, 836, 788, 766, 733, 701, 675

UV-Vis: $\left(D C M: 7.91 \times 10^{-5} \mathrm{M}\right) \lambda_{\max 1}=455 \mathrm{~nm}\left(\varepsilon=478 \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 2}=325 \mathrm{~nm}(\varepsilon=1.33$ $\left.\times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 3}=299 \mathrm{~nm}\left(\varepsilon=1.32 \times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 4}=252 \mathrm{~nm}\left(\varepsilon=8.03 \times 10^{3}\right.$ $\left.\mathrm{L} \cdot \mathrm{mol}^{-1} \cdot \mathrm{~cm}^{-1}\right)$.

EA: (\%): calc'd. (found) for $\mathrm{C}_{28} \mathrm{H}_{32} \mathrm{~N}_{2} \mathrm{O}_{6} \mathrm{Cu}: \mathrm{C} 60.47$ (60.66); H 5.80 (5.61); N 5.04 (5.08).
MS: $(\mathrm{m} / \mathrm{z})$ found (calc'd) $[\mathrm{M}]^{+}=556.3$ (556.1)

4.5.4 Chelation of $\mathbf{4 d}$ to Copper metal to obtain 7d

A round-bottom flask was charged with $\mathbf{4 d}(0.149 \mathrm{~g}, 0.607 \mathrm{mmol})$ and $\mathrm{EtOH}(10 \mathrm{~mL})$. After the yellow-coloured solids were completely dissolved, $\mathrm{Cu}\left(\mathrm{NO}_{3}\right)_{2} \cdot 2.5 \mathrm{H}_{2} \mathrm{O}(0.069 \mathrm{~g}, 0.30 \mathrm{mmol})$, a bright blue-coloured compound, was dissolved in $\mathrm{EtOH}(5 \mathrm{~mL}$ ) and added to the solution. Upon addition of the two, the solution turned colour from yellow to a dark green. $\mathrm{NEt}_{3}(1.00 \mathrm{~mL}, 0.726$ $\mathrm{g}, 7.17 \mathrm{mmol}$ ) was added as a base. The solution stirred at room temperature for 1 hour. Following completion of the reaction, green precipitates were collected which were recrystallized in a mixture of $1: 1 \mathrm{DCM} / \mathrm{MeOH}$ ( $150 \mathrm{mg}, 91 \%$ yield). EA is pending.

Melting Point Range: $218-220^{\circ} \mathrm{C}$
IR: $\left(\mathrm{cm}^{-1}\right) 2961,1740,1590,1561,1526,1488,1457,1352,1308,1191,1129,1095,131,992$, 944, 881, 811, 764, 731, 700

UV-Vis: (DCM: $\left.1.45 \times 10^{-5} \mathrm{M}\right) \lambda_{\max 1}=443 \mathrm{~nm}\left(\varepsilon=1.72 \times 10^{3} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 2}=325 \mathrm{~nm}(\varepsilon=$ $\left.4.04 \times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 3}=293 \mathrm{~nm}\left(\varepsilon=5.18 \times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 4}=250 \mathrm{~nm}(\varepsilon=3.74$ $\left.\times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right)$.

EA: (\%): calc'd. (found) for $\mathrm{C}_{30} \mathrm{H}_{36} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{Cu}: \mathrm{C} 65.26$ (64.99); H 6.57 (6.50); N 5.07 (5.07).
MS: $(\mathrm{m} / \mathrm{z})$ found (calc'd) $[\mathrm{M}]^{+}=552.3$ (552.2)

4.5.5 Chelation of $\mathbf{4 e}$ to Copper metal to obtain 7e;

A round-bottom flask was charged with $\mathbf{4 e}(0.499 \mathrm{~g}, 1.88 \mathrm{mmol})$ and EtOH ( 20 mL ). After the yellow-coloured solids were completely dissolved, $\mathrm{Cu}\left(\mathrm{NO}_{3}\right)_{2} \cdot 2.5 \mathrm{H}_{2} \mathrm{O}(0.213 \mathrm{~g}, 0.918 \mathrm{mmol})$, a bright blue-coloured compound, was dissolved in $\mathrm{EtOH}(10 \mathrm{~mL}$ ) and added to the solution. Upon addition of the two, the solution turned colour from yellow to a dark green. The solution was stirred at room temperature for 18 hours. Following completion of the reaction, green precipitates were collected which were recrystallized in a mixture of $1: 1 \mathrm{DCM} / \mathrm{MeOH}(176 \mathrm{mg}, 32 \%$ yield $)$.

Melting Point Range: 207-209 ${ }^{\circ} \mathrm{C}$
IR: $\left(\mathrm{cm}^{-1}\right) 2963,1589,1529,1483,1457,1355,1305,1179,1114,1030,997,942,894,799,765$, 708

UV-Vis: (DCM: $\left.2.83 \times 10^{-5} \mathrm{M}\right) \lambda_{\max 1}=445 \mathrm{~nm}\left(\varepsilon=815 \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 2}=330 \mathrm{~nm}(\varepsilon=2.13$ $\left.\times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 3}=301 \mathrm{~nm}\left(\varepsilon=2.16 \times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 4}=244 \mathrm{~nm}\left(\varepsilon=1.99 \times 10^{4}\right.$ $\mathrm{L} \cdot \mathrm{mol}^{-1} \cdot \mathrm{~cm}^{-1}$ ).

EA: (\%): calc'd. (found) for $\mathrm{C}_{28} \mathrm{H}_{30} \mathrm{Cl}_{2} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{Cu}$ : C 56.71 (56.94); H 5.10 (5.16); N 4.72 (4.80).
MS: $(\mathrm{m} / \mathrm{z})$ found (calc'd) $[\mathrm{M}]^{+}=594.1$ (593.1)

4.5.6 Chelation of $\mathbf{4 f}$ to Copper metal to obtain 7f;

A round-bottom flask was charged with $\mathbf{4 f}(0.450 \mathrm{~g}, 1.69 \mathrm{mmol})$ and $\mathrm{EtOH}(10 \mathrm{~mL})$. After the yellow-coloured solids were completely dissolved, $\mathrm{Cu}\left(\mathrm{NO}_{3}\right)_{2} \cdot 2.5 \mathrm{H}_{2} \mathrm{O}(0.196 \mathrm{~g}, 0.839 \mathrm{mmol})$, a bright blue-coloured compound, was dissolved in $\mathrm{EtOH}(10 \mathrm{~mL})$ and added to the solution. Upon addition of the two, the solution turned colour from yellow to a dark green. The solution was stirred at room temperature for 16 hours. Following completion of the reaction, dark green precipitates were collected which were recrystallized in a mixture of $1: 1 \mathrm{DCM} / \mathrm{MeOH}(380 \mathrm{mg}, 76 \%$ yield).

Melting Point Range: $>210^{\circ} \mathrm{C}$ (decomp.)
IR: $\left(\mathrm{cm}^{-1}\right) 2959,2113,1750,1593,1563,1529,1466,1352,1307,1198,1102,1031,1002,946$, 878, 826, 807, 766, 731, 677

UV-Vis: $\left(D C M: 4.72 \times 10^{-5} \mathrm{M}\right) \lambda_{\max 1}=436 \mathrm{~nm}\left(\varepsilon=788 \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 2}=330 \mathrm{~nm}(\varepsilon=1.81$ $\left.\times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 3}=299 \mathrm{~nm}\left(\varepsilon=1.88 \times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 4}=247 \mathrm{~nm}\left(\varepsilon=1.79 \times 10^{4}\right.$ $\mathrm{L} \cdot \mathrm{mol}^{-1} \cdot \mathrm{~cm}^{-1}$ ).

EA: (\%): calc'd. (found) for $\mathrm{C}_{28} \mathrm{H}_{30} \mathrm{Cl}_{2} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{Cu}$ : C 56.71 (56.89); H 5.10 (5.01); N 4.72 (4.75).
MS: $(\mathrm{m} / \mathrm{z})$ found (calc'd) $\left[\mathrm{C}_{14} \mathrm{H}_{16} \mathrm{ClNO}_{2}\right]=266.1(265.7),[\mathrm{M}]^{+}=594.3$ (593.1)

4.5.7 Chelation of $\mathbf{4 g}$ to Copper metal to obtain $\mathbf{7 g}$;

A round-bottom flask was charged with $\mathbf{4 g}(0.299 \mathrm{~g}, 1.12 \mathrm{mmol})$ and $\mathrm{EtOH}(10 \mathrm{~mL})$. After the yellow-coloured solids were completely dissolved, $\mathrm{Cu}\left(\mathrm{NO}_{3}\right)_{2} \cdot 2.5 \mathrm{H}_{2} \mathrm{O}(0.128 \mathrm{~g}, 0.55 \mathrm{mmol})$, a bright blue-coloured compound, was dissolved in $\mathrm{EtOH}(5 \mathrm{~mL})$ and added to the solution. Upon addition of the two, the solution turned colour from yellow to a dark green. $\mathrm{NEt}_{3}(0.20 \mathrm{~mL}, 0.14$ $\mathrm{g}, 1.4 \mathrm{mmol}$ ) was added as a base. The solution stirred at room temperature for 1 hour. Following completion of the reaction, green precipitates were collected which were recrystallized in a mixture of $1: 1 \mathrm{DCM} / \mathrm{MeOH}(300 \mathrm{mg}, 91 \%$ yield $)$.

Melting Point Range: $171-173^{\circ} \mathrm{C}$
IR: $\left(\mathrm{cm}^{-1}\right) 3041,2955,2112,1916,1581,1548,1457,1420,1390,1352,1308,1260,1199,1174$, 1062, 1040, 1000, 935, 880, 771, 714, 669

UV-Vis: (DCM: $\left.2.01 \times 10^{-5} \mathrm{M}\right) \lambda_{\max 1}=425 \mathrm{~nm}\left(\varepsilon=1.21 \times 10^{3} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 2}=293 \mathrm{~nm}(\varepsilon=$ $\left.3.21 \times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 3}=247 \mathrm{~nm}\left(\varepsilon=3.33 \times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right)$.

EA: (\%): calc'd. (found) for $\mathrm{C}_{34} \mathrm{H}_{32} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{Cu}: \mathrm{C} 68.50$ (68.47); H 5.41 (5.34); N 4.70 (4.78).
MS: $(\mathrm{m} / \mathrm{z})$ found (calc'd) $[\mathrm{M}]^{+}=596.3$ (596.2)

4.5.8 Chelation of $\mathbf{4 h}$ to Copper metal to obtain $\mathbf{7 h}$

A round-bottom flask was charged with $\mathbf{4 h}(0.128 \mathrm{~g}, 0.649 \mathrm{mmol})$ and $\mathrm{EtOH}(10 \mathrm{~mL})$. After the yellow-coloured solids were completely dissolved, $\mathrm{Cu}\left(\mathrm{NO}_{3}\right)_{2} \cdot 2.5 \mathrm{H}_{2} \mathrm{O}(0.0740 \mathrm{~g}, 0.318 \mathrm{mmol})$, a bright blue-coloured compound, was dissolved in $\mathrm{EtOH}(10 \mathrm{~mL})$ and added to the solution. Upon addition of the two, the solution turned colour from yellow to a dark green. $\mathrm{NEt}_{3}(0.20 \mathrm{~mL}, 1.4$ mmol ) was added to as a base. The solution was stirred at room temperature for 1 hour. Following completion of the reaction, green precipitates were collected which recrystallized in a mixture of 1:1 DCM/MeOH ( $73 \mathrm{mg}, 50 \%$ yield). Analyses of this complex are consistent with those in the literature. ${ }^{66}$

Melting Point Range: 203-204 ${ }^{\circ} \mathrm{C}$
IR: $\left(\mathrm{cm}^{-1}\right) 2958,1590,1527,1474,1415,1349,1297,1249,1197,1153,1036,1003,945,890$, 848, 803, 788, 729

UV-Vis: $\left(D C M: 2.10 \times 10^{-5} \mathrm{M}\right) \lambda_{\max 1}=411 \mathrm{~nm}\left(\varepsilon=1.11 \times 10^{3} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 2}=309 \mathrm{~nm}(\varepsilon=$ $\left.8.15 \times 10^{3} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 3}=275 \mathrm{~nm}\left(\varepsilon=2.38 \times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right)$

EA: (\%): calc'd. (found) for $\mathrm{C}_{22} \mathrm{H}_{36} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{Cu}$ : C 57.94 (58.17); H 7.96 (7.85); N 6.14 (5.92).

4.5.9 Chelation of $\mathbf{4 i}$ to a Copper metal to obtain $\mathbf{7 i}$;

A round-bottom flask was charged with $\mathbf{4 i}(0.122 \mathrm{~g}, 0.465 \mathrm{mmol})$ and $\mathrm{EtOH}(10 \mathrm{~mL})$. After the yellow-coloured solids were completely dissolved, $\mathrm{Cu}\left(\mathrm{NO}_{3}\right)_{2} \cdot 2.5 \mathrm{H}_{2} \mathrm{O}(0.0530 \mathrm{~g}, 0.228 \mathrm{mmol})$, a bright blue-coloured compound, was dissolved in $\mathrm{EtOH}(10 \mathrm{~mL})$ and added to the solution. Upon addition of the two, the solution turned colour from yellow to a dark green. $\mathrm{NEt}_{3}(1.0 \mathrm{~mL}, 7.2$ mmol ) was added to as a base. The solution was stirred at room temperature for 1 hour. Following completion of the reaction, green precipitates were collected which were recrystallized in a mixture of 1:1 DCM/MeOH ( $120 \mathrm{mg}, 90 \%$ yield). Analyses of this complex are consistent with those in the literature. ${ }^{66}$

Melting Point Range: $217-218{ }^{\circ} \mathrm{C}$
IR: $\left(\mathrm{cm}^{-1}\right) 1584,1535,1514,1484,1341,1299,1250,1181,1108,1031,998,946,861,834,779$, 752, 750

UV-Vis: (solv: $\left.1.43 \times 10^{-5} \mathrm{M}\right) \lambda_{\max 1}=717 \mathrm{~nm}\left(\varepsilon=550 \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 2}=374 \mathrm{~nm}(\varepsilon=1.78 \times$ $\left.10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 3}=306 \mathrm{~nm}\left(\varepsilon=1.41 \times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 4}=269 \mathrm{~nm}\left(\varepsilon=3.11 \times 10^{4}\right.$ $\mathrm{L} \cdot \mathrm{mol}^{-1} \cdot \mathrm{~cm}^{-1}$ )

EA: (\%): calc'd. (found) for $\mathrm{C}_{26} \mathrm{H}_{26} \mathrm{~N}_{4} \mathrm{O}_{8} \mathrm{Cu}$ : C 53.29 (53.17); H 4.47 (4.45); N 9.56 (9.45).

### 4.6 Synthesis and Characterization of $\mathbf{C u}$ complexes made with 1b


4.6.1 Chelation of $\mathbf{6 a}$ to Copper metal to obtain $\mathbf{8 a}$

A round-bottom flask was charged with $\mathbf{6 a}(0.755 \mathrm{~g}, 3.99 \mathrm{mmol})$ and $\mathrm{MeOH}(15 \mathrm{~mL})$. After the pink-coloured solids were completely dissolved, $\mathrm{CuBr}_{2}(0.560 \mathrm{~g}, 2.51 \mathrm{mmol})$ was added to the solution. Upon addition of the two, the solution turned colour from pink to a pastel green. The solution was stirred at room temperature for 3 hours. Upon completion of the reaction a green precipitate was collected via vacuum filtration $(0.59 \mathrm{~g}, 70 \%$ yield $)$. The synthesized substance is unable to be properly characterized due to its extreme limited solubility in only THF.

Melting Point Range: $>260^{\circ} \mathrm{C}$ (decomp.)
IR: $\left(\mathrm{cm}^{-1}\right) 2890,1605,1578,1540,1487,1454,1414,1360,1328,1263,1200,1110,1063,995$, 951, 750, 689, 655

UV-Vis: $\left(D C M: 1.36 \times 10^{-4} \mathrm{M}\right) \lambda_{\max 1}=320 \mathrm{~nm}\left(\varepsilon=7.1710^{3} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 2}=285 \mathrm{~nm}(\varepsilon=$ $\left.8.58 \times 10^{3} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 3}=233 \mathrm{~nm}\left(\varepsilon=8.45 \times 10^{3} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right)$.

EA: (\%): calc'd. (found) for $\mathrm{C}_{22} \mathrm{H}_{20} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{Cu}: \mathrm{C} 60.06$ (59.89); H 4.58 (4.76); N 6.37 (6.36).
MS: ( $\mathrm{m} / \mathrm{z}$ ) found (calc'd): not detected (440.0)


### 4.6.2 Chelation of $\mathbf{6 b}$ to Copper metal to obtain $\mathbf{8 b}$

A round-bottom flask was charged with $\mathbf{6 b}(39 \mathrm{mg}, 0.15 \mathrm{mmol})$ and $\mathrm{EtOH}(2 \mathrm{~mL})$. After the yellow-coloured solids were completely dissolved, $\mathrm{Cu}\left(\mathrm{NO}_{3}\right)_{2} \cdot 2.5 \mathrm{H}_{2} \mathrm{O}(17 \mathrm{mg}, 0.073 \mathrm{mmol})$ dissolved in $\mathrm{EtOH}(3 \mathrm{~mL}$ ) was added to the solution. Upon addition of the two, the solution turned colour from yellow to a dark green. $\mathrm{NEt}_{3}(0.10 \mathrm{~mL}, 73 \mathrm{mg}, 72 \mathrm{mmol})$ was added to the reaction. The solution was stirred at room temperature for 1 hour. Upon completion of the reaction a pastel green-coloured precipitate was collected via vacuum filtration ( $30 \mathrm{mg}, 71 \%$ yield). The synthesized substance is unable to be properly characterized due to its extreme limited solubility in only THF. Characterization on this compound is pending. Crude characterization represents results like 8a.

### 4.7 Synthesis and Characterization of Co complexes made with 1a


4.7.1 Chelation of $\mathbf{4 a}$ to a Cobalt metal to obtain $\mathbf{9 a}$

A round-bottom flask was charged with $4 \mathbf{a}\left(1.01 \mathrm{~g}, 4.64 \mathrm{mmol}^{2}\right), \mathrm{NEt}_{3}(3.00 \mathrm{~mL}, 2.18 \mathrm{~g}, 21.5$ mmol ), and $\mathrm{EtOH}(10 \mathrm{~mL})$. After the yellow-coloured solids were completely dissolved, $\mathrm{Co}\left(\mathrm{NO}_{3}\right)_{2} \cdot 6 \mathrm{H}_{2} \mathrm{O}(0.671 \mathrm{~g}, 2.31 \mathrm{mmol})$, a pink compound, was dissolved in $\mathrm{EtOH}(5 \mathrm{~mL})$ and added to the solution. Upon addition of the two, the solution turned colour from yellow to a bright red. The solution was stirred at room temperature for 2 hours. Following completion of the reaction, red precipitates were collected which were recrystallized in a mixture of $1: 1 \mathrm{DCM} / \mathrm{MeOH}$ $(0.927 \mathrm{~g}, 81 \%$ yield $)$. Analyses of this compound are consistent with those in the literature. ${ }^{66}$

Melting Point Range: $198-201^{\circ} \mathrm{C}$
IR: $\left(\mathrm{cm}^{-1}\right) 2986,2889,1740,1589,1570,1520,1485,1471,1407,1353,1304,1172,1103,994$, 952, 860, 840, 754, 695, 653

UV-Vis: $\left(D C M: 5.70 \times 10^{-5} \mathrm{M}\right) \lambda_{\max 1}=534 \mathrm{~nm}\left(\varepsilon=60.0 \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 2}=314 \mathrm{~nm}(\varepsilon=2.39$ $\left.\times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 3}=232 \mathrm{~nm}\left(\varepsilon=2.14 \times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right)$.

EA: (\%): calc'd. (found) for $\mathrm{C}_{26} \mathrm{H}_{28} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{Co}$ : C 63.54 (63.49); H 5.74 (5.72); N 5.70 (5.43).
MS: $(\mathrm{m} / \mathrm{z})$ found $\left(\mathrm{calc}^{\prime} \mathrm{d}\right)[\mathrm{M}+\mathrm{H}]^{+}=492.3$ (491.5)

4.7.2 Chelation of $\mathbf{4 b}$ to a Cobalt metal to obtain $9 \mathbf{b}$

A round-bottom flask was charged with $\mathbf{4 b}(0.533 \mathrm{~g}, 1.86 \mathrm{mmol})$ and $\mathrm{MeOH}(10 \mathrm{~mL})$. After the yellow-coloured solids were completely dissolved, $\mathrm{Co}\left(\mathrm{NO}_{3}\right)_{2} \cdot 6 \mathrm{H}_{2} \mathrm{O}(0.27 \mathrm{~g}, 0.92 \mathrm{mmol})$, a pink compound, was dissolved in $\mathrm{MeOH}(15 \mathrm{~mL})$ and added to the solution. Upon addition of the two, the solution turned colour from yellow to a bright red. The solution was stirred at room temperature for 18 hours. Following completion of the reaction, orange precipitates were collected which were recrystallized in a mixture of $1: 1 \mathrm{DCM} / \mathrm{MeOH}$ ( $331 \mathrm{mg}, 56 \%$ yield). Analyses of this compound are consistent with those in the literature. ${ }^{66}$

Melting Point Range: $223-225^{\circ} \mathrm{C}$
IR: $\left(\mathrm{cm}^{-1}\right) 2960,1739,1581,1524,1461,1428,1354,1303,1256,1178,1141,1102,1025,878$, 766, 670

UV-Vis: $\left(D C M: 2.54 \times 10^{-5} \mathrm{M}\right) \lambda_{\max 1}=538 \mathrm{~nm}\left(\varepsilon=113 \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 2}=321 \mathrm{~nm}(\varepsilon=3.88$ $\left.\times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 3}=245 \mathrm{~nm}\left(\varepsilon=3.03 \times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right)$.

EA: (\%): calc'd. (found) for $\mathrm{C}_{26} \mathrm{H}_{24} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{Cl}_{4} \mathrm{Co}$ : C 49.63 (49.48); H 3.84 (3.90); N 4.45 (4.40).
MS: $(\mathrm{m} / \mathrm{z})$ found $\left(\mathrm{calc}^{\prime} \mathrm{d}\right)[\mathrm{M}+\mathrm{H}]^{+}=630.1$ (629.2)

4.7.3 Chelation of $\mathbf{4 c}$ to a Cobalt metal to obtain $9 \mathbf{c}$

A round-bottom flask was charged with $\mathbf{4 c}(0.103 \mathrm{~g}, 0.42 \mathrm{mmol})$ and $\mathrm{EtOH}(15 \mathrm{~mL}) . \mathrm{NEt}_{3}(0.10$ $\mathrm{mL}, 0.073 \mathrm{~g}, 0.72 \mathrm{mmol}$ ) was added to the solution. After the yellow-coloured solids were completely dissolved, $\mathrm{Co}\left(\mathrm{NO}_{3}\right)_{2} \cdot 6 \mathrm{H}_{2} \mathrm{O}(0.058 \mathrm{~g}, 0.20 \mathrm{mmol})$, a pink-coloured compound, was dissolved in $\mathrm{EtOH}(5 \mathrm{~mL})$ and added to the solution. Upon addition of the two, the solution turned colour to a dark red. The solution was stirred at room temperature for 18 hours. Following completion of the reaction, red precipitates were collected were recrystallized in a mixture of 1:1 $\mathrm{DCM} / \mathrm{MeOH}$ (118 mg, 99 \% yield). Analyses of this compound are consistent with those in the literature. ${ }^{66}$

Melting Point Range: $243-245^{\circ} \mathrm{C}$
IR: $\left(\mathrm{cm}^{-1}\right) 2969,2882,1610,1584,1560,1524,1498,1396,1355,1300,1253,1190,1167,1113$, 1026, 999, 842, 769, 680

UV-Vis: $\left(D C M: 1.27 \times 10^{-4} \mathrm{M}\right) \lambda_{\max 1}=540 \mathrm{~nm}\left(\varepsilon=30.0 \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 2}=316 \mathrm{~nm}(\varepsilon=1.14$ $\left.\times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 3}=263 \mathrm{~nm}\left(\varepsilon=7.32 \times 10^{3} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right)$.

EA: (\%): calc'd. (found) for $\mathrm{C}_{28} \mathrm{H}_{32} \mathrm{~N}_{2} \mathrm{O}_{6} \mathrm{Co}$ : C 60.98 (60.90); H 5.85 (5.74); N 5.08 (5.10).

4.7.4 Chelation of $\mathbf{4 d}$ to a Cobalt metal to obtain $9 \mathbf{d}$

A round-bottom flask was charged with $\mathbf{4 d}(0.088 \mathrm{~g}, 0.34 \mathrm{mmol})$ and $\mathrm{EtOH}(3 \mathrm{~mL}) . \mathrm{NEt}_{3}(0.20$ $\mathrm{mL}, 0.15 \mathrm{~g}, 1.4 \mathrm{mmol}$ ) was added to the solution. After the yellow-coloured solids were completely dissolved, $\mathrm{Co}\left(\mathrm{NO}_{3}\right)_{2} \cdot 6 \mathrm{H}_{2} \mathrm{O}(0.048 \mathrm{~g}, 0.17 \mathrm{mmol})$, a pink-coloured compound, was dissolved in $\mathrm{EtOH}(2 \mathrm{~mL})$ and added to the solution. Upon addition of the two, the solution turned colour to a dark red. The solution was stirred at room temperature for 1 hour. Following completion of the reaction, red precipitates were collected were recrystallized in a mixture of $1: 1 \mathrm{DCM} / \mathrm{MeOH}(64$ $\mathrm{mg}, 71 \%$ yield).

Melting Point Range: $240^{\circ} \mathrm{C}$ (decomp.)
IR: $\left(\mathrm{cm}^{-1}\right) 2965,1584,1561,1522,1487,1457,1354,1308,1241,1185,1092,1023,991,807$, 768

UV-Vis: $\left(D C M: 4.39 \times 10^{-5} \mathrm{M}\right) \lambda_{\max 1}=542 \mathrm{~nm}\left(\varepsilon=66.0 \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 2}=315 \mathrm{~nm}(\varepsilon=2.96$ $\left.\times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 3}=257 \mathrm{~nm}\left(\varepsilon=1.78 \times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 4}=248 \mathrm{~nm}\left(\varepsilon=1.90 \times 10^{4}\right.$ $\left.\mathrm{L} \cdot \mathrm{mol}^{-1} \cdot \mathrm{~cm}^{-1}\right)$.

EA: (\%): calc'd. (found) for $\mathrm{C}_{30} \mathrm{H}_{36} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{Co}$ : C 63.71 (63.73); H 6.77 (6.57); N 4.95 (4.84).

- $\quad 1.0 \mathrm{H}_{2} \mathrm{O}$ found within lattice for elemental analysis

MS: $(\mathrm{m} / \mathrm{z})$ found $\left(\mathrm{calc}^{\prime} \mathrm{d}\right)[\mathrm{M}+\mathrm{H}]^{+}=548.3$ (547.6)

4.7.5 Chelation of $\mathbf{3 e}$ to a Cobalt metal to obtain $\mathbf{9 e}$

To a round-bottom flask containing $\mathrm{MeOH}(25 \mathrm{~mL}), \mathrm{KOH}(2.21 \mathrm{~g}, 39.4 \mathrm{mmol}, 1.58 \mathrm{M})$ was added and stirred till all solids were dissolved. Once dissolved, $\mathbf{3 e}(1.11 \mathrm{~g}, 2.65 \mathrm{mmol})$ was added. Separately, $\mathrm{Co}\left(\mathrm{NO}_{3}\right)_{2} \cdot 6 \mathrm{H}_{2} \mathrm{O}(0.373 \mathrm{~g}, 1.28 \mathrm{mmol})$ was dissolved in $\mathrm{MeOH}(5 \mathrm{~mL})$ and added to the swirling suspension. The resulting mixture was allowed the stir at room temperature for 6 hours. Following completion of the reaction all volatile components were removed via a rotary evaporator. The resulting solids were dissolved in DCM ( 50 mL ) and washed with a solution of $\mathrm{NaCl}(0.20 \mathrm{mmol}, 1.0 \mathrm{M})$. The organics were washed a second time with a solution of $\mathrm{Na}_{2} \mathrm{CO}_{3}$ ( $0.02 \mathrm{mmol}, 0.1 \mathrm{M})$. The organic phase was dried $\left(\mathrm{MgSO}_{4}\right)$, filtered and the remaining volatile components were removed via a rotary evaporator. The crude orange-coloured precipitates were recrystallized in a mixture of $1: 1 \mathrm{DCM} / \mathrm{MeOH}(0.519 \mathrm{~g}, 70 \%$ yield $)$

Melting Point Range: $233-235^{\circ} \mathrm{C}$
IR: $\left(\mathrm{cm}^{-1}\right) 2966,1583,1522,1481,1419,1353,1301,1183,1110,1045,1022,995,946,890,799$, 767, 740, 731, 700

UV-Vis: $\left(D C M: ~ 6.80 \times 10^{-5} \mathrm{M}\right) \lambda_{\max 1}=533 \mathrm{~nm}\left(\varepsilon=32.0 \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 2}=317 \mathrm{~nm}(\varepsilon=1.36$ $\left.\times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 3}=237 \mathrm{~nm}\left(\varepsilon=1.07 \times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right)$.

EA: (\%): calc'd. (found) for $\mathrm{C}_{28} \mathrm{H}_{30} \mathrm{Cl}_{2} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{Co}$ : C 57.16 (56.89); H 5.14 (5.16); N 4.76 (4.80).
MS: $(\mathrm{m} / \mathrm{z})$ found (calc'd) $[\mathrm{M}]^{+}=588.2$ (588.3)

4.7.6 Chelation of $\mathbf{4 f}$ to a Cobalt metal to obtain $9 \mathbf{f}$

A round-bottom flask was charged with $\mathbf{4 f}(0.425 \mathrm{~g}, 1.60 \mathrm{mmol})$ and $\mathrm{EtOH}(15 \mathrm{~mL})$. After the yellow-coloured solids were completely dissolved, $\mathrm{Co}\left(\mathrm{NO}_{3}\right)_{2} \cdot 2.5 \mathrm{H}_{2} \mathrm{O}(0.227 \mathrm{~g}, 0.779 \mathrm{mmol})$, a pink-coloured compound, was dissolved in $\mathrm{EtOH}(10 \mathrm{~mL})$ and added to the solution. Upon addition of the two, the solution turned colour from yellow to a dark red. The solution was stirred at room temperature for 18 hours. Following completion of the reaction, orange precipitates were collected were recrystallized in a mixture of $1: 1 \mathrm{DCM} / \mathrm{MeOH}$ collected ( $459 \mathrm{mg}, 61 \%$ yield).

Melting Point Range: $234-236^{\circ} \mathrm{C}$
IR: $\left(\mathrm{cm}^{-1}\right) 2967,2114,1738,1583,1562,1521,1470,1424,1354,1306,1198,1178,1148,1100$, 1045, 1023, 993, 946, 877, 831, 802, 767, 690

UV-Vis: (DCM: $\left.1.04 \times 10^{-4} \mathrm{M}\right) \lambda_{\max 1}=536 \mathrm{~nm}\left(\varepsilon=41.0 \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 2}=317 \mathrm{~nm}(\varepsilon=1.96$ $\left.\times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 3}=292 \mathrm{~nm}\left(\varepsilon=1.56 \times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 4}=247 \mathrm{~nm}\left(\varepsilon=1.59 \times 10^{4}\right.$ $\mathrm{L} \cdot \mathrm{mol}^{-1} \cdot \mathrm{~cm}^{-1}$ ).

EA: (\%): calc'd. (found) for $\mathrm{C}_{28} \mathrm{H}_{30} \mathrm{Cl}_{2} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{Co}$ : C 57.16 (56.88); H 5.14 (5.22); N 4.76 (4.77).
MS: $(\mathrm{m} / \mathrm{z})$ found (calc'd) $[\mathrm{M}]^{+}=588.3$ (588.3)

4.7.7 Chelation of $\mathbf{4 g}$ to a Cobalt metal to obtain $\mathbf{9 g}$

A round-bottom flask was charged with $\mathbf{4 g}(0.237 \mathrm{~g}, 0.887 \mathrm{mmol}), \mathrm{NEt}_{3}(1.25 \mathrm{~mL}, 0.908 \mathrm{~g}, 8.97$ mmol ) and $\mathrm{EtOH}(10 \mathrm{~mL})$. After the yellow-coloured solids were completely dissolved, $\mathrm{Co}\left(\mathrm{NO}_{3}\right)_{2} \cdot 6 \mathrm{H}_{2} \mathrm{O}(0.127 \mathrm{~g}, 0.436 \mathrm{mmol})$, a bright pink-coloured compound, was dissolved in EtOH $(5 \mathrm{~mL})$ and added to the solution. Upon addition of the two, the solution turned colour from yellow to a dark red. The solution was stirred at room temperature for 1 hour. Following completion of the reaction, dark red precipitates were collected which were recrystallized in a mixture of $1: 1$ DCM/MeOH ( $246 \mathrm{mg}, 95 \%$ yield). Analyses of this compound are consistent with those in the literature. ${ }^{66}$

Melting Point Range: 201-202 ${ }^{\circ} \mathrm{C}$
IR: $\left(\mathrm{cm}^{-1}\right) 3044,2967,2890,1572,1519,1412,1383,1352,1302,1259,1193,1165,1034,989$, 744, 666

UV-Vis: (DCM: $\left.2.37 \times 10^{-5} \mathrm{M}\right) \lambda_{\max 1}=537 \mathrm{~nm}\left(\varepsilon=226 \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 2}=314 \mathrm{~nm}(\varepsilon=5.50$ $\left.\times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 3}=297 \mathrm{~nm}\left(\varepsilon=6.13 \times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 4}=274 \mathrm{~nm}\left(\varepsilon=4.62 \times 10^{4}\right.$ $\mathrm{L} \cdot \mathrm{mol}^{-1} \cdot \mathrm{~cm}^{-1}$ ).

EA: (\%): calc'd. (found) for $\mathrm{C}_{34} \mathrm{H}_{32} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{Co}$ : C 69.03 (69.02); H 5.45 (5.44); N 4.74 (4.79).
MS: $(\mathrm{m} / \mathrm{z})$ found (calc'd) $[\mathrm{M}]^{+}=592.3$ (591.6)

4.7.8 Chelation of $\mathbf{4 h}$ to a Cobalt metal to obtain $\mathbf{9 h}$

A round-bottom flask was charged with $\mathbf{4 h}(0.119 \mathrm{~g}, 0.603 \mathrm{mmol})$ and $\mathrm{EtOH}(10 \mathrm{~mL})$. After the yellow-coloured solids were completely dissolved, $\mathrm{Co}\left(\mathrm{NO}_{3}\right)_{2} \cdot 6 \mathrm{H}_{2} \mathrm{O}(0.0850 \mathrm{~g}, 0.292 \mathrm{mmol})$, a bright pink-coloured compound, was dissolved in $\mathrm{EtOH}(10 \mathrm{~mL})$ and added to the solution. Upon addition of the two, the solution turned colour from yellow to a dark red. $\mathrm{NEt}_{3}(0.20 \mathrm{~mL}, 1.4 \mathrm{mmol})$ was added as a base. The solution was stirred at room temperature for 1 hour. Following completion of the reaction, pink precipitates were collected which were recrystallized in a mixture of 1:1 DCM/MeOH ( $105 \mathrm{mg}, 79 \%$ yield). Analyses of this compound are consistent with those in the literature. ${ }^{66}$

Melting Point Range: $>220^{\circ} \mathrm{C}$ (decomp.)
IR: $\left(\mathrm{cm}^{-1}\right) 2959,1576,1525,1473,1416,1353,1295,1195,1155,1000,948,898,803,770,729$
UV-Vis: (solv: $\left.1.77 \times 10^{-5} \mathrm{M}\right) \lambda_{\max 1}=537 \mathrm{~nm}\left(\varepsilon=647 \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 2}=321 \mathrm{~nm}(\varepsilon=1.14 \times$ $\left.10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 3}=280 \mathrm{~nm}\left(\varepsilon=8.37 \times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right)$

EA: (\%): calc'd. (found) for $\mathrm{C}_{22} \mathrm{H}_{36} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{Co}$ : C 58.53 (58.29); H 8.04 (8.07); N 6.21 (5.97).

4.7.9 Chelation of $\mathbf{4 i}$ to a Cobalt metal to obtain $\mathbf{9 i}$

A round-bottom flask was charged with $\mathbf{4 i}(0.120 \mathrm{~g}, 0.458 \mathrm{mmol})$ and $\mathrm{EtOH}(10 \mathrm{~mL})$. After the yellow-coloured solids were completely dissolved, $\mathrm{Co}\left(\mathrm{NO}_{3}\right)_{2} \cdot 6 \mathrm{H}_{2} \mathrm{O}(0.0670 \mathrm{~g}, 0.230 \mathrm{mmol})$, a bright pink-coloured compound, was dissolved in $\mathrm{EtOH}(10 \mathrm{~mL})$ and added to the solution. Upon addition of the two, the solution turned colour from yellow to a dark red. $\mathrm{NEt}_{3}(1.0 \mathrm{~mL}, 7.2 \mathrm{mmol})$ was added as a base. The solution was stirred at room temperature for 1 hour. Following completion of the reaction, orange precipitates were collected which were recrystallized in a mixture of $1: 1 \mathrm{DCM} / \mathrm{MeOH}$ collected ( $97 \mathrm{mg}, 73 \%$ yield). Analyses of this compound are consistent with those in the literature. ${ }^{66}$

Melting Point Range: $>240{ }^{\circ} \mathrm{C}$ (decomp.)
IR: $\left(\mathrm{cm}^{-1}\right) 2967,1577,1512,1482,1341,1300,1173,1108,1025,992,945,862,833,777,753$, 703

UV-Vis: (solv: $\left.6.88 \times 10^{-6} \mathrm{M}\right) \lambda_{\max 1}=363 \mathrm{~nm}\left(\varepsilon=2.47 \times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 2}=264 \mathrm{~nm}(\varepsilon=$ $3.33 \times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}$ )

EA: (\%): calc'd. (found) for $\mathrm{C}_{26} \mathrm{H}_{26} \mathrm{~N}_{4} \mathrm{O}_{8} \mathrm{Co}$ : C 51.02 (51.39); H 4.36 (4.28); N 8.98 (8.82).

- $\quad 0.5 \mathrm{DCM}$ found within lattice for elemental analysis

4.7.10 Chelation of $\mathbf{4} \mathbf{j}$ to a Cobalt metal to obtain $\mathbf{9 j}$

A round-bottom flask was charged with $\mathbf{4} \mathbf{j}\left(0.503 \mathrm{~g}, 3.24 \mathrm{mmol}^{2}\right), \mathrm{NEt}_{3}(1.00 \mathrm{~mL}, 0.726 \mathrm{~g}, 7.17$ $\mathrm{mmol})$, and $\mathrm{EtOH}(10 \mathrm{~mL})$. Afterwards, $\mathrm{Co}\left(\mathrm{NO}_{3}\right)_{2} \cdot 6 \mathrm{H}_{2} \mathrm{O}(0.435 \mathrm{~g}, 150 \mathrm{mmol})$, a bright pinkcoloured compound, was dissolved in $\mathrm{EtOH}(5 \mathrm{~mL})$ and added to the solution. Upon addition of the two, the solution turned colour from yellow to a bright pink. The solution was stirred at room temperature for 1 hour. Following completion of the reaction, bright pink precipitates were collected which were recrystallized in a mixture of $1: 1 \mathrm{DCM} / \mathrm{MeOH}$ ( $300 \mathrm{mg}, 57 \%$ yield).

Melting Point Range: $>210^{\circ} \mathrm{C}$ (decomp.)
IR: $\left(\mathrm{cm}^{-1}\right) 2964,1577,1508,1405,1351,1297,1221,1190,1165,1045,991,932,760$.
UV-Vis: $\left(\mathrm{DCM}: 1.09 \times 10^{-5} \mathrm{M}\right) \lambda_{\max 1}=536 \mathrm{~nm}\left(\varepsilon=786 \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 2}=278 \mathrm{~nm}(\varepsilon=1.52$ $\times 10^{5} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}$ )

EA: (\%): calc'd. (found) for $\mathrm{C}_{16} \mathrm{H}_{24} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{Co}: \mathrm{C} 52.32$ (52.07); H 6.59 (6.37); N 7.63 (742).

4.7.11 Chelation of $\mathbf{4 k}$ to a Cobalt metal to obtain $\mathbf{9 k}$

A round-bottom flask was charged with $\mathbf{4 k}(0.502 \mathrm{~g}, 2.40 \mathrm{mmol})$ and $\mathrm{EtOH}(5 \mathrm{~mL})$. After the transparent solids were completely dissolved, $\mathrm{NEt}_{3}(1.00 \mathrm{~mL}, 0.726 \mathrm{~g}, 7.17 \mathrm{mmol})$ was added. Afterwards, $\mathrm{Co}\left(\mathrm{NO}_{3}\right)_{2} \cdot 6 \mathrm{H}_{2} \mathrm{O}(0.317 \mathrm{~g}, 1.09 \mathrm{mmol})$, a bright pink-coloured compound, was dissolved in $\mathrm{EtOH}(5 \mathrm{~mL})$ and added to the solution. Upon addition of the two, the solution turned colour from transparent to a bright pink. The solution was stirred at room temperature for 18 hours. Following completion of the reaction, bright pink precipitates were collected which were recrystallized in a mixture of $1: 1 \mathrm{DCM} / \mathrm{MeOH}(478 \mathrm{mg}, 93 \%$ yield $)$.

Melting Point Range: $220^{\circ} \mathrm{C}$ (decomp.)
IR: $\left(\mathrm{cm}^{-1}\right) 2975,1608,1560,1463,1360,1314,1250,1173,1126,1028,992,971,872,751,749$, 699.

UV-Vis: $\left(\right.$ solv: $\left.1.94 \times 10^{-5} \mathrm{M}\right) \lambda_{\max 1}=534 \mathrm{~nm}\left(\varepsilon=389 \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 2}=273 \mathrm{~nm}(\varepsilon=7.38 \times$ $10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}$ )

EA: (\%): calc'd. (found) for $\mathrm{C}_{16} \mathrm{H}_{18} \mathrm{~F}_{6} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{Co}$ : C 40.44 (40.54); H 3.82 (3.77); N 5.89 (5.98).

4.7.12 Chelation of $\mathbf{4 I}$ to a Cobalt metal to obtain 91

A round-bottom flask was charged with $\mathbf{4 l}(0.500 \mathrm{~g}, 1.93 \mathrm{mmol})$ and $\mathrm{EtOH}(5 \mathrm{~mL})$. After the transparent solids were completely dissolved, $\mathrm{NEt}_{3}(1.00 \mathrm{~mL}, 0.726 \mathrm{~g}, 7.17 \mathrm{mmol})$ was added. Afterwards, $\mathrm{Co}\left(\mathrm{NO}_{3}\right)_{2} \cdot 6 \mathrm{H}_{2} \mathrm{O}(0.268 \mathrm{~g}, 0.920 \mathrm{mmol})$, a bright pink-coloured compound, was dissolved in $\operatorname{EtOH}(5 \mathrm{~mL})$ and added to the solution. Upon addition of the two, the solution turned colour from transparent to a bright pink. The solution was stirred at room temperature for 18 hours. Following completion of the reaction, pale pink precipitates were collected which were recrystallized in a mixture of $1: 1 \mathrm{DCM} / \mathrm{MeOH}(500 \mathrm{mg}, 95 \%$ yield $)$.

Melting Point Range: $184{ }^{\circ} \mathrm{C}$ (decomp.)
IR: $\left(\mathrm{cm}^{-1}\right) 2970,2895,1596,1524,1458,1352,1281,1199,1031,1005,960,936,828,802,758$, 671

UV-Vis: $\left(\right.$ solv: $\left.2.10 \times 10^{-4} \mathrm{M}\right) \lambda_{\max 1}=536 \mathrm{~nm}\left(\varepsilon=72.0 \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 2}=489 \mathrm{~nm}(\varepsilon=51.0$ $\left.\mathrm{L} \cdot \mathrm{mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 3}=285 \mathrm{~nm}\left(\varepsilon=1.56 \times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right)$

EA: (\%): calc'd. (found) for $\mathrm{C}_{16} \mathrm{H}_{18} \mathrm{~F}_{6} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{Co}: \mathrm{C} 40.44$ (33.48); H 3.82 (3.77); N 5.89 (5.98).

### 4.8 Synthesis and Characterization of Co complexes made with 1a



### 4.8.1 Chelation of Cobalt metal to obtain 10a

A round-bottom flask was charged with compound $\mathbf{6 a}(0.764 \mathrm{~g}, 4.04 \mathrm{mmol})$ and $\mathrm{MeOH}(15 \mathrm{~mL})$. After the pinkish solid completely dissolved $\mathrm{CoCl}_{2} \cdot 6 \mathrm{H}_{2} \mathrm{O}(0.598 \mathrm{~g}, 2.51 \mathrm{mmol})$ was added to the solution. Upon addition of the two compounds the solution turned colour from pink to a wine red. The solution was stirred at room temperature for 3 hours. Upon completion of the reaction a tancoloured precipitate was collected via vacuum filtration ( 0.587 g ). The crude complex was recrystallized from a $1: 1$ mixture of warm $\mathrm{CHCl}_{3}$ and diffusing with room temperature diethyl ether. The pure complex was obtained as a bright red solid ( $0.35 \mathrm{~g}, 39 \%$ yield $)$.

Melting Point Range: $240^{\circ} \mathrm{C}$ (decomp.)
IR: $\left(\mathrm{cm}^{-1}\right) 2968,2903,1591,1569,1527,1486,1418,1354,1261,1192,1108,989,945,865,746$, 696, 668

UV-Vis: $\left(D C M: 9.19 \times 10^{-5} \mathrm{M}\right) \lambda_{\max 1}=527 \mathrm{~nm}\left(\varepsilon=58.0 \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 2}=311 \mathrm{~nm}(\varepsilon=1.63$ $\left.\times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 3}=282 \mathrm{~nm}\left(\varepsilon=1.52 \times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 4}=236 \mathrm{~nm}\left(\varepsilon=1.82 \times 10^{4}\right.$ $\mathrm{L} \cdot \mathrm{mol}^{-1} \cdot \mathrm{~cm}^{-1}$ ).

EA: (\%): calc'd. (found) for $\mathrm{C}_{22} \mathrm{H}_{20} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{Co}$ : C 60.70 (60.49); H 4.63 (4.70); N 6.43 (6.49).
MS: $(\mathrm{m} / \mathrm{z})$ found $\left(\right.$ calc' $\left.^{\prime} \mathrm{d}\right)[\mathrm{M}+\mathrm{H}]^{+}=436.1$ (435.3)


### 4.8.1.1 Oxidation of 10a to 11a

A round-bottom flask was charged with compound $\mathbf{6 a}(0.764 \mathrm{~g}, 4.04 \mathrm{mmol})$ and $\mathrm{MeOH}(15 \mathrm{~mL})$. After the pink-solids completely dissolved $\mathrm{CoCl}_{2} \cdot 6 \mathrm{H}_{2} \mathrm{O}(0.598 \mathrm{~g}, 2.51 \mathrm{mmol})$ was added to the solution. Upon addition of the two compounds the solution turned colour from pink to a black-red. The solution was stirred at room temperature for 3 hours. Upon completion of the reaction a tancoloured precipitate was collected via vacuum filtration ( 0.114 g ). The crude complex $(0.034 \mathrm{~g})$ was recrystallized from a $1: 1$ mixture of hot DCM and layering on top $\operatorname{cool} \mathrm{MeOH}$, which led to oxidation of the metal forming the octahedral complex $11 \mathbf{a}(0.032 \mathrm{mg})$. The pure complex was obtained as a blackish-green solid (49 \%) and structurally determined via x-ray crystallography.

Melting Point Range: $235^{\circ} \mathrm{C}$ (decomp.)
IR: $\left(\mathrm{cm}^{-1}\right) 2921,2108,1612,1526,1478,1454,1420,1353,1317,1266,186,1109,1066,990$, 948, 871, 791, 736, 695

UV-Vis: $\left(D C M: 5.77 \times 10^{-6} \mathrm{M}\right) \lambda_{\max 1}=556 \mathrm{~nm}\left(\varepsilon=556 \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 2}=441 \mathrm{~nm}(\varepsilon=1.31$ $\left.\times 10^{3} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 3}=347 \mathrm{~nm}\left(\varepsilon=2.28 \times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 4}=268 \mathrm{~nm}\left(\varepsilon=8.99 \times 10^{4}\right.$ $\left.\mathrm{L} \cdot \mathrm{mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 5}=262 \mathrm{~nm}\left(\varepsilon=9.72 \times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 6}=258 \mathrm{~nm}\left(\varepsilon=9.37 \times 10^{4}\right.$ $\left.\mathrm{L} \cdot \mathrm{mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 7}=245 \mathrm{~nm}\left(\varepsilon=8.71 \times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right)$.

EA: (\%): calc'd. (found) for $\mathrm{C}_{33} \mathrm{H}_{30} \mathrm{~N}_{3} \mathrm{O}_{6} \mathrm{Co}$ : C 60.41 (61.05); H 4.96 (4.69); N 6.31 (5.99).

- $\quad 0.5 \mathrm{DCM}$ found within lattice for elemental analysis

4.8.2 Chelation of Cobalt metal to obtain 10b

A round-bottom flask was charged with $\mathbf{6 b}(42 \mathrm{mg}, 0.16 \mathrm{mmol})$ and $\mathrm{EtOH}(2 \mathrm{~mL})$. After the yellow-coloured solids were completely dissolved, $\mathrm{Co}\left(\mathrm{NO}_{3}\right)_{2} \cdot 6 \mathrm{H}_{2} \mathrm{O}$ ( $23 \mathrm{mg}, 0.079 \mathrm{mmol}$ ) dissolved in $\mathrm{EtOH}(3 \mathrm{~mL}$ ) and added to the solution. Upon addition of the two, the solution turned colour from yellow to a dark orange. $\mathrm{NEt}_{3}(0.1 \mathrm{~mL}, 73 \mathrm{mg}, 72 \mathrm{mmol})$ was added to the reaction. The solution was stirred at room temperature for 1 hour. Upon completion of the reaction a tancoloured precipitate was collected via vacuum filtration. The crude complex was recrystallized from a 1:1 mixture of warm $\mathrm{CHCl}_{3}$ and diffusing with room temperature diethyl ether. The pure complex was obtained as a bright red solid ( $36 \mathrm{mg}, 79 \%$ yield).

Melting Point Range: $221^{\circ} \mathrm{C}$ (decomp.)
IR: $\left(\mathrm{cm}^{-1}\right) 1592,1529,1462,1437,1359,1280,1240,1194,1134,1107,1058,1025,995,949$, 899, 801, 761, 677

UV-Vis: $\left(D C M: 7.00 \times 10^{-5} \mathrm{M}\right) \lambda_{\max 1}=524 \mathrm{~nm}\left(\varepsilon=94.0 \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 2}=321 \mathrm{~nm}(\varepsilon=2.11$ $\left.\times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 3}=296 \mathrm{~nm}\left(\varepsilon=1.51 \times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 4}=243 \mathrm{~nm}\left(\varepsilon=1.91 \times 10^{4}\right.$ $\mathrm{L} \cdot \mathrm{mol}^{-1} \cdot \mathrm{~cm}^{-1}$ ).

EA: (\%): calc'd. (found) for $\mathrm{C}_{22} \mathrm{H}_{16} \mathrm{Cl}_{4} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{Co}: \mathrm{C} 43.90$ (44.43); H 2.75 (2.78); N 4.55 (4.66).

- $\quad 0.5 \mathrm{DCM}$ found within lattice for elemental analysis

4.8.3 Chelation of Cobalt metal to obtain 10c

A round-bottom flask was charged with $\mathbf{6 c}(0.630 \mathrm{~g}, 2.87 \mathrm{mmol})$ and $\mathrm{EtOH}(10 \mathrm{~mL})$. After the yellow-coloured solids were completely dissolved, $\mathrm{Co}\left(\mathrm{NO}_{3}\right)_{2} \cdot 6 \mathrm{H}_{2} \mathrm{O}(0.412 \mathrm{~g}, 1.42 \mathrm{mmol})$ dissolved in $\mathrm{EtOH}(10 \mathrm{~mL})$ and added to the solution. Upon addition of the two, the solution turned colour from yellow to a dark orange. $\mathrm{NEt}_{3}(0.60 \mathrm{~mL}, 0.44 \mathrm{~g}, 4.3 \mathrm{mmol})$ was added to the reaction. The solution was stirred at room temperature for 1 hour. Upon completion of the reaction a tancoloured precipitate was collected via vacuum filtration. The crude complex was recrystallized from a 1:1 mixture of warm DCM and diffusing with room temperature diethyl ether. The pure complex was obtained as a bright red solid ( $595 \mathrm{mg}, 85 \%$ yield).

Melting Point Range: $250^{\circ} \mathrm{C}$ (decomp.)
IR: $\left(\mathrm{cm}^{-1}\right) 2960,1587,1566,1531,1498,1396,1358,1321,1301,1245,1194,1170,1113,1056$, 1028, 992, 948, 869, 838, 770, 672

UV-Vis: $\left(D C M: 1.94 \times 10^{-5} \mathrm{M}\right) \lambda_{\max 1}=547 \mathrm{~nm}\left(\varepsilon=73.0 \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 2}=317 \mathrm{~nm}(\varepsilon=4.04$ $\left.\times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 3}=263 \mathrm{~nm}\left(\varepsilon=2.32 \times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 4}=242 \mathrm{~nm}\left(\varepsilon=2.06 \times 10^{4}\right.$ $\mathrm{L} \cdot \mathrm{mol}^{-1} \cdot \mathrm{~cm}^{-1}$ ).

EA: (\%): calc'd. (found) for $\mathrm{C}_{24} \mathrm{H}_{24} \mathrm{~N}_{2} \mathrm{O}_{6} \mathrm{Co}$ : C 49.18 (49.12); H 4.37 (4.80); N 4.50 (5.17).

- $\quad 1.5 \mathrm{DCM}$ found within lattice for elemental analysis

MS: $(\mathrm{m} / \mathrm{z})$ found $\left(\right.$ calc' $\left.^{\prime} \mathrm{d}\right)[\mathrm{M}+\mathrm{H}]^{+}=495.4$ (496.2)


### 4.8.3.1 Oxidation of 10c to 11c

A round-bottom flask was charged with $\mathbf{6 c}(0.630 \mathrm{~g}, 2.87 \mathrm{mmol})$ and $\mathrm{EtOH}(10 \mathrm{~mL})$. After the yellow-coloured solids were completely dissolved, $\mathrm{Co}\left(\mathrm{NO}_{3}\right)_{2} \cdot 6 \mathrm{H}_{2} \mathrm{O}(0.412 \mathrm{~g}, 1.42 \mathrm{mmol})$ dissolved in $\mathrm{EtOH}(10 \mathrm{~mL})$ and added to the solution. Upon addition of the two, the solution turned colour from yellow to a dark orange. $\mathrm{NEt}_{3}(0.60 \mathrm{~mL}, 0.43 \mathrm{~g}, 4.30 \mathrm{mmol})$ was added to the reaction. The solution was stirred at room temperature for 1 hour. Upon completion of the reaction a tancoloured precipitate was collected via vacuum filtration ( $595 \mathrm{mg}, 85 \%$ yield). The precipitates (40 mg ) were dissolved in a vial containing only DCM, which led to oxidation of the metal forming the octahedral complex 11c. The pure complex was obtained as a blackish-green crystalline solid ( $50 \mathrm{mg}, 86 \%$ yield.).

Melting Point Range: $>230^{\circ} \mathrm{C}$ (decomp.)
IR: $\left(\mathrm{cm}^{-1}\right) 2923,1599,1529,1495,1437,1358,1319,1299,1244,1167,1111,1071,126,992$, 950, 876, 837, 756, 723

UV-Vis: $\left(D C M: 5.61 \times 10^{-6} \mathrm{M}\right) \lambda_{\max 1}=553 \mathrm{~nm}\left(\varepsilon=683 \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 2}=429 \mathrm{~nm}(\varepsilon=1.34$ $\left.\times 10^{3} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 3}=343 \mathrm{~nm}\left(\varepsilon=2.06 \times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 4}=276 \mathrm{~nm}\left(\varepsilon=6.38 \times 10^{4}\right.$ $\left.\mathrm{L} \cdot \mathrm{mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 5}=269 \mathrm{~nm}\left(\varepsilon=7.43 \times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 6}=265 \mathrm{~nm}\left(\varepsilon=7.15 \times 10^{4}\right.$ $\left.\mathrm{L} \cdot \mathrm{mol}^{-1} \cdot \mathrm{~cm}^{-1}\right), \lambda_{\max 7}=244 \mathrm{~nm}\left(\varepsilon=4.46 \times 10^{4} \mathrm{~L} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~cm}^{-1}\right)$

EA: (\%): calc'd. (found) for $\mathrm{C}_{36} \mathrm{H}_{36} \mathrm{~N}_{3} \mathrm{O}_{9} \mathrm{Co}$ : C 59.47 (59.84); H 5.20 (5.54); N 5.78 (5.04).

- $\quad 0.75 \mathrm{H}_{2} \mathrm{O}$ found within lattice for elemental analysis


### 4.9 Attempted Oxidation of Co complexes made with 1a



4.9.1 Attempted oxidation of $\mathbf{9 a}$ to $\mathbf{9 a X}$;

For quantities and general procedure, see below;
To a $25-\mathrm{mL}$ round-bottom flask, $\mathbf{9}$ a and solvent were added. $\mathbf{X}_{2}$ was added to the flask. The contents of the flask were stirred at room temperature for (mins). At the termination of the reaction, the solvent was removed in vacuo.

For all bromine reactions, removal of the excess $\mathrm{Br}_{2}$ revealed a bright blue-green gum. The dried gum was insoluble in most common laboratory solvents with the exclusion of acetone and water. Once dissolved the solution turned from a teal colour to a bright blue. NMR spectral analysis turned no positive results as the lack of any ligand signals. Dissolving commercially available $\mathrm{CoBr}_{2} \cdot 6 \mathrm{H}_{2} \mathrm{O}$ and the synthesized product in water confirmed the formation of $\mathrm{CoBr}_{2}$ occurred.

For all iodine reactions, the resultant red power was vacuum filtered, washed with cold methanol then left to dry. Further analysis revealed the persistency of the starting material 9a with absence of any iodine. [See $\underline{\text { Sec. 2.5.3.1 }}$ for full discussion]

Table 15: Trials for oxidative addition of halogens to $\mathbf{9 a}$

| Trial | $\mathrm{Co}(\mathrm{L2})_{2}$ <br> $(\mathrm{mg})$ | $\mathrm{X}_{2}$ | Molar Equiv. <br> $\left(\mathrm{X}_{2}: \mathrm{Co}\right)$ | Solvent | Time <br> $(\mathrm{mins})$ | light? <br> $(\mathrm{Y} / \mathrm{N})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 251 | Br | $1: 1$ | neat | 60 | Y |
| 2 | 507 | Br | $1: 2$ | neat | 15 | N |
| 3 | 108 | I | $1: 1$ | toluene | 60 | Y |
| 4 | 105 | I | $1: 1$ | acetone | 60 | Y |


4.9.2 Attempted oxidation of $\mathbf{9 h}$ to $\mathbf{9 h} \mathbf{- 1}$ and then $\mathbf{9 h} \mathbf{- 2}$

In a $100-\mathrm{mL}$ round-bottom flask, $9 \mathrm{~h}(445 \mathrm{mg}, 0.986 \mathrm{mmol})$, a bright pink compound, was dissolved in acetonitrile ( 20 mL ). Upon mixing, the solution turned to a dark purple suggesting coordination of either one or two ACN molecules. To this, bromine ( $0.070 \mathrm{~mL}, 0.22 \mathrm{~g}, 1.3 \mathrm{mmol}$ ) was added dropwise. The solution was stirred at room temperature in the dark (wrapped in aluminum foil) for 1 hour. After completion of the reaction, volatile components were removed in vacuo. What was left behind was a green resin. This green resin is water soluble and insoluble in most organic solvents. Thus, it was determined not to be the target complex.

### 4.10 Using 9h in ATRP


4.10.1 Polymerization of MMA with $\mathbf{9 h}$ to PMMA

Into a flame dried 10-mL Schlenk flask, a mixture of dry solvent ( 3 mL ), $\mathrm{TsCl}(0.3 \mathrm{~mol} \%)$ and $\mathbf{9 h}$ ( $2 \mathrm{~mol} \%$ ) were added. To the flask, MMA ( $1.70 \mathrm{~mL}, 1.60 \mathrm{~g}, 16.0 \mathrm{mmol}$ ) was added. The mixture of materials was sparged for 30 minutes with $\mathrm{N}_{2(\mathrm{~g})}$. The reaction was left to stir at $60{ }^{\circ} \mathrm{C}$ for 24 hours. After completion of the reaction, the solvent was removed in vacuo. The polymer was diluted with a small amount of THF ( $\sim 1 \mathrm{~mL}$ ) and dropped into rapidly stirring $-26^{\circ} \mathrm{C} \mathrm{MeOH}$. This cleaning procedure was repeated at 3-4 times to ensure complete removal of all starting materials. The catalyst ( $\mathbf{9 h}$ ) was quantitatively recovered by removal of MeOH by rotary evaporator. PMMA was isolated by removing excess solvent (MeOH/THF) in vacuo till dry ( $658 \mathrm{mg}, 42 \%$ conversion). GPC analysis revealed a PDI of 1.19 and a molecular weight for PMMA of 50,000 Da. Conversions are similar to other Co catalysts. ${ }^{74}$
${ }^{\mathbf{1}} \mathbf{H}$-NMR: ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta \mathbf{0 . 8 0 - 0 . 9 7}$ (m, 3H, 2-syndio/isotactic), $\mathbf{1 . 3 8}$ (m, 2H, 1-isotactic), 1.76-1.92 (m, 2H, 1-syndiotactic), 3.54 (m, 3H, 5-syndiotactic), $\mathbf{3 . 6 9}$ (m, 3H, 5-isotactic)
${ }^{13}$ C-NMR: ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 16.5$ (2-syndio); 18.7 (2-syndio); 25.6 (1-iso); 30.3 (1-syndio); 44.5 (3-iso); 44.9 (3-syndio); 51.8 (5-syndio); 54.1 (1-iso); 54.4 (1-syndio); 67.8 (5-iso); 176.9 (4-iso); 177.7 (4-syndio);


### 4.10.2 Attempted polymerization of THF with $\mathbf{9 h}$

Into a flame dried $10-\mathrm{mL}$ Schlenk flask, a mixture of dry THF ( 5 mL ), $\mathrm{TsCl}(11 \mathrm{mg}, 0.058 \mathrm{mmol})$ and $9 \mathbf{h}(101 \mathrm{mg}, 0.226 \mathrm{mmol})$ were added. The mixture of materials was sparged for 30 minutes with $\mathrm{N}_{2(\mathrm{~g})}$. The reaction was left to stir at $60^{\circ} \mathrm{C}$, under static vacuum, for 24 . After the completion of the reaction, purification yielded no trace of poly(THF).

| Trial | Mol\% <br> cat. | Solvent | Time | Temperature <br> $\left({ }^{\circ} \mathrm{C}\right)$ | Initiator : <br> mol \% | Mw : <br> PDI | $\%$ <br> Conversion |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 65 | THF | 24 | 60 (static vac.) | $\mathrm{TsCl}: 16$ | N/A | 0 |

### 4.11 Synthesis of Other Group 9 Complexes


4.11.1 Synthesis of Vaska's complex $\left(\operatorname{IrCl}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2}\right)(\mathbf{1 2})$

Analyses of this compound are consistent with those in the literature. ${ }^{89}$
${ }^{31}$ P-NMR: $\left(161 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right) \delta+24 \mathrm{ppm},+5 \mathrm{ppm}$
${ }^{\mathbf{1}} \mathbf{H}-\mathbf{N M R}:\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.36-7.40(\mathrm{~m}, 18 \mathrm{H}), 7.72-7.73(\mathrm{~m}, 12 \mathrm{H})$
TLC: $20 \%$ EtOAc $/ n$-hexanes $\mathrm{R}_{\mathrm{f}}=0.29$

IR: $\left(\mathrm{cm}^{-1}\right) 2109,1948_{(v=\mathrm{CO})}, 1477,1433,1306,1181,1095,1027,997,844,744,689$.

4.11.2 Synthesis of bis(1,5-cyclooctadiene)diiridium(I)dichloride (14)

Analyses of this compound are consistent with those in the literature. ${ }^{56}$
${ }^{1} \mathbf{H}-$ NMR: $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta \mathbf{1 . 5 2}(\mathrm{q}, J=8.0 \mathrm{~Hz}, 4 \mathrm{H}), \mathbf{2 . 2 4 - 2 . 2 6}(\mathrm{m}, 4 \mathrm{H}), \mathbf{4 . 2 2}(\mathrm{s}, 4 \mathrm{H})$
${ }^{13}$ C-NMR: $\left(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 31.9 ; 62.3$

4.11.3 Substitution of $\mathbf{1 4}$ with $\mathbf{4 a}$ to give $\mathbf{1 5}$

A $50-\mathrm{mL}$ three-necked round-bottom flask was charged with both $14(0.608 \mathrm{mg}, 0.905 \mathrm{mmol})$ and $4 \mathbf{a}(0.512 \mathrm{mg}, 2.36 \mathrm{mmol})$. This flask was purged and back filled with an $\mathrm{N}_{2(\mathrm{~g})}$ atmosphere. To the flask, toluene ( 6 mL ) and $\mathrm{NEt}_{3}(1.0 \mathrm{~mL}, 0.726 \mathrm{~g}, 7.2 \mathrm{mmol})$ were added. As soon as the base was added, the reaction mixture immediately changed colour from dark red-orange to a bright yellow. The reaction was left to stir at room temperature for 1 hour under a constant nitrogen atmosphere. Once completed, the solvent mixture was removed in vacuo leaving behind a yellow powder. The powder was washed with ice cold $\mathrm{MeOH}(\sim 5 \mathrm{~mL} \times 5)$ and the solution decanted from the yellow solids. The solids were dried over vacuum after being washed one last time with ice cold MeOH . The fine yellow powder was determined to be the chelated product, 15 ( $894 \mathrm{mg}, 90 \%$ yield).

Melting Point: $>150{ }^{\circ} \mathrm{C}$ (decomp.)
TLC: $30 \%$ EtOAc $/ n$-hexanes $\mathrm{R}_{\mathrm{f}}=0.30$
IR: $\left(\mathrm{cm}^{-1}\right) 2988,2927,2877,2832,1586,1560,1533,1486,1357,1315,1255,1196,1176,1155$, 1114, 1019, 969, 936, 907, 866, 834, 798, 774, 738, 696.
${ }^{1} H-N M R:\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 1.40(\mathrm{~s}, 6 \mathrm{H}, \mathbf{1}), \mathbf{1 . 5 0 - 1 . 5 8}(\mathrm{m}, 2 \mathrm{H}, \mathbf{1 2}, 13)$, 1.69-1.76 (m, 2 H , 12,13), 2.16-2.25 (m, 2H, 12,13), 2.29-2.39 (m, 2H, 12,13), 3.89 (s, 2H, 2), 4.27 (t, J = 3.0 Hz, $2 \mathrm{H}, 11,14), 4.35(\mathrm{t}, J=3.0 \mathrm{~Hz}, 2 \mathrm{H}, 11,14), 5.59(\mathrm{~s}, 1 \mathrm{H}, 5), 7.30-7.36(\mathrm{~m}, 3 \mathrm{H}, \mathbf{9 , 1 0})$, 7.75-7.78 (m, 2H, 8),
${ }^{13}$ C-NMR: (101 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta 27.5$ (1); 28.5 (12-13); 33.5 (12-13); 53.0 (11,14); 65.7 (11,14); 72.0 (3); 79.4 (2); 81.7 (5); 126.7 (8); 128.1 (9); 129.8 (10); 138.6 (7); 168.6 (4); 176.5 (6)

EA: (\%): calc'd. (found) for $\mathrm{C}_{21} \mathrm{H}_{26} \mathrm{NO}_{2}$ Ir: C 48.82 (49.11); H 5.07 (5.20); N 2.71 (2.79).

4.11.4 Oxidative addition of methyl iodide to $\mathbf{1 5}$

In a $25-\mathrm{mL}$ round-bottom flask, dry toluene $(10 \mathrm{~mL})$ was added to dissolve $15(201 \mathrm{mg}, 0.368$ $\mathrm{mmol})$. Once fully dissolved, MeI ( $0.11 \mathrm{~mL}, 1.8 \mathrm{mmol}$ ) was added dropwise. The solution was stirred under and atmosphere of $\mathrm{N}_{2(\mathrm{~g})}$ for 24 hours. The yellow coloured solution turned to a darker orange. Upon completion of the reaction, excess toluene was removed via a rotary evaporator where the mixture solidified. To purify, the crude solids were dissolved in a minimal amount of toluene and dropped into $-26^{\circ} \mathrm{C} n$-hexanes. This revealed the product as light brown solids which then the target product was isolated via vacuum filtration. The solids were recrystallized from a mixture of $1: 1 \mathrm{C}_{6} \mathrm{D}_{6} / n$-hexanes to give brown spherical plates ( $101 \mathrm{mg}, 42 \%$ yield).

TLC: 30 \% EtOAc $/ n$-hexanes $\mathrm{R}_{\mathrm{f}}=0.33$
IR: $\left(\mathrm{cm}^{-1}\right) 2925,2870,1591,1543,1486,1448,1361,1307,1249,1190,1117,1068,1037,937$, 870, 839, 776, 726, 697.
${ }^{\mathbf{1}} \mathbf{H}-N M R:\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta \mathbf{1 . 3 8}$ (d, $\left.J=18.4 \mathrm{~Hz}, 6 \mathrm{H}, \mathbf{1}, 1 \mathrm{a}\right), \mathbf{1 . 6 5 - 1 . 7 4}$ (m, $\left.1 \mathrm{H},(\mathbf{1 1 / 1 4}) \mathrm{a}\right), \mathbf{2 . 0 3 -}$ 2.11 (m, 1H, (11/14)a), 2.22-2.28 (m, 1H, (11/14)a), 2.33 (s, 3H, 15), 2.42-2.51 (m, 2H, (11/14)a), 2.62-2.72 (m, 1H, (11/14)a), 3.01-3.10 (m, 1H, (11/14)a), 3.27-3.37 (m, 1H, (11/14)a), 3.89 (ABq, $J=8.0,2 \mathrm{H}, \mathbf{2}, 2 \mathrm{a}), 4.43$ (td, $J=3.8,8.5 \mathrm{~Hz}, 1 \mathrm{H},(12-13) \mathrm{a}), 4.70-4.73$ (m, 1H, (12-13)a), 5.46-5.50 (m, 2H, 5 and (12-13)a), 5.71 (td, $J=3.4,8.4 \mathrm{~Hz}, 1 \mathrm{H}(12-13) \mathrm{a}), 7.29-7.34$ (m, 3H, 9,10), 7.647.66 (m, 2H, 8)
${ }^{13}$ C-NMR: (101 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta 11.3$ (15); 25.1 ((11/14a)); 25.3 (1,1a); 28.6 (1,1a); 31.6 ((11/14a)); 32.1 ((11/14a)); 34.7 ((11/14a)); 71.2 ((12-13)a); 71.6 (3); 74.0 ((12-13)a); 79.6 (2,2a); 82.4 (5); 86.9 ((12-13)a); 88.0 ((12-13)a); 126.7 (8); 128.0 (9); 129.8 (10); 138.7 (7); 165.6 (4); 174.5 (6)

EA: (\%): calc'd. (found) for $\mathrm{C}_{22} \mathrm{H}_{29} \mathrm{INO}_{2} \mathrm{Ir}$ : C 40.12 (39.99); H 4.44 (4.50); N 2.13 (2.11).

4.11.5 Synthesis and oxidative addition of triphenylstannane to $\mathbf{1 5}$

In the glovebox, $\mathrm{Et}_{2} \mathrm{O}(100 \mathrm{~mL})$ was combined with $\mathrm{ClSnPh}_{3}(7.261 \mathrm{~g}, 18.84 \mathrm{mmol})$ in a Schlenk flask and cooled to $0{ }^{\circ} \mathrm{C}$. $\mathrm{LiAlH}_{4}(18.00 \mathrm{~mL}, 18.00 \mathrm{mmol})$ was added and stirred at $0{ }^{\circ} \mathrm{C}$ for 4 hours. The reaction was quenched with degassed $\mathrm{dH}_{2} \mathrm{O}(50 \mathrm{~mL})$. The orgnic components were extracted, dried $\left(\mathrm{MgSO}_{4}\right)$, filtered and all volatile components were removed in vacuo to reveal $\mathrm{HSnPh}_{3}\left(6.61 \mathrm{~g}, 94 \%\right.$ yield). In a $25-\mathrm{mL}$ round-bottom flask in the glovebox, $\mathrm{HSnPh}_{3}$ ( 149 mg , $0.425 \mathrm{mmol})$ and $15(100 \mathrm{mg}, 0.183 \mathrm{mmol})$ were weighed out and dissolved in $\mathrm{C}_{6} \mathrm{D}_{6}(1.66 \mathrm{~mL})$. The mixture was stirred at room temperature under a constant nitrogen atmosphere for 20 hours. The mixture is concentrated under vacuum, $\mathrm{DCM}(0.5 \mathrm{~mL})$ is added to dissolve the complex then dry $n$-hexanes ( 10 mL ) was added. The complex, 18, is collected by vacuum filtration as a yellow powder (128 mg, 80 \% yield).

IR: $\left(\mathrm{cm}^{-1}\right) 2956,2884,1600,1574,1537,1424,1359,1307,1254,1191,1112,1064,1011,922$, 861, 726, 693
${ }^{1} H-N M R:\left(400 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right) \delta \mathbf{- 1 7 . 4 0}\left(\mathrm{s}, J_{S n-H}=23.0 \mathrm{~Hz}, 1 \mathrm{H}, 19\right), \mathbf{0 . 8 5}(\mathrm{d}, J=34.0 \mathrm{~Hz}, 6 \mathrm{H}, 1,1 \mathrm{a})$, 1.01-1.12 (m, 2H, (12-13)a), 1.58-1.68 (m, 2H, (12-13)a), 2.00-2.08 (m, 1H, (12-13)a), 2.15-2.35 (m, 2H, (12-13)a), 2.75-2.80 (m, 1H, (12-13)a), 3.11 (ABq, $J=7.8 \mathrm{~Hz}, 2 \mathrm{H}, 2,2 \mathrm{a})$, 4.52-4.57 (m, $1 \mathrm{H},(11-14) \mathrm{a})$, 4.74-4.78 (m, 2H, (11-14)a), 4.99-5.08 (m, 2H, (11-14)a), 5.74 (s, 1H, 5), 7.187.25 (m, 12H, 9-10/17-18, 7.88-7.98 (m, 6H, 16), 8.04-8.05 (m, 2H, 8),
${ }^{13}$ C-NMR: (101 MHz, C ${ }_{6} \mathrm{D}_{6}$ ) $\delta 26.7$ ((12-13)a); 27.2 ((12-13)a); 27.3 (1/1a); 27.7 (1/1a); 28.8 ((12-13)a); 41.2 ((12-13)a); 68.3 (3); 70.0 ((11/14)a); 76.0 ((11/14)a); 76.8 (2/2a); 80.6 (5); 95.3 ((11/14)a); 99.8 ((11/14)a); 126.5 (8); 127.6 (9); 127.8 (17/18); 128.2 (10); 129.5 (17/18); 137.7 ( $\left.J_{S n-C}=17.0 \mathrm{~Hz},(16)\right) ; 139.9$ (15); 144.1 (7); 162.8 (4); 175.6 (6);
${ }^{119}$ Sn-NMR: $\left(149 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right) \delta-178.1,\left(149 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ $\qquad$
EA: (\%): calc'd. (found) for $\mathrm{C}_{39} \mathrm{H}_{42} \mathrm{SnNO}_{2} \mathrm{Ir}$ : C 52.13 (52.18); H 4.76 (4.58); N 1.54 (1.41).
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KM-04901
KM-L2 (to test $\bar{T}_{\text {- }}$ shift of CDCl 3 )
 $\infty^{\circ} \infty \infty \infty$




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$\stackrel{m}{i}$






A8: ${ }^{1} \mathrm{H}-\mathrm{NMR}$ of $\mathbf{4 a}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$





A11: ${ }^{13} \mathrm{C}-\mathrm{NMR}$ of $\mathbf{3 b}$ in $\mathrm{CDCl}_{3}$ *


A12: ${ }^{1} \mathrm{H}-\mathrm{NMR}$ of $\mathbf{4 b}$ in $\mathrm{CDCl}_{3}{ }^{*}$






|  | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |  | 1 | 1 |  | 1 |  |  |  |  | 1 |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 210 | 200 | 190 | 180 | 170 | 160 | 150 | 140 | 130 | 120 | $\underset{\substack{110}}{ }$ | $100$ | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 | 0 |

A17: ${ }^{13} \mathrm{C}-\mathrm{NMR}$ of $\mathbf{3} \mathbf{c}$ in $\mathrm{CDCl}_{3} *$


A18: ${ }^{1} \mathrm{H}-\mathrm{NMR}$ of $\mathbf{4} \mathbf{c}$ in $\mathrm{CDCl}_{3} *$





A22: ${ }^{1} \mathrm{H}-\mathrm{NMR}$ of $\mathbf{3 d}$ in $\mathrm{CDCl}_{3}$ *





A25: ${ }^{13} \mathrm{C}-\mathrm{NMR}$ of $\mathbf{4 d}$ in $\mathrm{CDCl}_{3} *$


A26: COSY NMR of $\mathbf{4 d}$ in $\mathrm{CDCl}_{3}$


A27: HSQC NMR of $\mathbf{4 d}$ in $\mathrm{CDCl}_{3}$

KM-03-66
$\begin{aligned} & \text { Int-6 } \\ & 1 \mathrm{H} \text { in } \mathrm{CDCl} 3\end{aligned}$


184


A28: ${ }^{1} \mathrm{H}-\mathrm{NMR}$ of $\mathbf{3 e}$ in $\mathrm{CDCl}_{3}$ *



A29: ${ }^{13} \mathrm{C}-\mathrm{NMR}$ of $\mathbf{3 e}$ in $\mathrm{CDCl}_{3}$ *


A30: ${ }^{1} \mathrm{H}-\mathrm{NMR}$ of $\mathbf{4 e}$ in $\mathrm{CDCl}_{3}$ *



|  | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 210 | 200 | 190 | 180 | 170 | 160 | 150 | 140 | 130 | 120 | 110 | 100 | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 | 0 |
| A31: ${ }^{13} \mathrm{C}-\mathrm{NMR}$ of $\mathbf{4 e}$ in $\mathrm{CDCl}_{3}$ * |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |














A42: COSY NMR of $\mathbf{4} \mathbf{g}$ in $\mathrm{CDCl}_{3}$



KM-03-94
Ligand-9 13 C in CDCl 3


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Nogmoy



| $\infty$ |
| :--- |
| $\stackrel{\omega}{\sim}$ |

-134.57
-132.50
-130.17
-128.99
$-126.04$
12

201


A45: ${ }^{13} \mathrm{C}-\mathrm{NMR}$ of $\mathbf{6 b}$ in $\mathrm{CDCl}_{3} *$









|  | 1 | 1 | 1 | 1 | 1 | 15 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |  | 1 |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 210 | 200 | 190 | 180 | 170 | 160 | 150 | 140 | 130 | 120 |  | ${ }^{100}$ | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 | 0 |

A53: ${ }^{13} \mathrm{C}-\mathrm{NMR}$ of $\mathbf{3 h}$ in $\mathrm{CDCl}_{3} *$







## (2)





A62: ${ }^{1} \mathrm{H}-\mathrm{NMR}$ of $\mathbf{4 k}$ in $\mathrm{CDCl}_{3}{ }^{*}$


KM-03-174
Ligand-15
19F in CDCl3


A64: ${ }^{19}$ F-NMR of $\mathbf{4 k}$ in $\mathrm{CDCl}_{3}{ }^{*}$



KM-03-175



KM-03-175
Ligand-16 13 C in CDCl 3

$\stackrel{\sim}{\stackrel{\infty}{1}}$







KM-04-30 [IrCODCl]2 13 C in CDCl 3
$\stackrel{\infty}{\stackrel{\infty}{\dot{N}}}$
$\stackrel{\infty}{\stackrel{\infty}{+}}$


A72: ${ }^{13} \mathrm{C}-\mathrm{NMR}$ of $\mathbf{1 4}$ in $\mathrm{CDCl}_{3}$ *



|  | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 200 | 190 | 180 | 170 | 160 | 150 | 140 | 130 | 120 | 110 | $\begin{gathered} 100 \\ \mathrm{f} 1(\mathrm{ppm}) \end{gathered}$ | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 | 0 |

A74: ${ }^{13} \mathrm{C}-\mathrm{NMR}$ of $\mathbf{1 5}$ in $\mathrm{CDCl}_{3} *$




KM-04-26
(COD)Ir(L2)MeI 1 H in CDCl 3

† $\mathcal{~}$



A78: ${ }^{1} \mathrm{H}-\mathrm{NMR}$ of $\mathbf{1 6}$ in $\mathrm{CDCl}_{3} *$







KM-04-32
HSnPh 3
119Sn in C6D6




KM-04-33
(COD)Ir(L2)HSnPh3
119Sn in C6D6




A87: ${ }^{119} \mathrm{Sn}-\mathrm{NMR}$ of $\mathbf{1 8}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$




A90: HSQC NMR of $\mathbf{1 8}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$




A92: ${ }^{13} \mathrm{C}-\mathrm{NMR}$ of PMMA in $\mathrm{CDCl}_{3} *$
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## Agilent Resolutions Pro



Wavenumber

| Name |
| :--- |
| $\operatorname{Co}($ oxme $) 2-\mathrm{L} 2 \quad$ |

B1: IR spectrum for $\mathbf{9 a}$

Agilent Resolutions Pro

252


Wavenumber

| Name |
| :--- |
| $\mathrm{Co}(\mathrm{Cl2}) 2-\mathrm{L} 3$ |

## Agilent Resolutions Pro


wavenumber

| Name |
| :--- |
| $\mathrm{Co}(\mathrm{OMe}) 2-\mathrm{L} 4 \quad$ |

## Agilent Resolutions Pro



| Name |
| :--- |
| $\mathrm{Co}(\mathrm{Me2}) 2$ - L5 |

## Agilent Resolutions Pro



## Wavenumber

B5: IR spectrum for $\mathbf{9 e}$

Agilent Resolutions Pro


Wavenumber
B6: IR spectrum for $9 \mathbf{f}$

## Agilent Resolutions Pro



## Wavenumber

B7: IR spectrum for $\mathbf{9 g}$

Agilent Resolutions Pro

258


| Name |
| :--- |
| $\operatorname{Co}(\mathrm{L} 12) 2$ |

B8: IR spectrum for 9 h

## Agilent Resolutions Pro

259


Wavenumber

| Name |
| :--- |
| $\mathrm{Co}(\mathrm{L} 13) 2 \quad$ |

B9: IR spectrum for $\mathbf{9 i}$

## Agilent Resolutions Pro



Wavenumber

| Name |
| :--- | :--- |
| $\mathrm{Co}(\mathrm{Me}) 2 \quad$ |

B10: IR spectrum for $\mathbf{9} \mathbf{j}$

## Agilent Resolutions Pro



## Wavenumber

| Name |
| :--- |
| $\mathrm{Co}(\mathrm{CF} 3) 2 \quad$ |

B11: IR spectrum for $\mathbf{9 k}$

## Agilent Resolutions Pro



B12: IR spectrum for 91

## Agilent Resolutions Pro



Wavenumber

| Name |
| :--- |
| Co (ox) $2-\mathrm{L} 1 \quad$ |

B13: IR spectrum for 10a

## Agilent Resolutions Pro



Wavenumber

| Name |
| :--- |
| Co (L9) $2 \quad$ |

B14: IR spectrum for $\mathbf{1 0 b}$

## Agilent Resolutions Pro



Wavenumber

| Name |
| :--- |
| $\mathrm{Co}(\mathrm{L} 10) 2 \quad$ |

B15: IR spectrum for 10c

Agilent Resolutions Pro

266


Wavenumber

| Name |
| :--- |
| $\mathrm{Co}(\mathrm{ox}) 3$ - L1 $\quad$ |

B16: IR spectrum for $\mathbf{1 1 a}$

## Agilent Resolutions Pro



| Name |
| :--- |
| Co (L10) $3 \quad$ |

B17: IR spectrum for 11c

## Agilent Resolutions Pro



Wavenumber

| Name |
| :--- |
| $\mathrm{Cu}(\mathrm{ox}) 2$ - L1 $\quad$ |

B18: IR spectrum for $\mathbf{8 a}$

## Agilent Resolutions Pro



Wavenumber

| Name |  |
| :--- | :--- |
| Cu (oxme) $2-\mathrm{L} 2 \quad-$ |  |

B19: IR spectrum for 7a (brown)

## Agilent Resolutions Pro



Wavenumber

| Name |
| :--- | :--- |
| Cu (oxme) $2-\mathrm{L} 2 \quad-$ |

B20: IR spectrum for 7a (green)

## Agilent Resolutions Pro



Wavenumber

| Name |
| :--- |
| $\mathrm{Cu}(\mathrm{Cl} 2) 2-\mathrm{L} 3 \quad$ |

Agilent Resolutions Pro

272


| Name |
| :--- |
| $\mathrm{Cu}(\mathrm{OMe}) 2-\mathrm{L} 4$ |

B22: IR spectrum for 7c

## Agilent Resolutions Pro

273


Wavenumber

| Name |
| :--- |
| $\mathrm{Cu}(\mathrm{Me} 2) 2-\mathrm{L} 5-$ |

## Agilent Resolutions Pro



Wavenumber

## Agilent Resolutions Pro



[^0]
## Agilent Resolutions Pro



[^1]
## Agilent Resolutions Pro



| Name |
| :--- |
| $\mathrm{Cu}(\mathrm{L} 9) 2 \quad 2$ |

B27: IR spectrum for $\mathbf{8 b}$

## Agilent Resolutions Pro



| Name |
| :--- |
| $\mathrm{Cu}(\mathrm{L} 12) 2$ |

B28: IR spectrum for 7 h

## Agilent Resolutions Pro

279


B29: IR spectrum for $\mathbf{7 i}$

## Agilent Resolutions Pro



| Name |
| :--- |
| Kathy $-\operatorname{IrCl}(\mathrm{CO})(\mathrm{PPh} 3) 2$ |

B30: IR spectrum for 12

## Agilent Resolutions Pro

281


Wavenumber

| Name |
| :--- |
| (COD) Ir (L2) $\quad$ |

B31: IR spectrum for $\mathbf{1 5}$

## Agilent Resolutions Pro

282


B32: IR spectrum for 16

## Agilent Resolutions Pro



[^2]B33: IR spectrum for $\mathbf{1 8}$
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C7: UV-Vis Trace of $\mathbf{9 e}$ ..... 291
C8: UV-Vis Trace of $\mathbf{9 f}$ ..... 292
C9: UV-Vis Trace of $\mathbf{9 g}$ ..... 293
C10: UV-Vis Trace of $\mathbf{1 0 b}$ ..... 300
C11: UV-Vis Trace of $\mathbf{1 0 c}$ ..... 301
C12: UV-Vis Trace of 11c ..... 303
C13: UV-Vis Trace of $\mathbf{9 h}$ ..... 294
C14: UV-Vis Trace of $\mathbf{9 i}$ ..... 295
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C25: UV-Vis Trace of $\mathbf{7 g}$ ..... 311
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C2: UV-Vis Trace of 9b


C3: UV-Vis Trace of 9c



C5: UV-Vis Trace of $\mathbf{9 e}$





C9: UV-Vis Trace of $\mathbf{9 i}$



C11: UV-Vis Trace of $\mathbf{9 k}$

UV-Vis trace of $\mathrm{Co}(16)_{2}$ in $\operatorname{DCM}\left(1.39 \times 10^{-4}\right)$


C12: UV-Vis Trace of 91


C13: UV-Vis Trace of $\mathbf{1 0 a}$



C15: UV-Vis Trace of 10c

UV-Vis trace of $\mathrm{Co}(\mathrm{L} 1)_{3}$ in $\operatorname{DCM}\left(5.77 \times 10^{-6}\right)$


C16: UV-Vis Trace of 11a



C18: UV-Vis Trace of 7a (brown)


C19: UV-Vis Trace of 7a (green)




C22: UV-Vis Trace of 7d





C26: UV-Vis Trace for $\mathbf{8 b}$



C28: UV-Vis Trace of 7i
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D1: Voltammogram of $\mathbf{9 a}$


D2: Voltammogram of 9b


D3: Voltammogram of 9c


D4: Voltammogram of 9d


D5: Voltammogram of $9 \mathbf{e}$


D6: Voltammogram of $\mathbf{9 f}$


D7: Voltammogram of $9 \mathbf{g}$


D8: Voltammogram of $\mathbf{9 h}$


D9: Voltammogram of $\mathbf{9 i}$


D10: Voltammogram of $\mathbf{9 j}$


D11: Voltammogram of $\mathbf{9 k}$


D12: Voltammogram of 91


D13: Voltammogram of $\mathbf{1 0 a}$


D14: Voltammogram of $\mathbf{1 0 c}$


D15: Voltammogram of 11a


D16: Voltammogram of 11c


D17: Voltammogram of 7a (brown)


D18: Voltammogram of 7a (green)


D19: Voltammogram of 7b


D20: Voltammogram of 7c


D21: Voltammogram of 7d


D22: Voltammogram of 7e


D23: Voltammogram of 7f


D24: Voltammogram of $\mathbf{7 g}$


D25: Voltammogram of 7h


D26: Voltammogram of 7i

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E1: GPC Trace of PMMA (approximate $\mathrm{Rt}=15.5 \mathrm{mins}$ )
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F1: Crystal data and structure refinement for d1759_a (10a).

| Identification code | d1759_a (10a2) |
| :---: | :---: |
| Empirical formula | C22 H20 Co N2 O4 |
| Formula weight | 435.33 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 £ |
| Crystal system | Monoclinic |
| Space group | $\mathrm{P} 21 / \mathrm{n}$ |
| Unit cell dimensions | $a=12.3954(7) \AA \quad a=90^{\circ}$. |
|  | $b=10.2361(5) \AA \quad b=103.402(2)^{\circ}$. |
|  | $\mathrm{c}=15.3565(8) \AA \quad \mathrm{g}=90^{\circ}$. |
| Volume | 1895.38(17) $\AA^{3}$ |
| Z | 4 |
| Density (calculated) | $1.526 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.938 \mathrm{~mm}^{-1}$ |
| F(000) | 900 |
| Crystal size | $0.300 \times 0.250 \times 0.040 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 1.909 to $27.543^{\circ}$. |
| Index ranges | $-16<=\mathrm{h}<=16,-13<=\mathrm{k}<=13,-19<=1<=19$ |
| Reflections collected | 27284 |

Independent reflections
Completeness to theta $=25.242^{\circ}$
Absorption correction
Max. and min. transmission
Refinement method
Data / restraints / parameters
Goodness-of-fit on $\mathrm{F}^{2}$
Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ]
R indices (all data)
Extinction coefficient
Largest diff. peak and hole
$4360[\mathrm{R}(\mathrm{int})=0.0392]$
100.0 \%

Semi-empirical from equivalents
0.7456 and 0.6452

Full-matrix least-squares on $\mathrm{F}^{2}$
4360 / 0 / 262
1.041
$\mathrm{R} 1=0.0290, \mathrm{wR} 2=0.0694$
$\mathrm{R} 1=0.0430, \mathrm{wR} 2=0.0786$
$\mathrm{n} / \mathrm{a}$
0.348 and -0.315 e. $\AA^{-3}$

Table 2. Atomic coordinates ( $\times 10^{4}$ ) and equivalent isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for $\mathrm{d} 1759 \_\mathrm{a}$. $\mathrm{U}(\mathrm{eq})$ is defined as one third of the trace of the orthogonalized $\mathrm{U}^{\mathrm{ij}}$ tensor.

|  | X | y | z | U(eq) |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{Co}(1)$ | 7235(1) | 7531(1) | 7396(1) | 22(1) |
| $\mathrm{O}(1)$ | 6093(1) | 8841(1) | 7040(1) | 27(1) |
| $\mathrm{O}(2)$ | 5406(1) | 6725(1) | 9239(1) | 28(1) |
| $\mathrm{O}(3)$ | 7133(1) | 6296(1) | 6425(1) | 25(1) |
| $\mathrm{O}(4)$ | 10290(1) | 8143(1) | 6866(1) | 26(1) |
| N(1) | 6688(1) | 6895(1) | 8419(1) | 22(1) |
| N(2) | 8760(1) | 8058(1) | 7415(1) | 21(1) |
| C(1) | 7151(2) | 5918(2) | 9113(1) | 28(1) |
| C(2) | 6216(2) | 5717(2) | 9603(1) | 30(1) |
| C(3) | 5746(1) | 7313(2) | 8555(1) | 21(1) |
| C(4) | 5025(1) | 8280(2) | 8080(1) | 21(1) |
| C(5) | 5225(1) | 8977(2) | 7363(1) | 20(1) |
| C(6) | 4393(1) | 9946(2) | 6876(1) | 21(1) |
| C(7) | 4569(2) | 10534(2) | 6102(1) | 29(1) |
| C(8) | 3794(2) | 11394(2) | 5609(1) | 36(1) |
| C(9) | 2838(2) | 11692(2) | 5889(1) | 34(1) |
| C(10) | 2659(2) | 11121(2) | 6659(1) | 35(1) |
| C(11) | 3423(2) | 10256(2) | 7148(1) | 29(1) |
| C(12) | 9513(1) | 8955(2) | 8020(1) | 25(1) |
| C(13) | 10480(1) | 9127(2) | 7566(1) | 27(1) |
| C(14) | 9266(1) | 7623(2) | 6821(1) | 19(1) |
| C(15) | 8896(1) | 6698(2) | 6130(1) | 21(1) |
| C(16) | 7885(1) | 6072(2) | 5984(1) | 18(1) |
| C(17) | 7572(1) | 5073(2) | 5256(1) | 18(1) |
| C(18) | 6470(1) | 4665(2) | 4998(1) | 23(1) |
| C(19) | 6141(1) | 3721(2) | 4339(1) | 26(1) |
| C(20) | 6912(2) | 3181(2) | 3923(1) | 26(1) |
| C(21) | 8011(2) | 3570(2) | 4172(1) | 29(1) |
| C(22) | 8337(1) | 4508(2) | 4835(1) | 26(1) |

Table 3. Bond lengths $[\AA]$ and angles $\left[{ }^{\circ}\right]$ for d1759_a.

| $\mathrm{Co}(1)-\mathrm{O}(1)$ | 1.9348(12) |
| :---: | :---: |
| $\mathrm{Co}(1)-\mathrm{O}(3)$ | 1.9360(12) |
| $\mathrm{Co}(1)-\mathrm{N}(2)$ | 1.9588(14) |
| $\mathrm{Co}(1)-\mathrm{N}(1)$ | 1.9621(14) |
| $\mathrm{O}(1)-\mathrm{C}(5)$ | 1.2923(19) |
| $\mathrm{O}(2)-\mathrm{C}(3)$ | 1.359(2) |
| $\mathrm{O}(2)-\mathrm{C}(2)$ | 1.458(2) |
| $\mathrm{O}(3)-\mathrm{C}(16)$ | 1.2926(19) |
| $\mathrm{O}(4)-\mathrm{C}(14)$ | 1.3632(19) |
| $\mathrm{O}(4)-\mathrm{C}(13)$ | 1.452(2) |
| $\mathrm{N}(1)-\mathrm{C}(3)$ | $1.305(2)$ |
| $\mathrm{N}(1)-\mathrm{C}(1)$ | 1.476(2) |
| $\mathrm{N}(2)-\mathrm{C}(14)$ | 1.301(2) |
| $\mathrm{N}(2)-\mathrm{C}(12)$ | 1.474(2) |
| $\mathrm{C}(1)-\mathrm{C}(2)$ | 1.535(3) |
| $\mathrm{C}(1)-\mathrm{H}(1 \mathrm{~A})$ | 0.9900 |
| $\mathrm{C}(1)-\mathrm{H}(1 \mathrm{~B})$ | 0.9900 |
| $\mathrm{C}(2)-\mathrm{H}(2 \mathrm{~A})$ | 0.9900 |
| $\mathrm{C}(2)-\mathrm{H}(2 \mathrm{~B})$ | 0.9900 |
| $\mathrm{C}(3)-\mathrm{C}(4)$ | 1.417(2) |
| $\mathrm{C}(4)-\mathrm{C}(5)$ | 1.382(2) |
| $\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(5)-\mathrm{C}(6)$ | 1.499(2) |
| $\mathrm{C}(6)-\mathrm{C}(7)$ | 1.395(2) |
| $\mathrm{C}(6)-\mathrm{C}(11)$ | 1.397(2) |
| $\mathrm{C}(7)-\mathrm{C}(8)$ | 1.391(3) |
| $\mathrm{C}(7)-\mathrm{H}(7 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(8)-\mathrm{C}(9)$ | 1.385(3) |
| $\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(9)-\mathrm{C}(10)$ | 1.383(3) |
| $\mathrm{C}(9)-\mathrm{H}(9 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(10)-\mathrm{C}(11)$ | 1.384(3) |
| $\mathrm{C}(10)-\mathrm{H}(10 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(11)-\mathrm{H}(11 \mathrm{~A})$ | 0.9500 |


| $\mathrm{C}(12)-\mathrm{C}(13)$ | 1.529(2) |
| :---: | :---: |
| $\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~A})$ | 0.9900 |
| $\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~B})$ | 0.9900 |
| $\mathrm{C}(13)-\mathrm{H}(13 \mathrm{~A})$ | 0.9900 |
| $\mathrm{C}(13)-\mathrm{H}(13 \mathrm{~B})$ | 0.9900 |
| $\mathrm{C}(14)-\mathrm{C}(15)$ | 1.417(2) |
| $\mathrm{C}(15)-\mathrm{C}(16)$ | 1.378(2) |
| $\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(16)-\mathrm{C}(17)$ | 1.499 (2) |
| $\mathrm{C}(17)-\mathrm{C}(22)$ | 1.391(2) |
| $\mathrm{C}(17)-\mathrm{C}(18)$ | 1.396(2) |
| $\mathrm{C}(18)-\mathrm{C}(19)$ | 1.391(2) |
| $\mathrm{C}(18)-\mathrm{H}(18 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(19)-\mathrm{C}(20)$ | 1.382(2) |
| $\mathrm{C}(19)-\mathrm{H}(19 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(20)-\mathrm{C}(21)$ | $1.385(3)$ |
| $\mathrm{C}(20)-\mathrm{H}(20 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(21)-\mathrm{C}(22)$ | 1.390 (2) |
| $\mathrm{C}(21)-\mathrm{H}(21 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(22)-\mathrm{H}(22 \mathrm{~A})$ | 0.9500 |
| $\mathrm{O}(1)-\mathrm{Co}(1)-\mathrm{O}(3)$ | 108.80(5) |
| $\mathrm{O}(1)-\mathrm{Co}(1)-\mathrm{N}(2)$ | 116.97(6) |
| $\mathrm{O}(3)-\mathrm{Co}(1)-\mathrm{N}(2)$ | 94.75(5) |
| $\mathrm{O}(1)-\mathrm{Co}(1)-\mathrm{N}(1)$ | 95.14(6) |
| $\mathrm{O}(3)-\mathrm{Co}(1)-\mathrm{N}(1)$ | 115.29(6) |
| $\mathrm{N}(2)-\mathrm{Co}(1)-\mathrm{N}(1)$ | 126.20(6) |
| $\mathrm{C}(5)-\mathrm{O}(1)-\mathrm{Co}(1)$ | 125.93(11) |
| $\mathrm{C}(3)-\mathrm{O}(2)-\mathrm{C}(2)$ | 107.50(13) |
| $\mathrm{C}(16)-\mathrm{O}(3)-\mathrm{Co}(1)$ | 126.28(11) |
| $\mathrm{C}(14)-\mathrm{O}(4)-\mathrm{C}(13)$ | 107.31(13) |
| $\mathrm{C}(3)-\mathrm{N}(1)-\mathrm{C}(1)$ | 108.65(14) |
| $\mathrm{C}(3)-\mathrm{N}(1)-\mathrm{Co}(1)$ | 120.48(12) |
| $\mathrm{C}(1)-\mathrm{N}(1)-\mathrm{Co}(1)$ | 130.84(11) |
| $\mathrm{C}(14)-\mathrm{N}(2)-\mathrm{C}(12)$ | 108.45(14) |
| $\mathrm{C}(14)-\mathrm{N}(2)-\mathrm{Co}(1)$ | 121.03(11) |


| $\mathrm{C}(12)-\mathrm{N}(2)-\mathrm{Co}(1)$ | 130.50(11) |
| :---: | :---: |
| $\mathrm{N}(1)-\mathrm{C}(1)-\mathrm{C}(2)$ | 103.48(14) |
| $\mathrm{N}(1)-\mathrm{C}(1)-\mathrm{H}(1 \mathrm{~A})$ | 111.1 |
| $\mathrm{C}(2)-\mathrm{C}(1)-\mathrm{H}(1 \mathrm{~A})$ | 111.1 |
| $\mathrm{N}(1)-\mathrm{C}(1)-\mathrm{H}(1 \mathrm{~B})$ | 111.1 |
| $\mathrm{C}(2)-\mathrm{C}(1)-\mathrm{H}(1 \mathrm{~B})$ | 111.1 |
| $\mathrm{H}(1 \mathrm{~A})-\mathrm{C}(1)-\mathrm{H}(1 \mathrm{~B})$ | 109.0 |
| $\mathrm{O}(2)-\mathrm{C}(2)-\mathrm{C}(1)$ | 104.36(14) |
| $\mathrm{O}(2)-\mathrm{C}(2)-\mathrm{H}(2 \mathrm{~A})$ | 110.9 |
| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{H}(2 \mathrm{~A})$ | 110.9 |
| $\mathrm{O}(2)-\mathrm{C}(2)-\mathrm{H}(2 \mathrm{~B})$ | 110.9 |
| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{H}(2 \mathrm{~B})$ | 110.9 |
| $\mathrm{H}(2 \mathrm{~A})-\mathrm{C}(2)-\mathrm{H}(2 \mathrm{~B})$ | 108.9 |
| $\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{O}(2)$ | 115.26(15) |
| $\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{C}(4)$ | 128.92(16) |
| $\mathrm{O}(2)-\mathrm{C}(3)-\mathrm{C}(4)$ | 115.82(15) |
| $\mathrm{C}(5)-\mathrm{C}(4)-\mathrm{C}(3)$ | 124.23(15) |
| $\mathrm{C}(5)-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~A})$ | 117.9 |
| $\mathrm{C}(3)-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~A})$ | 117.9 |
| $\mathrm{O}(1)-\mathrm{C}(5)-\mathrm{C}(4)$ | 124.66(16) |
| $\mathrm{O}(1)-\mathrm{C}(5)-\mathrm{C}(6)$ | 114.71(14) |
| $\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{C}(6)$ | 120.61(15) |
| $\mathrm{C}(7)-\mathrm{C}(6)-\mathrm{C}(11)$ | 118.19(16) |
| $\mathrm{C}(7)-\mathrm{C}(6)-\mathrm{C}(5)$ | 119.02(16) |
| $\mathrm{C}(11)-\mathrm{C}(6)-\mathrm{C}(5)$ | 122.75(16) |
| $\mathrm{C}(8)-\mathrm{C}(7)-\mathrm{C}(6)$ | 120.83(18) |
| $\mathrm{C}(8)-\mathrm{C}(7)-\mathrm{H}(7 \mathrm{~A})$ | 119.6 |
| $\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{H}(7 \mathrm{~A})$ | 119.6 |
| $\mathrm{C}(9)-\mathrm{C}(8)-\mathrm{C}(7)$ | 120.21(19) |
| $\mathrm{C}(9)-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~A})$ | 119.9 |
| $\mathrm{C}(7)-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~A})$ | 119.9 |
| $\mathrm{C}(10)-\mathrm{C}(9)-\mathrm{C}(8)$ | 119.42(18) |
| $\mathrm{C}(10)-\mathrm{C}(9)-\mathrm{H}(9 \mathrm{~A})$ | 120.3 |
| $\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{H}(9 \mathrm{~A})$ | 120.3 |
| $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(11)$ | 120.61(19) |
| $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{H}(10 \mathrm{~A})$ | 119.7 |


| $\mathrm{C}(11)-\mathrm{C}(10)-\mathrm{H}(10 \mathrm{~A})$ | 119.7 |
| :---: | :---: |
| $\mathrm{C}(10)-\mathrm{C}(11)-\mathrm{C}(6)$ | 120.73(18) |
| $\mathrm{C}(10)-\mathrm{C}(11)-\mathrm{H}(11 \mathrm{~A})$ | 119.6 |
| $\mathrm{C}(6)-\mathrm{C}(11)-\mathrm{H}(11 \mathrm{~A})$ | 119.6 |
| $\mathrm{N}(2)-\mathrm{C}(12)-\mathrm{C}(13)$ | 103.51(13) |
| $\mathrm{N}(2)-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~A})$ | 111.1 |
| $\mathrm{C}(13)-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~A})$ | 111.1 |
| $\mathrm{N}(2)-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~B})$ | 111.1 |
| $\mathrm{C}(13)-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~B})$ | 111.1 |
| $\mathrm{H}(12 \mathrm{~A})-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~B})$ | 109.0 |
| $\mathrm{O}(4)-\mathrm{C}(13)-\mathrm{C}(12)$ | 104.36(13) |
| $\mathrm{O}(4)-\mathrm{C}(13)-\mathrm{H}(13 \mathrm{~A})$ | 110.9 |
| $\mathrm{C}(12)-\mathrm{C}(13)-\mathrm{H}(13 \mathrm{~A})$ | 110.9 |
| $\mathrm{O}(4)-\mathrm{C}(13)-\mathrm{H}(13 \mathrm{~B})$ | 110.9 |
| $\mathrm{C}(12)-\mathrm{C}(13)-\mathrm{H}(13 \mathrm{~B})$ | 110.9 |
| $\mathrm{H}(13 \mathrm{~A})-\mathrm{C}(13)-\mathrm{H}(13 \mathrm{~B})$ | 108.9 |
| $\mathrm{N}(2)-\mathrm{C}(14)-\mathrm{O}(4)$ | 115.19(14) |
| $\mathrm{N}(2)-\mathrm{C}(14)-\mathrm{C}(15)$ | 128.96(15) |
| $\mathrm{O}(4)-\mathrm{C}(14)-\mathrm{C}(15)$ | 115.84(14) |
| $\mathrm{C}(16)-\mathrm{C}(15)-\mathrm{C}(14)$ | 123.83(15) |
| $\mathrm{C}(16)-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~A})$ | 118.1 |
| $\mathrm{C}(14)-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~A})$ | 118.1 |
| $\mathrm{O}(3)-\mathrm{C}(16)-\mathrm{C}(15)$ | 124.87(15) |
| $\mathrm{O}(3)-\mathrm{C}(16)-\mathrm{C}(17)$ | 114.71(14) |
| $\mathrm{C}(15)-\mathrm{C}(16)-\mathrm{C}(17)$ | 120.40(14) |
| $\mathrm{C}(22)-\mathrm{C}(17)-\mathrm{C}(18)$ | 118.12(15) |
| $\mathrm{C}(22)-\mathrm{C}(17)-\mathrm{C}(16)$ | 123.01(15) |
| $\mathrm{C}(18)-\mathrm{C}(17)-\mathrm{C}(16)$ | 118.85(14) |
| $\mathrm{C}(19)-\mathrm{C}(18)-\mathrm{C}(17)$ | 121.11(16) |
| $\mathrm{C}(19)-\mathrm{C}(18)-\mathrm{H}(18 \mathrm{~A})$ | 119.4 |
| $\mathrm{C}(17)-\mathrm{C}(18)-\mathrm{H}(18 \mathrm{~A})$ | 119.4 |
| $\mathrm{C}(20)-\mathrm{C}(19)-\mathrm{C}(18)$ | 119.79(16) |
| $\mathrm{C}(20)-\mathrm{C}(19)-\mathrm{H}(19 \mathrm{~A})$ | 120.1 |
| $\mathrm{C}(18)-\mathrm{C}(19)-\mathrm{H}(19 \mathrm{~A})$ | 120.1 |
| $\mathrm{C}(19)-\mathrm{C}(20)-\mathrm{C}(21)$ | 119.95(16) |
| $\mathrm{C}(19)-\mathrm{C}(20)-\mathrm{H}(20 \mathrm{~A})$ | 120.0 |


| $\mathrm{C}(21)-\mathrm{C}(20)-\mathrm{H}(20 \mathrm{~A})$ | 120.0 |
| :--- | :--- |
| $\mathrm{C}(20)-\mathrm{C}(21)-\mathrm{C}(22)$ | $120.04(17)$ |
| $\mathrm{C}(20)-\mathrm{C}(21)-\mathrm{H}(21 \mathrm{~A})$ | 120.0 |
| $\mathrm{C}(22)-\mathrm{C}(21)-\mathrm{H}(21 \mathrm{~A})$ | 120.0 |
| $\mathrm{C}(21)-\mathrm{C}(22)-\mathrm{C}(17)$ | $120.97(16)$ |
| $\mathrm{C}(21)-\mathrm{C}(22)-\mathrm{H}(22 \mathrm{~A})$ | 119.5 |
| $\mathrm{C}(17)-\mathrm{C}(22)-\mathrm{H}(22 \mathrm{~A})$ | 119.5 |

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for d1759_a. The anisotropic displacement factor exponent takes the form: $-2 p^{2}\left[h^{2} a^{* 2} U^{11}+\ldots+2 h k a^{*} b^{*} U^{12}\right]$

|  | $\mathrm{U}^{11}$ | $\mathrm{U}^{22}$ | $\mathrm{U}^{33}$ | $\mathrm{U}^{23}$ | $\mathrm{U}^{13}$ | $\mathrm{U}^{12}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{Co}(1)$ | 20(1) | 26(1) | 23(1) | -4(1) | 10(1) | 1(1) |
| $\mathrm{O}(1)$ | 26(1) | 30(1) | 30(1) | 5(1) | 14(1) | 4(1) |
| $\mathrm{O}(2)$ | 26(1) | 33(1) | 26(1) | 8(1) | 11(1) | 4(1) |
| $\mathrm{O}(3)$ | 20(1) | 31(1) | 27(1) | -8(1) | 12(1) | -4(1) |
| $\mathrm{O}(4)$ | 19(1) | 27(1) | 35(1) | -12(1) | 10(1) | -4(1) |
| N(1) | 22(1) | 23(1) | 22(1) | -2(1) | $6(1)$ | 1(1) |
| $\mathrm{N}(2)$ | 21(1) | 20(1) | 22(1) | -3(1) | 5(1) | 1(1) |
| C(1) | 27(1) | 28(1) | 27(1) | 1(1) | $6(1)$ | 6(1) |
| $\mathrm{C}(2)$ | 32(1) | 28(1) | 29(1) | 5(1) | 8(1) | 5(1) |
| C(3) | 21(1) | 24(1) | 18(1) | -3(1) | 5(1) | -4(1) |
| C(4) | 17(1) | 25(1) | 22(1) | -2(1) | 6 (1) | $0(1)$ |
| C(5) | 18(1) | 19(1) | 22(1) | -5(1) | 5(1) | -3(1) |
| C(6) | 22(1) | 18(1) | 22(1) | -4(1) | 3(1) | -3(1) |
| C(7) | 30(1) | 30(1) | 29(1) | 2(1) | 8(1) | -1(1) |
| C(8) | 43(1) | 33(1) | 30(1) | 8(1) | 4(1) | -2(1) |
| C(9) | 31(1) | 25(1) | 40(1) | 4(1) | -4(1) | 1(1) |
| C(10) | 28(1) | 30(1) | 47(1) | 4(1) | 9(1) | 6(1) |
| $\mathrm{C}(11)$ | 28(1) | 27(1) | 34(1) | 5(1) | 10(1) | 3(1) |
| $\mathrm{C}(12)$ | 23(1) | 25(1) | 26(1) | -8(1) | 6 (1) | $0(1)$ |
| C(13) | 23(1) | 24(1) | 32(1) | -11(1) | 5(1) | -2(1) |
| C(14) | 15(1) | 19(1) | 23(1) | 1(1) | 4(1) | 2(1) |
| C(15) | 18(1) | 22(1) | 22(1) | -4(1) | 8(1) | 1(1) |
| C(16) | 18(1) | 19(1) | 18(1) | 1(1) | $6(1)$ | 3(1) |
| C(17) | 19(1) | 18(1) | 18(1) | 2(1) | 4(1) | 1(1) |
| C(18) | 19(1) | 27(1) | 23(1) | $0(1)$ | $6(1)$ | $0(1)$ |
| C(19) | 20(1) | 29(1) | 26(1) | $0(1)$ | 2(1) | -3(1) |
| C(20) | 30(1) | 22(1) | 24(1) | -6(1) | 2(1) | -2(1) |
| C(21) | 26(1) | 31(1) | 32(1) | -10(1) | 11(1) | 1(1) |
| C(22) | 17(1) | 31(1) | 31(1) | -9(1) | 8(1) | -2(1) |

Table 5. Hydrogen coordinates ( $\times 10^{4}$ ) and isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for d1759_a.

|  | x | y | z | $\mathrm{U}(\mathrm{eq})$ |
| :---: | :---: | :---: | :---: | :---: |
| H(1A) | 7830 | 6252 | 9526 | 33 |
| H(1B) | 7328 | 5093 | 8840 | 33 |
| H(2A) | 5886 | 4835 | 9482 | 36 |
| H(2B) | 6494 | 5826 | 10257 | 36 |
| H(4A) | 4361 | 8461 | 8267 | 25 |
| H(7A) | 5227 | 10346 | 5909 | 35 |
| H(8A) | 3920 | 11777 | 5077 | 43 |
| H(9A) | 2311 | 12285 | 5555 | 41 |
| H(10A) | 2005 | 11323 | 6854 | 42 |
| H(11A) | 3287 | 9868 | 7675 | 35 |
| H(12A) | 9768 | 8569 | 8624 | 30 |
| H(12B) | 9146 | 9801 | 8072 | 30 |
| H(13A) | 10476 | 10015 | 7308 | 32 |
| H(13B) | 11198 | 8982 | 7996 | 32 |
| H(15A) | 9372 | 6496 | 5745 | 25 |
| H(18A) | 5935 | 5039 | 5278 | 27 |
| H(19A) | 5388 | 3448 | 4175 | 31 |
| H(20A) | 6689 | 2543 | 3468 | 31 |
| H(21A) | 8542 | 3195 | 3889 | 35 |
| H(22A) | 9092 | 4768 | 5003 | 31 |

Table 6. Torsion angles [ ${ }^{\circ}$ ] for d1759_a.

| $\mathrm{C}(3)-\mathrm{N}(1)-\mathrm{C}(1)-\mathrm{C}(2)$ | 7.36(19) |
| :---: | :---: |
| $\mathrm{Co}(1)-\mathrm{N}(1)-\mathrm{C}(1)-\mathrm{C}(2)$ | -170.37(12) |
| $\mathrm{C}(3)-\mathrm{O}(2)-\mathrm{C}(2)-\mathrm{C}(1)$ | 6.99(18) |
| $\mathrm{N}(1)-\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{O}(2)$ | -8.50(18) |
| $\mathrm{C}(1)-\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{O}(2)$ | -3.3(2) |
| $\mathrm{Co}(1)-\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{O}(2)$ | 174.70(11) |
| $\mathrm{C}(1)-\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{C}(4)$ | 177.69(17) |
| $\mathrm{Co}(1)-\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{C}(4)$ | -4.3(2) |
| $\mathrm{C}(2)-\mathrm{O}(2)-\mathrm{C}(3)-\mathrm{N}(1)$ | -2.61(19) |
| $\mathrm{C}(2)-\mathrm{O}(2)-\mathrm{C}(3)-\mathrm{C}(4)$ | 176.52(14) |
| $\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{C}(4)-\mathrm{C}(5)$ | -0.6(3) |
| $\mathrm{O}(2)-\mathrm{C}(3)-\mathrm{C}(4)-\mathrm{C}(5)$ | -179.59(15) |
| $\mathrm{Co}(1)-\mathrm{O}(1)-\mathrm{C}(5)-\mathrm{C}(4)$ | 6.6(2) |
| $\mathrm{Co}(1)-\mathrm{O}(1)-\mathrm{C}(5)-\mathrm{C}(6)$ | -171.60(10) |
| $\mathrm{C}(3)-\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{O}(1)$ | -0.4(3) |
| $\mathrm{C}(3)-\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{C}(6)$ | 177.60(15) |
| $\mathrm{O}(1)-\mathrm{C}(5)-\mathrm{C}(6)-\mathrm{C}(7)$ | 4.6(2) |
| $\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{C}(6)-\mathrm{C}(7)$ | -173.60(16) |
| $\mathrm{O}(1)-\mathrm{C}(5)-\mathrm{C}(6)-\mathrm{C}(11)$ | -177.68(16) |
| $\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{C}(6)-\mathrm{C}(11)$ | 4.1(2) |
| $\mathrm{C}(11)-\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{C}(8)$ | -0.7(3) |
| $\mathrm{C}(5)-\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{C}(8)$ | 177.06(16) |
| $\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{C}(8)-\mathrm{C}(9)$ | 0.9(3) |
| $\mathrm{C}(7)-\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{C}(10)$ | -0.6(3) |
| $\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(11)$ | 0.0(3) |
| $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(11)-\mathrm{C}(6)$ | 0.2(3) |
| $\mathrm{C}(7)-\mathrm{C}(6)-\mathrm{C}(11)-\mathrm{C}(10)$ | 0.2(3) |
| $\mathrm{C}(5)-\mathrm{C}(6)-\mathrm{C}(11)-\mathrm{C}(10)$ | -177.54(17) |
| $\mathrm{C}(14)-\mathrm{N}(2)-\mathrm{C}(12)-\mathrm{C}(13)$ | 9.02(18) |
| $\mathrm{Co}(1)-\mathrm{N}(2)-\mathrm{C}(12)-\mathrm{C}(13)$ | -169.80(12) |
| $\mathrm{C}(14)-\mathrm{O}(4)-\mathrm{C}(13)-\mathrm{C}(12)$ | 8.85(18) |
| $\mathrm{N}(2)-\mathrm{C}(12)-\mathrm{C}(13)-\mathrm{O}(4)$ | -10.62(18) |
| $\mathrm{C}(12)-\mathrm{N}(2)-\mathrm{C}(14)-\mathrm{O}(4)$ | -3.8(2) |
| $\mathrm{Co}(1)-\mathrm{N}(2)-\mathrm{C}(14)-\mathrm{O}(4)$ | 175.11(11) |


| $\mathrm{C}(12)-\mathrm{N}(2)-\mathrm{C}(14)-\mathrm{C}(15)$ | $176.83(16)$ |
| :--- | :---: |
| $\mathrm{Co}(1)-\mathrm{N}(2)-\mathrm{C}(14)-\mathrm{C}(15)$ | $-4.2(2)$ |
| $\mathrm{C}(13)-\mathrm{O}(4)-\mathrm{C}(14)-\mathrm{N}(2)$ | $-3.51(19)$ |
| $\mathrm{C}(13)-\mathrm{O}(4)-\mathrm{C}(14)-\mathrm{C}(15)$ | $175.90(14)$ |
| $\mathrm{N}(2)-\mathrm{C}(14)-\mathrm{C}(15)-\mathrm{C}(16)$ | $-0.8(3)$ |
| $\mathrm{O}(4)-\mathrm{C}(14)-\mathrm{C}(15)-\mathrm{C}(16)$ | $179.93(15)$ |
| $\mathrm{Co}(1)-\mathrm{O}(3)-\mathrm{C}(16)-\mathrm{C}(15)$ | $-0.7(2)$ |
| $\mathrm{Co}(1)-\mathrm{O}(3)-\mathrm{C}(16)-\mathrm{C}(17)$ | $-179.18(10)$ |
| $\mathrm{C}(14)-\mathrm{C}(15)-\mathrm{C}(16)-\mathrm{O}(3)$ | $3.6(3)$ |
| $\mathrm{C}(14)-\mathrm{C}(15)-\mathrm{C}(16)-\mathrm{C}(17)$ | $-178.03(15)$ |
| $\mathrm{O}(3)-\mathrm{C}(16)-\mathrm{C}(17)-\mathrm{C}(22)$ | $-166.48(16)$ |
| $\mathrm{C}(15)-\mathrm{C}(16)-\mathrm{C}(17)-\mathrm{C}(22)$ | $15.0(2)$ |
| $\mathrm{O}(3)-\mathrm{C}(16)-\mathrm{C}(17)-\mathrm{C}(18)$ | $12.1(2)$ |
| $\mathrm{C}(15)-\mathrm{C}(16)-\mathrm{C}(17)-\mathrm{C}(18)$ | $-166.41(16)$ |
| $\mathrm{C}(22)-\mathrm{C}(17)-\mathrm{C}(18)-\mathrm{C}(19)$ | $0.0(3)$ |
| $\mathrm{C}(16)-\mathrm{C}(17)-\mathrm{C}(18)-\mathrm{C}(19)$ | $-178.69(15)$ |
| $\mathrm{C}(17)-\mathrm{C}(18)-\mathrm{C}(19)-\mathrm{C}(20)$ | $-0.6(3)$ |
| $\mathrm{C}(18)-\mathrm{C}(19)-\mathrm{C}(20)-\mathrm{C}(21)$ | $0.7(3)$ |
| $\mathrm{C}(19)-\mathrm{C}(20)-\mathrm{C}(21)-\mathrm{C}(22)$ | $-0.4(3)$ |
| $\mathrm{C}(20)-\mathrm{C}(21)-\mathrm{C}(22)-\mathrm{C}(17)$ | $-0.2(3)$ |
| $\mathrm{C}(18)-\mathrm{C}(17)-\mathrm{C}(22)-\mathrm{C}(21)$ | $0.4(3)$ |
| $\mathrm{C}(16)-\mathrm{C}(17)-\mathrm{C}(22)-\mathrm{C}(21)$ | $179.02(16)$ |

Symmetry transformations used to generate equivalent atoms:


F2: Crystal data and structure refinement for d1747_a (11a).

Identification code
Empirical formula
Formula weight
Temperature
Wavelength
Crystal system
Space group
Unit cell dimensions

Volume

Z

Density (calculated)
Absorption coefficient
F(000)
Crystal size
Theta range for data collection
Index ranges
Reflections collected
Independent reflections
Completeness to theta $=67.549 \propto$
Absorption correction
d1747_a (11a)
C33 H30 Co N3 O6
623.53

150(2) K
$1.54178 \approx$
Triclinic
P-1
$\mathrm{a}=10.7799(4) \approx \quad \alpha=72.051(2) \infty$.
$b=10.7875(4) \approx \quad \beta=84.462(2) \infty$.
$\mathrm{c}=13.4524(5) \approx \quad \gamma=68.638(2) \infty$.
$1385.76(9) \approx^{3}$
2
$1.494 \mathrm{Mg} / \mathrm{m}^{3}$
$5.301 \mathrm{~mm}^{-1}$
648
$0.160 \times 0.050 \times 0.040 \mathrm{~mm}^{3}$
3.454 to $67.549 \infty$.
$-12<=\mathrm{h}<=12,-12<=\mathrm{k}<=12,-16<=1<=16$
34303
$4927[\mathrm{R}(\mathrm{int})=0.0638]$
98.6 \%

Semi-empirical from equivalents

Max. and min. transmission
Refinement method
Data / restraints / parameters
Goodness-of-fit on $\mathrm{F}^{2}$
Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ]
R indices (all data)
Extinction coefficient
Largest diff. peak and hole
0.7529 and 0.5658

Full-matrix least-squares on $\mathrm{F}^{2}$
4927 / 0 / 388
1.022
$\mathrm{R} 1=0.0401, \mathrm{wR} 2=0.0984$
$\mathrm{R} 1=0.0479, w R 2=0.1032$
n/a
0.506 and -0.411 e. $\approx^{-3}$

Table 2. Atomic coordinates $\left(\times 10^{4}\right)$ and equivalent isotropic displacement parameters $\left(\approx^{2} \times 10^{3}\right)$ for $\mathrm{d} 1747 \_\mathrm{a}$. $\mathrm{U}(\mathrm{eq})$ is defined as one third of the trace of the orthogonalized $\mathrm{U}^{\mathrm{ij}}$ tensor.

|  | x | y | z | U(eq) |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{Co}(1)$ | 5074(1) | 7355(1) | 7297(1) | 22(1) |
| $\mathrm{O}(1)$ | 3619(2) | 6986(2) | 8080(1) | 27(1) |
| $\mathrm{O}(2)$ | 2799(2) | 7544(2) | 4971(1) | 40(1) |
| $\mathrm{O}(3)$ | 5932(2) | 5406(2) | 7486(1) | 26(1) |
| $\mathrm{O}(4)$ | 8708(2) | 7371(2) | 6154(1) | 35(1) |
| $\mathrm{O}(5)$ | 4095(2) | 9288(2) | 7038(1) | 26(1) |
| $\mathrm{O}(6)$ | 5751(2) | 7681(2) | 10102(1) | 34(1) |
| N(1) | 4335(2) | 7463(2) | 6015(2) | 24(1) |
| N(2) | 6574(2) | 7777(2) | 6608(2) | 26(1) |
| N(3) | 5751(2) | 7134(2) | 8629(2) | 26(1) |
| C(1) | 2440(2) | 7329(2) | 7708(2) | 26(1) |
| C(2) | 2113(2) | 7669(3) | 6671(2) | 29(1) |
| C(3) | 3119(2) | 7570(2) | 5914(2) | 26(1) |
| C(4) | 4024(3) | 7217(3) | 4395(2) | 33(1) |
| C(5) | 5078(2) | 7210(3) | 5082(2) | 32(1) |
| C(6) | 1404(2) | 7286(3) | 8528(2) | 29(1) |
| C(7) | 443(3) | 6732(3) | 8483(2) | 39(1) |
| C(8) | -481(3) | 6669(3) | 9273(3) | 50(1) |
| C(9) | -462(3) | 7182(4) | 10097(2) | 51(1) |
| C(10) | 483(3) | 7757(3) | 10135(2) | 45(1) |
| C(11) | 1427(3) | 7781(3) | 9360(2) | 36(1) |
| C(12) | 7164(2) | 4773(3) | 7303(2) | 25(1) |
| C(13) | 8088(2) | 5396(3) | 6911(2) | 30(1) |
| C(14) | 7746(2) | 6844(3) | 6579(2) | 27(1) |
| C(15) | 8120(3) | 8866(3) | 5924(2) | 37(1) |
| C(16) | 6657(3) | 9163(3) | 6157(2) | 40(1) |
| C(17) | 7567(2) | 3237(3) | 7570(2) | 26(1) |
| C(18) | 8639(3) | 2445(3) | 7087(2) | 33(1) |
| C(19) | 9008(3) | 1024(3) | 7359(2) | 38(1) |
| C(20) | 8316(3) | 347(3) | 8108(2) | 39(1) |
| C(21) | 7245(3) | 1112(3) | 8586(2) | 35(1) |
|  |  | 359 |  |  |


| $\mathrm{C}(22)$ | $6876(2)$ | $2542(3)$ | $8319(2)$ | $29(1)$ |
| :--- | ---: | ---: | ---: | ---: |
| $\mathrm{C}(23)$ | $4012(2)$ | $10027(3)$ | $7666(2)$ | $26(1)$ |
| $\mathrm{C}(24)$ | $4583(2)$ | $9519(3)$ | $8649(2)$ | $27(1)$ |
| $\mathrm{C}(25)$ | $5359(2)$ | $8110(3)$ | $9083(2)$ | $26(1)$ |
| $\mathrm{C}(26)$ | $6466(3)$ | $6182(3)$ | $10386(2)$ | $32(1)$ |
| $\mathrm{C}(27)$ | $6416(3)$ | $5784(3)$ | $9398(2)$ | $33(1)$ |
| $\mathrm{C}(28)$ | $3254(2)$ | $11538(3)$ | $7217(2)$ | $26(1)$ |
| $\mathrm{C}(29)$ | $3593(3)$ | $12550(3)$ | $7461(2)$ | $33(1)$ |
| $\mathrm{C}(30)$ | $2956(3)$ | $13948(3)$ | $6989(2)$ | $40(1)$ |
| $\mathrm{C}(31)$ | $1934(3)$ | $14381(3)$ | $6263(2)$ | $39(1)$ |
| $\mathrm{C}(32)$ | $1583(2)$ | $13406(3)$ | $6008(2)$ | $35(1)$ |
| $\mathrm{C}(33)$ | $2238(2)$ | $11998(3)$ | $6481(2)$ | $33(1)$ |
|  |  |  |  |  |

Table 3. Bond lengths [ $\approx]$ and angles [ $\infty$ ] for d1747_a.

| $\mathrm{Co}(1)-\mathrm{O}(5)$ | $1.8983(16)$ |
| :---: | :---: |
| $\mathrm{Co}(1)-\mathrm{O}(1)$ | $1.8993(16)$ |
| $\mathrm{Co}(1)-\mathrm{O}(3)$ | $1.9072(16)$ |
| $\mathrm{Co}(1)-\mathrm{N}(3)$ | $1.9144(19)$ |
| $\mathrm{Co}(1)-\mathrm{N}(2)$ | $1.915(2)$ |
| $\mathrm{Co}(1)-\mathrm{N}(1)$ | $1.9219(19)$ |
| $\mathrm{O}(1)-\mathrm{C}(1)$ | $1.292(3)$ |
| $\mathrm{O}(2)-\mathrm{C}(3)$ | $1.356(3)$ |
| $\mathrm{O}(2)-\mathrm{C}(4)$ | $1.449(3)$ |
| $\mathrm{O}(3)-\mathrm{C}(12)$ | $1.292(3)$ |
| $\mathrm{O}(4)-\mathrm{C}(14)$ | $1.357(3)$ |
| $\mathrm{O}(4)-\mathrm{C}(15)$ | $1.444(3)$ |
| $\mathrm{O}(5)-\mathrm{C}(23)$ | $1.307(3)$ |
| $\mathrm{O}(6)-\mathrm{C}(25)$ | $1.360(3)$ |
| $\mathrm{O}(6)-\mathrm{C}(26)$ | $1.457(3)$ |
| $\mathrm{N}(1)-\mathrm{C}(3)$ | $1.291(3)$ |
| $\mathrm{N}(1)-\mathrm{C}(5)$ | $1.467(3)$ |
| $\mathrm{N}(2)-\mathrm{C}(14)$ | $1.304(3)$ |
| $\mathrm{N}(2)-\mathrm{C}(16)$ | $1.463(3)$ |
| $\mathrm{N}(3)-\mathrm{C}(25)$ | $1.296(3)$ |
| $\mathrm{N}(3)-\mathrm{C}(27)$ | $1.470(3)$ |
| $\mathrm{C}(1)-\mathrm{C}(2)$ | 1.375(3) |
| $\mathrm{C}(1)-\mathrm{C}(6)$ | 1.494(3) |
| $\mathrm{C}(2)-\mathrm{C}(3)$ | 1.413(3) |
| $\mathrm{C}(2)-\mathrm{H}(2 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(4)-\mathrm{C}(5)$ | 1.528(3) |
| $\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~A})$ | 0.9900 |
| $\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~B})$ | 0.9900 |
| $\mathrm{C}(5)-\mathrm{H}(5 \mathrm{~A})$ | 0.9900 |
| $\mathrm{C}(5)-\mathrm{H}(5 \mathrm{~B})$ | 0.9900 |
| $\mathrm{C}(6)-\mathrm{C}(7)$ | 1.385(4) |
| $\mathrm{C}(6)-\mathrm{C}(11)$ | 1.387(4) |
| $\mathrm{C}(7)-\mathrm{C}(8)$ | 1.387(4) |
| $\mathrm{C}(7)-\mathrm{H}(7 \mathrm{~A})$ | 0.9500 |


| $\mathrm{C}(8)-\mathrm{C}(9)$ | 1.388(4) |
| :---: | :---: |
| $\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~A})$ | 0.9500 |
| C(9)-C(10) | 1.384(4) |
| $\mathrm{C}(9)-\mathrm{H}(9 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(10)-\mathrm{C}(11)$ | 1.386(4) |
| $\mathrm{C}(10)-\mathrm{H}(10 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(11)-\mathrm{H}(11 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(12)-\mathrm{C}(13)$ | 1.374( |
| $\mathrm{C}(12)-\mathrm{C}(17)$ | 1.484 (3) |
| $\mathrm{C}(13)-\mathrm{C}(14)$ | 1.399(4 |
| $\mathrm{C}(13)-\mathrm{H}(13 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(15)-\mathrm{C}(16)$ | 1.513(4) |
| $\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~A})$ | 0.9900 |
| $\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~B})$ | 0.9900 |
| $\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~A})$ | 0.9900 |
| $\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~B})$ | 0.9900 |
| $\mathrm{C}(17)-\mathrm{C}(22)$ | 1.389(3) |
| $\mathrm{C}(17)-\mathrm{C}(18)$ | $1.402(3$ |
| $\mathrm{C}(18)-\mathrm{C}(19)$ | 1.372(4) |
| $\mathrm{C}(18)-\mathrm{H}(18 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(19)-\mathrm{C}(20)$ | 1.380(4 |
| $\mathrm{C}(19)-\mathrm{H}(19 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(20)-\mathrm{C}(21)$ | 1.384(4) |
| $\mathrm{C}(20)-\mathrm{H}(20 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(21)-\mathrm{C}(22)$ | 1.380(4 |
| $\mathrm{C}(21)-\mathrm{H}(21 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(22)-\mathrm{H}(22 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(23)-\mathrm{C}(24)$ | 1.375(3) |
| $\mathrm{C}(23)-\mathrm{C}(28)$ | $1.485(3$ |
| $\mathrm{C}(24)$ - $\mathrm{C}(25)$ | $1.405(4$ |
| $\mathrm{C}(24)-\mathrm{H}(24 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(26)-\mathrm{C}(27)$ | 1.528(3 |
| $\mathrm{C}(26)-\mathrm{H}(26 \mathrm{~A})$ | 0.9900 |
| $\mathrm{C}(26)-\mathrm{H}(26 \mathrm{~B})$ | 0.9900 |
| $\mathrm{C}(27)-\mathrm{H}(27 \mathrm{~A})$ | 0.9900 |
| C(27)-H(27B) | 0.9900 |


| C(28)-C(33) | 1.392(3) |
| :---: | :---: |
| C(28)-C(29) | 1.403(3) |
| $\mathrm{C}(29)$-C(30) | 1.374(4) |
| $\mathrm{C}(29)-\mathrm{H}(29 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(30)-\mathrm{C}(31)$ | 1.392(4) |
| $\mathrm{C}(30)-\mathrm{H}(30 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(31)-\mathrm{C}(32)$ | 1.380(4) |
| $\mathrm{C}(31)-\mathrm{H}(31 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(32)-\mathrm{C}(33)$ | 1.386(4) |
| $\mathrm{C}(32)-\mathrm{H}(32 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(33)-\mathrm{H}(33 \mathrm{~A})$ | 0.9500 |
| $\mathrm{O}(5)-\mathrm{Co}(1)-\mathrm{O}(1)$ | 88.61(7) |
| $\mathrm{O}(5)-\mathrm{Co}(1)-\mathrm{O}(3)$ | 174.68(7) |
| $\mathrm{O}(1)-\mathrm{Co}(1)-\mathrm{O}(3)$ | 89.04(7) |
| $\mathrm{O}(5)-\mathrm{Co}(1)-\mathrm{N}(3)$ | 94.33(7) |
| $\mathrm{O}(1)-\mathrm{Co}(1)-\mathrm{N}(3)$ | 84.09(8) |
| $\mathrm{O}(3)-\mathrm{Co}(1)-\mathrm{N}(3)$ | 90.18(8) |
| $\mathrm{O}(5)-\mathrm{Co}(1)-\mathrm{N}(2)$ | 89.78(8) |
| $\mathrm{O}(1)-\mathrm{Co}(1)-\mathrm{N}(2)$ | 174.84(7) |
| $\mathrm{O}(3)-\mathrm{Co}(1)-\mathrm{N}(2)$ | 92.96(8) |
| $\mathrm{N}(3)-\mathrm{Co}(1)-\mathrm{N}(2)$ | 91.15(8) |
| $\mathrm{O}(5)-\mathrm{Co}(1)-\mathrm{N}(1)$ | 88.15(7) |
| $\mathrm{O}(1)-\mathrm{Co}(1)-\mathrm{N}(1)$ | 92.11(7) |
| $\mathrm{O}(3)-\mathrm{Co}(1)-\mathrm{N}(1)$ | 87.16(7) |
| $\mathrm{N}(3)-\mathrm{Co}(1)-\mathrm{N}(1)$ | 175.40(8) |
| $\mathrm{N}(2)-\mathrm{Co}(1)-\mathrm{N}(1)$ | 92.73(8) |
| $\mathrm{C}(1)-\mathrm{O}(1)-\mathrm{Co}(1)$ | 125.40(15) |
| $\mathrm{C}(3)-\mathrm{O}(2)-\mathrm{C}(4)$ | 107.09(18) |
| $\mathrm{C}(12)-\mathrm{O}(3)-\mathrm{Co}(1)$ | 126.63(15) |
| $\mathrm{C}(14)-\mathrm{O}(4)-\mathrm{C}(15)$ | 107.23(19) |
| $\mathrm{C}(23)-\mathrm{O}(5)-\mathrm{Co}(1)$ | 126.15(15) |
| $\mathrm{C}(25)-\mathrm{O}(6)-\mathrm{C}(26)$ | 107.56(18) |
| $\mathrm{C}(3)-\mathrm{N}(1)-\mathrm{C}(5)$ | 109.44(19) |
| $\mathrm{C}(3)-\mathrm{N}(1)-\mathrm{Co}(1)$ | 123.46(16) |
| $\mathrm{C}(5)-\mathrm{N}(1)-\mathrm{Co}(1)$ | 126.38(15) |


| $\mathrm{C}(14)-\mathrm{N}(2)-\mathrm{C}(16)$ | 108.9(2) |
| :---: | :---: |
| $\mathrm{C}(14)-\mathrm{N}(2)-\mathrm{Co}(1)$ | 124.12(17) |
| $\mathrm{C}(16)-\mathrm{N}(2)-\mathrm{Co}(1)$ | 126.54(16) |
| $\mathrm{C}(25)-\mathrm{N}(3)-\mathrm{C}(27)$ | 109.74(19) |
| $\mathrm{C}(25)-\mathrm{N}(3)-\mathrm{Co}(1)$ | 123.18(17) |
| $\mathrm{C}(27)-\mathrm{N}(3)-\mathrm{Co}(1)$ | 124.44(15) |
| $\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(2)$ | 125.7(2) |
| $\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(6)$ | 113.6(2) |
| $\mathrm{C}(2)-\mathrm{C}(1)-\mathrm{C}(6)$ | 120.6(2) |
| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)$ | 120.2(2) |
| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{H}(2 \mathrm{~A})$ | 119.9 |
| $\mathrm{C}(3)-\mathrm{C}(2)-\mathrm{H}(2 \mathrm{~A})$ | 119.9 |
| $\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{O}(2)$ | 115.1(2) |
| $\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{C}(2)$ | 127.7(2) |
| $\mathrm{O}(2)-\mathrm{C}(3)-\mathrm{C}(2)$ | 117.2(2) |
| $\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{C}(5)$ | 104.92(18) |
| $\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~A})$ | 110.8 |
| $\mathrm{C}(5)-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~A})$ | 110.8 |
| $\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~B})$ | 110.8 |
| $\mathrm{C}(5)-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~B})$ | 110.8 |
| $\mathrm{H}(4 \mathrm{~A})-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~B})$ | 108.8 |
| $\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(4)$ | 103.03(19) |
| $\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{H}(5 \mathrm{~A})$ | 111.2 |
| $\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{H}(5 \mathrm{~A})$ | 111.2 |
| $\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{H}(5 \mathrm{~B})$ | 111.2 |
| $\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{H}(5 \mathrm{~B})$ | 111.2 |
| $\mathrm{H}(5 \mathrm{~A})-\mathrm{C}(5)-\mathrm{H}(5 \mathrm{~B})$ | 109.1 |
| $\mathrm{C}(7)-\mathrm{C}(6)-\mathrm{C}(11)$ | 119.5(2) |
| $\mathrm{C}(7)-\mathrm{C}(6)-\mathrm{C}(1)$ | 121.3(2) |
| $\mathrm{C}(11)-\mathrm{C}(6)-\mathrm{C}(1)$ | 119.2(2) |
| $\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{C}(8)$ | 119.8(3) |
| $\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{H}(7 \mathrm{~A})$ | 120.1 |
| $\mathrm{C}(8)-\mathrm{C}(7)-\mathrm{H}(7 \mathrm{~A})$ | 120.1 |
| $\mathrm{C}(7)-\mathrm{C}(8)-\mathrm{C}(9)$ | 120.3(3) |
| $\mathrm{C}(7)-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~A})$ | 119.8 |
| $\mathrm{C}(9)-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~A})$ | 119.8 |


| $\mathrm{C}(10)-\mathrm{C}(9)-\mathrm{C}(8)$ | 119.9(3) |
| :---: | :---: |
| $\mathrm{C}(10)-\mathrm{C}(9)-\mathrm{H}(9 \mathrm{~A})$ | 120.0 |
| $\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{H}(9 \mathrm{~A})$ | 120.0 |
| $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(11)$ | 119.5(3) |
| $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{H}(10 \mathrm{~A})$ | 120.3 |
| $\mathrm{C}(11)-\mathrm{C}(10)-\mathrm{H}(10 \mathrm{~A})$ | 120.3 |
| $\mathrm{C}(10)-\mathrm{C}(11)-\mathrm{C}(6)$ | 120.8(3) |
| $\mathrm{C}(10)-\mathrm{C}(11)-\mathrm{H}(11 \mathrm{~A})$ | 119.6 |
| $\mathrm{C}(6)-\mathrm{C}(11)-\mathrm{H}(11 \mathrm{~A})$ | 119.6 |
| $\mathrm{O}(3)-\mathrm{C}(12)-\mathrm{C}(13)$ | 125.8(2) |
| $\mathrm{O}(3)-\mathrm{C}(12)-\mathrm{C}(17)$ | 114.5(2) |
| $\mathrm{C}(13)-\mathrm{C}(12)-\mathrm{C}(17)$ | 119.6(2) |
| $\mathrm{C}(12)-\mathrm{C}(13)-\mathrm{C}(14)$ | 122.2(2) |
| $\mathrm{C}(12)-\mathrm{C}(13)-\mathrm{H}(13 \mathrm{~A})$ | 118.9 |
| $\mathrm{C}(14)-\mathrm{C}(13)-\mathrm{H}(13 \mathrm{~A})$ | 118.9 |
| $\mathrm{N}(2)-\mathrm{C}(14)-\mathrm{O}(4)$ | 114.7(2) |
| $\mathrm{N}(2)-\mathrm{C}(14)-\mathrm{C}(13)$ | 127.1(2) |
| $\mathrm{O}(4)-\mathrm{C}(14)-\mathrm{C}(13)$ | 118.2(2) |
| $\mathrm{O}(4)-\mathrm{C}(15)-\mathrm{C}(16)$ | 105.2(2) |
| $\mathrm{O}(4)-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~A})$ | 110.7 |
| $\mathrm{C}(16)-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~A})$ | 110.7 |
| $\mathrm{O}(4)-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~B})$ | 110.7 |
| $\mathrm{C}(16)-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~B})$ | 110.7 |
| $\mathrm{H}(15 \mathrm{~A})-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~B})$ | 108.8 |
| $\mathrm{N}(2)-\mathrm{C}(16)-\mathrm{C}(15)$ | 103.6(2) |
| $\mathrm{N}(2)-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~A})$ | 111.0 |
| $\mathrm{C}(15)-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~A})$ | 111.0 |
| $\mathrm{N}(2)-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~B})$ | 111.0 |
| $\mathrm{C}(15)-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~B})$ | 111.0 |
| $\mathrm{H}(16 \mathrm{~A})-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~B})$ | 109.0 |
| $\mathrm{C}(22)-\mathrm{C}(17)-\mathrm{C}(18)$ | 118.0(2) |
| $\mathrm{C}(22)-\mathrm{C}(17)-\mathrm{C}(12)$ | 120.0(2) |
| $\mathrm{C}(18)-\mathrm{C}(17)-\mathrm{C}(12)$ | 122.0(2) |
| $\mathrm{C}(19)-\mathrm{C}(18)-\mathrm{C}(17)$ | 121.0(3) |
| $\mathrm{C}(19)-\mathrm{C}(18)-\mathrm{H}(18 \mathrm{~A})$ | 119.5 |
| $\mathrm{C}(17)-\mathrm{C}(18)-\mathrm{H}(18 \mathrm{~A})$ | 119.5 |


| $\mathrm{C}(18)-\mathrm{C}(19)-\mathrm{C}(20)$ | 120.3(2) |
| :---: | :---: |
| $\mathrm{C}(18)-\mathrm{C}(19)-\mathrm{H}(19 \mathrm{~A})$ | 119.9 |
| $\mathrm{C}(20)-\mathrm{C}(19)-\mathrm{H}(19 \mathrm{~A})$ | 119.9 |
| $\mathrm{C}(19)-\mathrm{C}(20)-\mathrm{C}(21)$ | 119.6(3) |
| $\mathrm{C}(19)-\mathrm{C}(20)-\mathrm{H}(20 \mathrm{~A})$ | 120.2 |
| $\mathrm{C}(21)-\mathrm{C}(20)-\mathrm{H}(20 \mathrm{~A})$ | 120.2 |
| $\mathrm{C}(22)-\mathrm{C}(21)-\mathrm{C}(20)$ | 120.2(3) |
| $\mathrm{C}(22)-\mathrm{C}(21)-\mathrm{H}(21 \mathrm{~A})$ | 119.9 |
| $\mathrm{C}(20)-\mathrm{C}(21)-\mathrm{H}(21 \mathrm{~A})$ | 119.9 |
| $\mathrm{C}(21)-\mathrm{C}(22)-\mathrm{C}(17)$ | 120.9(2) |
| $\mathrm{C}(21)-\mathrm{C}(22)-\mathrm{H}(22 \mathrm{~A})$ | 119.6 |
| $\mathrm{C}(17)-\mathrm{C}(22)-\mathrm{H}(22 \mathrm{~A})$ | 119.6 |
| $\mathrm{O}(5)-\mathrm{C}(23)-\mathrm{C}(24)$ | 125.4(2) |
| $\mathrm{O}(5)-\mathrm{C}(23)-\mathrm{C}(28)$ | 113.9(2) |
| $\mathrm{C}(24)-\mathrm{C}(23)-\mathrm{C}(28)$ | 120.6(2) |
| $\mathrm{C}(23)-\mathrm{C}(24)-\mathrm{C}(25)$ | 122.5(2) |
| $\mathrm{C}(23)-\mathrm{C}(24)-\mathrm{H}(24 \mathrm{~A})$ | 118.8 |
| $\mathrm{C}(25)-\mathrm{C}(24)-\mathrm{H}(24 \mathrm{~A})$ | 118.8 |
| $\mathrm{N}(3)-\mathrm{C}(25)-\mathrm{O}(6)$ | 114.5(2) |
| $\mathrm{N}(3)-\mathrm{C}(25)-\mathrm{C}(24)$ | 127.7(2) |
| $\mathrm{O}(6)-\mathrm{C}(25)-\mathrm{C}(24)$ | 117.8(2) |
| $\mathrm{O}(6)-\mathrm{C}(26)-\mathrm{C}(27)$ | 104.79(19) |
| $\mathrm{O}(6)-\mathrm{C}(26)-\mathrm{H}(26 \mathrm{~A})$ | 110.8 |
| $\mathrm{C}(27)-\mathrm{C}(26)-\mathrm{H}(26 \mathrm{~A})$ | 110.8 |
| $\mathrm{O}(6)-\mathrm{C}(26)-\mathrm{H}(26 \mathrm{~B})$ | 110.8 |
| $\mathrm{C}(27)-\mathrm{C}(26)-\mathrm{H}(26 \mathrm{~B})$ | 110.8 |
| $\mathrm{H}(26 \mathrm{~A})-\mathrm{C}(26)-\mathrm{H}(26 \mathrm{~B})$ | 108.9 |
| $\mathrm{N}(3)-\mathrm{C}(27)-\mathrm{C}(26)$ | 103.1(2) |
| $\mathrm{N}(3)-\mathrm{C}(27)-\mathrm{H}(27 \mathrm{~A})$ | 111.1 |
| $\mathrm{C}(26)-\mathrm{C}(27)-\mathrm{H}(27 \mathrm{~A})$ | 111.1 |
| $\mathrm{N}(3)-\mathrm{C}(27)-\mathrm{H}(27 \mathrm{~B})$ | 111.1 |
| $\mathrm{C}(26)-\mathrm{C}(27)-\mathrm{H}(27 \mathrm{~B})$ | 111.1 |
| $\mathrm{H}(27 \mathrm{~A})-\mathrm{C}(27)-\mathrm{H}(27 \mathrm{~B})$ | 109.1 |
| $\mathrm{C}(33)-\mathrm{C}(28)-\mathrm{C}(29)$ | 117.6(2) |
| $\mathrm{C}(33)-\mathrm{C}(28)-\mathrm{C}(23)$ | 120.7(2) |
| C(29)-C(28)-C(23) | 121.5(2) |


| $\mathrm{C}(30)-\mathrm{C}(29)-\mathrm{C}(28)$ | $121.5(2)$ |
| :--- | :--- |
| $\mathrm{C}(30)-\mathrm{C}(29)-\mathrm{H}(29 \mathrm{~A})$ | 119.2 |
| $\mathrm{C}(28)-\mathrm{C}(29)-\mathrm{H}(29 \mathrm{~A})$ | 119.2 |
| $\mathrm{C}(29)-\mathrm{C}(30)-\mathrm{C}(31)$ | $119.7(3)$ |
| $\mathrm{C}(29)-\mathrm{C}(30)-\mathrm{H}(30 \mathrm{~A})$ | 120.2 |
| $\mathrm{C}(31)-\mathrm{C}(30)-\mathrm{H}(30 \mathrm{~A})$ | 120.2 |
| $\mathrm{C}(32)-\mathrm{C}(31)-\mathrm{C}(30)$ | $119.9(3)$ |
| $\mathrm{C}(32)-\mathrm{C}(31)-\mathrm{H}(31 \mathrm{~A})$ | 120.1 |
| $\mathrm{C}(30)-\mathrm{C}(31)-\mathrm{H}(31 \mathrm{~A})$ | 120.1 |
| $\mathrm{C}(31)-\mathrm{C}(32)-\mathrm{C}(33)$ | $120.1(2)$ |
| $\mathrm{C}(31)-\mathrm{C}(32)-\mathrm{H}(32 \mathrm{~A})$ | 119.9 |
| $\mathrm{C}(33)-\mathrm{C}(32)-\mathrm{H}(32 \mathrm{~A})$ | 119.9 |
| $\mathrm{C}(32)-\mathrm{C}(33)-\mathrm{C}(28)$ | $121.1(2)$ |
| $\mathrm{C}(32)-\mathrm{C}(33)-\mathrm{H}(33 \mathrm{~A})$ | 119.5 |
| $\mathrm{C}(28)-\mathrm{C}(33)-\mathrm{H}(33 \mathrm{~A})$ | 119.5 |
|  |  |

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters $\left(\approx^{2} \times 10^{3}\right)$ for d1747_a. The anisotropic displacement factor exponent takes the form: $-2 \pi^{2}\left[h^{2} a^{* 2} U^{11}+\ldots+2 h k a^{*} b^{*} U^{12}\right]$

|  | $\mathrm{U}^{11}$ | $\mathrm{U}^{22}$ | $\mathrm{U}^{33}$ | $\mathrm{U}^{23}$ | $\mathrm{U}^{13}$ | $\mathrm{U}^{12}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{Co}(1)$ | 23(1) | 20(1) | 24(1) | -9(1) | -3(1) | -4(1) |
| $\mathrm{O}(1)$ | 23(1) | 26(1) | 27(1) | -9(1) | -3(1) | -3(1) |
| $\mathrm{O}(2)$ | 34(1) | 62(1) | 30(1) | -20(1) | -3(1) | -17(1) |
| $\mathrm{O}(3)$ | 23(1) | 25(1) | 30(1) | -10(1) | -1(1) | -5(1) |
| $\mathrm{O}(4)$ | 30(1) | 34(1) | 45(1) | -14(1) | 5(1) | -14(1) |
| $\mathrm{O}(5)$ | 28(1) | 23(1) | 28(1) | -11(1) | -4(1) | -4(1) |
| $\mathrm{O}(6)$ | 46(1) | 29(1) | 23(1) | -9(1) | -7(1) | -5(1) |
| $\mathrm{N}(1)$ | 25(1) | 22(1) | 25(1) | -9(1) | -1(1) | -5(1) |
| N(2) | 29(1) | 22(1) | 29(1) | -9(1) | -3(1) | -9(1) |
| N(3) | 26(1) | 21(1) | 27(1) | -9(1) | -4(1) | -3(1) |
| C(1) | 26(1) | 17(1) | 32(1) | -9(1) | -1(1) | -2(1) |
| C(2) | 22(1) | 29(1) | 34(1) | -11(1) | -3(1) | -5(1) |
| C(3) | 29(1) | 20(1) | 26(1) | -7(1) | -6(1) | -4(1) |
| C(4) | 36(1) | 35(2) | 31(1) | -16(1) | 1(1) | -10(1) |
| C(5) | 31(1) | 40(2) | 26(1) | -16(1) | 1(1) | -7(1) |
| C(6) | 24(1) | 24(1) | 32(1) | -7(1) | -3(1) | -1(1) |
| C(7) | 38(2) | 35(2) | 45(2) | -15(1) | 4(1) | -12(1) |
| C(8) | 43(2) | 48(2) | 63(2) | -18(2) | 12(2) | -23(2) |
| C(9) | 45(2) | 59(2) | 44(2) | -11(2) | 10(1) | -18(2) |
| $\mathrm{C}(10)$ | 36(2) | 62(2) | 33(1) | -18(1) | -1(1) | -10(1) |
| $\mathrm{C}(11)$ | 28(1) | 45(2) | 30(1) | -10(1) | -3(1) | -7(1) |
| $\mathrm{C}(12)$ | 24(1) | 25(1) | 23(1) | -10(1) | -4(1) | -3(1) |
| C(13) | 23(1) | 28(2) | 36(1) | -12(1) | 1(1) | -5(1) |
| C(14) | 25(1) | 31(2) | 29(1) | -13(1) | 0(1) | -10(1) |
| C(15) | 42(2) | 32(2) | 44(2) | -16(1) | 5(1) | -18(1) |
| C(16) | 39(2) | 26(2) | 54(2) | -10(1) | 2(1) | -12(1) |
| C(17) | 26(1) | 23(1) | 25(1) | -9(1) | -7(1) | -2(1) |
| C(18) | 33(1) | 30(2) | 35(1) | -14(1) | 2(1) | -6(1) |
| C(19) | 36(1) | 31(2) | 47(2) | -20(1) | 1(1) | -1(1) |
| C(20) | 42(2) | 24(2) | 46(2) | -11(1) | -7(1) | -4(1) |
| $\mathrm{C}(21)$ | 37(1) | 29(2) | 38(1) | -8(1) | -2(1) | -10(1) |
| 368 |  |  |  |  |  |  |


| $\mathrm{C}(22)$ | $28(1)$ | $26(1)$ | $31(1)$ | $-11(1)$ | $-2(1)$ | $-4(1)$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $\mathrm{C}(23)$ | $25(1)$ | $25(1)$ | $29(1)$ | $-12(1)$ | $2(1)$ | $-8(1)$ |
| $\mathrm{C}(24)$ | $34(1)$ | $25(1)$ | $25(1)$ | $-12(1)$ | $1(1)$ | $-10(1)$ |
| $\mathrm{C}(25)$ | $25(1)$ | $30(1)$ | $23(1)$ | $-8(1)$ | $-1(1)$ | $-9(1)$ |
| $\mathrm{C}(26)$ | $33(1)$ | $28(2)$ | $31(1)$ | $-9(1)$ | $-6(1)$ | $-2(1)$ |
| $\mathrm{C}(27)$ | $36(1)$ | $27(2)$ | $28(1)$ | $-7(1)$ | $-6(1)$ | $-3(1)$ |
| $\mathrm{C}(28)$ | $28(1)$ | $25(1)$ | $25(1)$ | $-12(1)$ | $3(1)$ | $-5(1)$ |
| $\mathrm{C}(29)$ | $41(2)$ | $28(2)$ | $29(1)$ | $-11(1)$ | $-2(1)$ | $-7(1)$ |
| $\mathrm{C}(30)$ | $58(2)$ | $25(2)$ | $33(1)$ | $-12(1)$ | $-1(1)$ | $-7(1)$ |
| $\mathrm{C}(31)$ | $44(2)$ | $24(2)$ | $35(1)$ | $-8(1)$ | $0(1)$ | $3(1)$ |
| $\mathrm{C}(32)$ | $27(1)$ | $35(2)$ | $37(1)$ | $-11(1)$ | $-1(1)$ | $-1(1)$ |
| $\mathrm{C}(33)$ | $29(1)$ | $32(2)$ | $34(1)$ | $-12(1)$ | $0(1)$ | $-6(1)$ |

Table 5. Hydrogen coordinates $\left(\times 10^{4}\right)$ and isotropic displacement parameters $\left(\approx^{2} \times 10^{3}\right)$ for d1747_a.

|  | x | y | z | U(eq) |
| :---: | :---: | :---: | :---: | :---: |
| H(2A) | 1207 | 7971 | 6463 | 35 |
| H(4A) | 3937 | 7930 | 3708 | 40 |
| H(4B) | 4258 | 6295 | 4281 | 40 |
| H(5A) | 5820 | 6300 | 5259 | 39 |
| H(5B) | 5439 | 7955 | 4732 | 39 |
| H(7A) | 416 | 6395 | 7914 | 47 |
| H(8A) | -1130 | 6274 | 9249 | 60 |
| H(9A) | -1097 | 7137 | 10636 | 61 |
| H(10A) | 485 | 8133 | 10687 | 54 |
| H(11A) | 2099 | 8141 | 9399 | 43 |
| H(13A) | 8988 | 4824 | 6862 | 36 |
| H(15A) | 8244 | 9329 | 5182 | 45 |
| H(15B) | 8528 | 9198 | 6370 | 45 |
| H(16A) | 6362 | 9713 | 6661 | 48 |
| H(16B) | 6105 | 9677 | 5511 | 48 |
| H(18A) | 9117 | 2900 | 6564 | 40 |
| H(19A) | 9744 | 502 | 7029 | 46 |
| H(20A) | 8572 | -637 | 8295 | 46 |
| H(21A) | 6762 | 652 | 9100 | 42 |
| H(22A) | 6139 | 3057 | 8651 | 35 |
| H(24A) | 4447 | 10144 | 9049 | 32 |
| H(26A) | 6028 | 5689 | 10971 | 39 |
| H(26B) | 7399 | 5952 | 10594 | 39 |
| H(27A) | 7324 | 5316 | 9174 | 39 |
| H(27B) | 5897 | 5163 | 9510 | 39 |
| H(29A) | 4280 | 12262 | 7965 | 40 |
| H(30A) | 3211 | 14615 | 7158 | 48 |
| H(31A) | 1479 | 15346 | 5943 | 46 |
| H(32A) | 891 | 13701 | 5508 | 42 |
| H(33A) | 1989 | 11335 | 6299 | 39 |

Table 6. Torsion angles [ $\infty$ ] for d1747_a.

| $\mathrm{O}(5)-\mathrm{Co}(1)-\mathrm{O}(1)-\mathrm{C}(1)$ | 63.96(18) |
| :---: | :---: |
| $\mathrm{O}(3)-\mathrm{Co}(1)-\mathrm{O}(1)-\mathrm{C}(1)$ | -111.26(18) |
| $\mathrm{N}(3)-\mathrm{Co}(1)-\mathrm{O}(1)-\mathrm{C}(1)$ | 158.46(19) |
| $\mathrm{N}(1)-\mathrm{Co}(1)-\mathrm{O}(1)-\mathrm{C}(1)$ | -24.14(19) |
| $\mathrm{O}(1)-\mathrm{Co}(1)-\mathrm{O}(5)-\mathrm{C}(23)$ | 82.72(18) |
| $\mathrm{N}(3)-\mathrm{Co}(1)-\mathrm{O}(5)-\mathrm{C}(23)$ | -1.25(19) |
| $\mathrm{N}(2)-\mathrm{Co}(1)-\mathrm{O}(5)-\mathrm{C}(23)$ | -92.38(18) |
| $\mathrm{N}(1)-\mathrm{Co}(1)-\mathrm{O}(5)-\mathrm{C}(23)$ | 174.88(18) |
| $\mathrm{Co}(1)-\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(2)$ | 18.5(3) |
| $\mathrm{Co}(1)-\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(6)$ | -163.39(15) |
| $\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)$ | 4.4(4) |
| $\mathrm{C}(6)-\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)$ | -173.5(2) |
| $\mathrm{C}(5)-\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{O}(2)$ | -5.2(3) |
| $\mathrm{Co}(1)-\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{O}(2)$ | -176.00(16) |
| $\mathrm{C}(5)-\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{C}(2)$ | 172.8(2) |
| $\mathrm{Co}(1)-\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{C}(2)$ | 2.1(4) |
| $\mathrm{C}(4)-\mathrm{O}(2)-\mathrm{C}(3)-\mathrm{N}(1)$ | 7.3(3) |
| $\mathrm{C}(4)-\mathrm{O}(2)-\mathrm{C}(3)-\mathrm{C}(2)$ | -171.0(2) |
| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)-\mathrm{N}(1)$ | -15.6(4) |
| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)-\mathrm{O}(2)$ | 162.5(2) |
| $\mathrm{C}(3)-\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{C}(5)$ | -5.9(3) |
| $\mathrm{C}(3)-\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(4)$ | 1.0(3) |
| $\mathrm{Co}(1)-\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(4)$ | 171.43(17) |
| $\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{N}(1)$ | 3.0(3) |
| $\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(6)-\mathrm{C}(7)$ | -137.5(2) |
| $\mathrm{C}(2)-\mathrm{C}(1)-\mathrm{C}(6)-\mathrm{C}(7)$ | 40.6(4) |
| $\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(6)-\mathrm{C}(11)$ | 41.0(3) |
| $\mathrm{C}(2)-\mathrm{C}(1)-\mathrm{C}(6)-\mathrm{C}(11)$ | -140.8(3) |
| $\mathrm{C}(11)-\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{C}(8)$ | -0.4(4) |
| $\mathrm{C}(1)-\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{C}(8)$ | 178.1(3) |
| $\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{C}(8)-\mathrm{C}(9)$ | 1.1(5) |
| $\mathrm{C}(7)-\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{C}(10)$ | -0.1(5) |
| $\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(11)$ | -1.8(5) |
| $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(11)-\mathrm{C}(6)$ | 2.5(4) |


| $\mathrm{C}(7)-\mathrm{C}(6)-\mathrm{C}(11)-\mathrm{C}(10)$ | -1.4(4) |
| :---: | :---: |
| $\mathrm{C}(1)-\mathrm{C}(6)-\mathrm{C}(11)-\mathrm{C}(10)$ | -180.0(2) |
| $\mathrm{Co}(1)-\mathrm{O}(3)-\mathrm{C}(12)-\mathrm{C}(13)$ | -1.7(3) |
| $\mathrm{Co}(1)-\mathrm{O}(3)-\mathrm{C}(12)-\mathrm{C}(17)$ | 177.36(14) |
| $\mathrm{O}(3)-\mathrm{C}(12)-\mathrm{C}(13)-\mathrm{C}(14)$ | -5.4(4) |
| $\mathrm{C}(17)-\mathrm{C}(12)-\mathrm{C}(13)-\mathrm{C}(14)$ | 175.6(2) |
| $\mathrm{C}(16)-\mathrm{N}(2)-\mathrm{C}(14)-\mathrm{O}(4)$ | -0.1(3) |
| $\mathrm{Co}(1)-\mathrm{N}(2)-\mathrm{C}(14)-\mathrm{O}(4)$ | -172.97(14) |
| $\mathrm{C}(16)-\mathrm{N}(2)-\mathrm{C}(14)-\mathrm{C}(13)$ | -178.4(2) |
| $\mathrm{Co}(1)-\mathrm{N}(2)-\mathrm{C}(14)-\mathrm{C}(13)$ | 8.8(3) |
| $\mathrm{C}(15)-\mathrm{O}(4)-\mathrm{C}(14)-\mathrm{N}(2)$ | 4.1(3) |
| $\mathrm{C}(15)-\mathrm{O}(4)-\mathrm{C}(14)-\mathrm{C}(13)$ | -177.5(2) |
| $\mathrm{C}(12)-\mathrm{C}(13)-\mathrm{C}(14)-\mathrm{N}(2)$ | 1.5(4) |
| $\mathrm{C}(12)-\mathrm{C}(13)-\mathrm{C}(14)-\mathrm{O}(4)$ | -176.7(2) |
| $\mathrm{C}(14)-\mathrm{O}(4)-\mathrm{C}(15)-\mathrm{C}(16)$ | -6.1(3) |
| $\mathrm{C}(14)-\mathrm{N}(2)-\mathrm{C}(16)-\mathrm{C}(15)$ | -3.6(3) |
| $\mathrm{Co}(1)-\mathrm{N}(2)-\mathrm{C}(16)-\mathrm{C}(15)$ | 168.96(16) |
| $\mathrm{O}(4)-\mathrm{C}(15)-\mathrm{C}(16)-\mathrm{N}(2)$ | 5.8(3) |
| $\mathrm{O}(3)-\mathrm{C}(12)-\mathrm{C}(17)-\mathrm{C}(22)$ | -24.8(3) |
| $\mathrm{C}(13)-\mathrm{C}(12)-\mathrm{C}(17)-\mathrm{C}(22)$ | 154.3(2) |
| $\mathrm{O}(3)-\mathrm{C}(12)-\mathrm{C}(17)-\mathrm{C}(18)$ | 155.3(2) |
| $\mathrm{C}(13)-\mathrm{C}(12)-\mathrm{C}(17)-\mathrm{C}(18)$ | -25.6(3) |
| $\mathrm{C}(22)-\mathrm{C}(17)-\mathrm{C}(18)-\mathrm{C}(19)$ | -1.0(4) |
| $\mathrm{C}(12)-\mathrm{C}(17)-\mathrm{C}(18)-\mathrm{C}(19)$ | 178.9(2) |
| $\mathrm{C}(17)-\mathrm{C}(18)-\mathrm{C}(19)-\mathrm{C}(20)$ | 0.7(4) |
| $\mathrm{C}(18)-\mathrm{C}(19)-\mathrm{C}(20)-\mathrm{C}(21)$ | -0.1(4) |
| $\mathrm{C}(19)-\mathrm{C}(20)-\mathrm{C}(21)-\mathrm{C}(22)$ | -0.3(4) |
| $\mathrm{C}(20)-\mathrm{C}(21)-\mathrm{C}(22)-\mathrm{C}(17)$ | 0.0(4) |
| $\mathrm{C}(18)-\mathrm{C}(17)-\mathrm{C}(22)-\mathrm{C}(21)$ | 0.7(3) |
| $\mathrm{C}(12)-\mathrm{C}(17)-\mathrm{C}(22)-\mathrm{C}(21)$ | -179.2(2) |
| $\mathrm{Co}(1)-\mathrm{O}(5)-\mathrm{C}(23)-\mathrm{C}(24)$ | -2.7(3) |
| $\mathrm{Co}(1)-\mathrm{O}(5)-\mathrm{C}(23)-\mathrm{C}(28)$ | 175.61(14) |
| $\mathrm{O}(5)-\mathrm{C}(23)-\mathrm{C}(24)-\mathrm{C}(25)$ | 1.2(4) |
| $\mathrm{C}(28)-\mathrm{C}(23)-\mathrm{C}(24)-\mathrm{C}(25)$ | -177.0(2) |
| $\mathrm{C}(27)-\mathrm{N}(3)-\mathrm{C}(25)-\mathrm{O}(6)$ | 5.6(3) |
| $\mathrm{Co}(1)-\mathrm{N}(3)-\mathrm{C}(25)-\mathrm{O}(6)$ | 167.83(15) |


| $\mathrm{C}(27)-\mathrm{N}(3)-\mathrm{C}(25)-\mathrm{C}(24)$ | $-173.8(2)$ |
| :--- | :---: |
| $\mathrm{Co}(1)-\mathrm{N}(3)-\mathrm{C}(25)-\mathrm{C}(24)$ | $-11.5(4)$ |
| $\mathrm{C}(26)-\mathrm{O}(6)-\mathrm{C}(25)-\mathrm{N}(3)$ | $-2.7(3)$ |
| $\mathrm{C}(26)-\mathrm{O}(6)-\mathrm{C}(25)-\mathrm{C}(24)$ | $176.7(2)$ |
| $\mathrm{C}(23)-\mathrm{C}(24)-\mathrm{C}(25)-\mathrm{N}(3)$ | $6.7(4)$ |
| $\mathrm{C}(23)-\mathrm{C}(24)-\mathrm{C}(25)-\mathrm{O}(6)$ | $-172.6(2)$ |
| $\mathrm{C}(25)-\mathrm{O}(6)-\mathrm{C}(26)-\mathrm{C}(27)$ | $-1.1(3)$ |
| $\mathrm{C}(25)-\mathrm{N}(3)-\mathrm{C}(27)-\mathrm{C}(26)$ | $-5.7(3)$ |
| $\mathrm{Co}(1)-\mathrm{N}(3)-\mathrm{C}(27)-\mathrm{C}(26)$ | $-167.71(16)$ |
| $\mathrm{O}(6)-\mathrm{C}(26)-\mathrm{C}(27)-\mathrm{N}(3)$ | $3.9(3)$ |
| $\mathrm{O}(5)-\mathrm{C}(23)-\mathrm{C}(28)-\mathrm{C}(33)$ | $29.1(3)$ |
| $\mathrm{C}(24)-\mathrm{C}(23)-\mathrm{C}(28)-\mathrm{C}(33)$ | $-152.5(2)$ |
| $\mathrm{O}(5)-\mathrm{C}(23)-\mathrm{C}(28)-\mathrm{C}(29)$ | $-146.4(2)$ |
| $\mathrm{C}(24)-\mathrm{C}(23)-\mathrm{C}(28)-\mathrm{C}(29)$ | $32.0(3)$ |
| $\mathrm{C}(33)-\mathrm{C}(28)-\mathrm{C}(29)-\mathrm{C}(30)$ | $-0.4(4)$ |
| $\mathrm{C}(23)-\mathrm{C}(28)-\mathrm{C}(29)-\mathrm{C}(30)$ | $175.3(2)$ |
| $\mathrm{C}(28)-\mathrm{C}(29)-\mathrm{C}(30)-\mathrm{C}(31)$ | $1.1(4)$ |
| $\mathrm{C}(29)-\mathrm{C}(30)-\mathrm{C}(31)-\mathrm{C}(32)$ | $-1.1(4)$ |
| $\mathrm{C}(30)-\mathrm{C}(31)-\mathrm{C}(32)-\mathrm{C}(33)$ | $0.6(4)$ |
| $\mathrm{C}(31)-\mathrm{C}(32)-\mathrm{C}(33)-\mathrm{C}(28)$ | $0.1(4)$ |
| $\mathrm{C}(29)-\mathrm{C}(28)-\mathrm{C}(33)-\mathrm{C}(32)$ | $-0.1(4)$ |
| $\mathrm{C}(23)-\mathrm{C}(28)-\mathrm{C}(33)-\mathrm{C}(32)$ | $-175.9(2)$ |

Symmetry transformations used to generate equivalent atoms:


F3: Crystal data and structure refinement for d1842_a (11c).


Refinement method
Data / restraints / parameters
Goodness-of-fit on $\mathrm{F}^{2}$
Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ]
R indices (all data)
Extinction coefficient
Largest diff. peak and hole

Full-matrix least-squares on $\mathrm{F}^{2}$
6112 / 0 / 454
1.031
$\mathrm{R} 1=0.0723, \mathrm{wR} 2=0.1654$
$R 1=0.1186, w R 2=0.1896$
n/a
0.591 and -0.590 e. $\sim^{-3}$

Table 2. Atomic coordinates $\left(\times 10^{4}\right)$ and equivalent isotropic displacement parameters $\left(\approx^{2} \times 10^{3}\right)$ for d1842_a. $\mathrm{U}(\mathrm{eq})$ is defined as one third of the trace of the orthogonalized $\mathrm{U}^{\mathrm{ij}}$ tensor.

|  | x | y | z | $\mathrm{U}(\mathrm{eq})$ |
| :--- | ---: | ---: | ---: | :--- |
|  |  |  |  |  |
| $\mathrm{Co}(1)$ | $7223(1)$ | $7132(1)$ | $6801(1)$ | $27(1)$ |
| $\mathrm{O}(1)$ | $5813(4)$ | $6646(1)$ | $6213(2)$ | $31(1)$ |
| $\mathrm{O}(2)$ | $8318(4)$ | $7420(2)$ | $4501(2)$ | $41(1)$ |
| $\mathrm{O}(3)$ | $-118(4)$ | $5565(2)$ | $4434(2)$ | $40(1)$ |
| $\mathrm{O}(4)$ | $5778(3)$ | $7693(1)$ | $6527(2)$ | $30(1)$ |
| $\mathrm{O}(5)$ | $4645(4)$ | $6946(1)$ | $8697(2)$ | $36(1)$ |
| $\mathrm{O}(6)$ | $569(5)$ | $9337(2)$ | $5243(2)$ | $52(1)$ |
| $\mathrm{O}(7)$ | $8620(3)$ | $6541(1)$ | $6960(2)$ | $29(1)$ |
| $\mathrm{O}(8)$ | $10565(4)$ | $7903(1)$ | $8256(2)$ | $31(1)$ |
| $\mathrm{O}(9)$ | $12778(5)$ | $4478(2)$ | $7441(3)$ | $62(1)$ |
| $\mathrm{N}(1)$ | $8147(4)$ | $7329(2)$ | $5845(2)$ | $28(1)$ |
| $\mathrm{N}(2)$ | $6316(4)$ | $6928(2)$ | $7755(3)$ | $31(1)$ |
| $\mathrm{N}(3)$ | $8520(4)$ | $7619(2)$ | $7436(2)$ | $28(1)$ |
| $\mathrm{C}(1)$ | $5393(5)$ | $6674(2)$ | $5439(3)$ | $29(1)$ |
| $\mathrm{C}(2)$ | $6146(5)$ | $6946(2)$ | $4881(3)$ | $30(1)$ |
| $\mathrm{C}(3)$ | $7532(5)$ | $7228(2)$ | $5109(3)$ | $30(1)$ |
| $\mathrm{C}(4)$ | $9704(6)$ | $7665(3)$ | $4890(3)$ | $48(2)$ |
| $\mathrm{C}(5)$ | $9593(6)$ | $7622(2)$ | $5795(3)$ | $40(1)$ |
| $\mathrm{C}(6)$ | $3936(5)$ | $6379(2)$ | $5182(3)$ | $31(1)$ |
| $\mathrm{C}(7)$ | $2719(6)$ | $6422(2)$ | $5636(3)$ | $36(1)$ |
| $\mathrm{C}(8)$ | $1328(6)$ | $6168(2)$ | $5400(3)$ | $37(1)$ |
| $\mathrm{C}(9)$ | $1193(5)$ | $5841(2)$ | $4718(3)$ | $32(1)$ |
| $\mathrm{C}(10)$ | $2416(6)$ | $5779(2)$ | $4259(3)$ | $40(1)$ |
| $\mathrm{C}(11)$ | $3775(6)$ | $6054(2)$ | $4484(3)$ | $40(1)$ |
| $\mathrm{C}(12)$ | $-1395(6)$ | $5602(2)$ | $4901(4)$ | $43(2)$ |
| $\mathrm{C}(13)$ | $4579(5)$ | $7804(2)$ | $6899(3)$ | $28(1)$ |
| $\mathrm{C}(14)$ | $4234(5)$ | $7582(2)$ | $7613(3)$ | $31(1)$ |
| $\mathrm{C}(15)$ | $5118(5)$ | $7158(2)$ | $8005(3)$ | $29(1)$ |
| $\mathrm{C}(16)$ | $5750(6)$ | $6529(2)$ | $8985(3)$ | $40(1)$ |
| $\mathrm{C}(17)$ | $6488(2)$ | $8325(3)$ | $37(1)$ |  |
| $\mathrm{C}(18)$ | $8211(2)$ | $6458(3)$ | $29(1)$ |  |
|  |  |  |  |  |


| $\mathrm{C}(19)$ | $3482(5)$ | $8257(2)$ | $5621(3)$ | $34(1)$ |
| :--- | ---: | ---: | ---: | ---: |
| $\mathrm{C}(20)$ | $2514(5)$ | $8630(2)$ | $5192(3)$ | $34(1)$ |
| $\mathrm{C}(21)$ | $1591(6)$ | $8963(2)$ | $5615(3)$ | $37(1)$ |
| $\mathrm{C}(22)$ | $1642(6)$ | $8925(2)$ | $6443(3)$ | $40(1)$ |
| $\mathrm{C}(23)$ | $2588(5)$ | $8554(2)$ | $6872(3)$ | $34(1)$ |
| $\mathrm{C}(24)$ | $466(8)$ | $9387(3)$ | $4391(4)$ | $56(2)$ |
| $\mathrm{C}(25)$ | $9949(5)$ | $6546(2)$ | $7403(3)$ | $28(1)$ |
| $\mathrm{C}(26)$ | $10584(5)$ | $6979(2)$ | $7831(3)$ | $30(1)$ |
| $\mathrm{C}(27)$ | $9848(5)$ | $7489(2)$ | $7818(3)$ | $28(1)$ |
| $\mathrm{C}(28)$ | $9533(5)$ | $8369(2)$ | $8190(3)$ | $37(1)$ |
| $\mathrm{C}(29)$ | $8159(6)$ | $8189(2)$ | $7615(3)$ | $35(1)$ |
| $\mathrm{C}(30)$ | $10744(5)$ | $6011(2)$ | $7429(3)$ | $29(1)$ |
| $\mathrm{C}(31)$ | $12333(6)$ | $5964(2)$ | $7595(3)$ | $37(1)$ |
| $\mathrm{C}(32)$ | $13059(6)$ | $5464(2)$ | $7611(4)$ | $45(2)$ |
| $\mathrm{C}(33)$ | $12191(7)$ | $4996(2)$ | $7466(4)$ | $42(1)$ |
| $\mathrm{C}(34)$ | $10607(6)$ | $5031(2)$ | $7284(3)$ | $37(1)$ |
| $\mathrm{C}(35)$ | $9910(6)$ | $5532(2)$ | $7266(3)$ | $34(1)$ |
| $\mathrm{C}(36)$ | $14396(7)$ | $4416(3)$ | $7647(5)$ | $80(3)$ |
| $\mathrm{O}(1 \mathrm{~W})$ | $6101(6)$ | $5506(2)$ | $6513(4)$ | $101(2)$ |

Table 3. Bond lengths [ $\approx]$ and angles [ $\infty$ ] for d1842_a.

| $\mathrm{Co}(1)-\mathrm{N}(3)$ | 1.892(4) |
| :---: | :---: |
| $\mathrm{Co}(1)-\mathrm{O}(4)$ | 1.896(3) |
| $\mathrm{Co}(1)-\mathrm{O}(7)$ | 1.902(3) |
| $\mathrm{Co}(1)-\mathrm{N}(2)$ | 1.906(4) |
| $\mathrm{Co}(1)-\mathrm{O}(1)$ | 1.912(3) |
| $\mathrm{Co}(1)-\mathrm{N}(1)$ | 1.913(4) |
| $\mathrm{O}(1)-\mathrm{C}(1)$ | 1.296(5) |
| $\mathrm{O}(2)-\mathrm{C}(3)$ | 1.361(6) |
| $\mathrm{O}(2)-\mathrm{C}(4)$ | 1.448(6) |
| $\mathrm{O}(3)-\mathrm{C}(9)$ | 1.376 (6) |
| $\mathrm{O}(3)-\mathrm{C}(12)$ | 1.429(6) |
| $\mathrm{O}(4)-\mathrm{C}(13)$ | 1.302(6) |
| $\mathrm{O}(5)-\mathrm{C}(15)$ | 1.362(6) |
| $\mathrm{O}(5)-\mathrm{C}(16)$ | 1.456(6) |
| $\mathrm{O}(6)-\mathrm{C}(21)$ | 1.383(6) |
| $\mathrm{O}(6)-\mathrm{C}(24)$ | 1.408(7) |
| $\mathrm{O}(7)-\mathrm{C}(25)$ | 1.312(5) |
| $\mathrm{O}(8)-\mathrm{C}(27)$ | 1.365(6) |
| $\mathrm{O}(8)-\mathrm{C}(28)$ | 1.457(6) |
| $\mathrm{O}(9)-\mathrm{C}(33)$ | 1.377(6) |
| $\mathrm{O}(9)-\mathrm{C}(36)$ | 1.434(7) |
| $\mathrm{N}(1)$-C(3) | 1.305(6) |
| $\mathrm{N}(1)-\mathrm{C}(5)$ | 1.469(6) |
| $\mathrm{N}(2)-\mathrm{C}(15)$ | 1.298(6) |
| $\mathrm{N}(2)-\mathrm{C}(17)$ | 1.477(6) |
| $\mathrm{N}(3)-\mathrm{C}(27)$ | 1.307(6) |
| $\mathrm{N}(3)-\mathrm{C}(29)$ | 1.473(6) |
| $\mathrm{C}(1)-\mathrm{C}(2)$ | 1.364(7) |
| $\mathrm{C}(1)-\mathrm{C}(6)$ | 1.494(7) |
| $\mathrm{C}(2)-\mathrm{C}(3)$ | 1.417(7) |
| $\mathrm{C}(2)-\mathrm{H}(2 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(4)-\mathrm{C}(5)$ | 1.513(7) |
| $\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~A})$ | 0.9900 |
| $\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~B})$ | 0.9900 |


| $\mathrm{C}(5)-\mathrm{H}(5 \mathrm{~A})$ | 0.9900 |
| :---: | :---: |
| $\mathrm{C}(5)-\mathrm{H}(5 \mathrm{~B})$ | 0.9900 |
| $\mathrm{C}(6)-\mathrm{C}(7)$ | 1.372(7) |
| $\mathrm{C}(6)-\mathrm{C}(11)$ | 1.399(7) |
| $\mathrm{C}(7)-\mathrm{C}(8)$ | 1.391(7) |
| $\mathrm{C}(7)-\mathrm{H}(7 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(8)-\mathrm{C}(9)$ | 1.380(7) |
| $\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(9)-\mathrm{C}(10)$ | 1.387(7) |
| $\mathrm{C}(10)-\mathrm{C}(11)$ | 1.388(7) |
| $\mathrm{C}(10)-\mathrm{H}(10 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(11)-\mathrm{H}(11 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~A})$ | 0.9800 |
| $\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~B})$ | 0.9800 |
| $\mathrm{C}(12)-\mathrm{H}(12 \mathrm{C})$ | 0.9800 |
| $\mathrm{C}(13)-\mathrm{C}(14)$ | 1.363(7) |
| $\mathrm{C}(13)-\mathrm{C}(18)$ | 1.496(7) |
| $\mathrm{C}(14)-\mathrm{C}(15)$ | 1.416(7) |
| $\mathrm{C}(14)-\mathrm{H}(14 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(16)-\mathrm{C}(17)$ | 1.525(7) |
| $\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~A})$ | 0.9900 |
| $\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~B})$ | 0.9900 |
| $\mathrm{C}(17)-\mathrm{H}(17 \mathrm{~A})$ | 0.9900 |
| $\mathrm{C}(17)-\mathrm{H}(17 \mathrm{~B})$ | 0.9900 |
| $\mathrm{C}(18)-\mathrm{C}(19)$ | 1.385(7) |
| $\mathrm{C}(18)$-C(23) | 1.409(7) |
| $\mathrm{C}(19)$-C(20) | 1.393(7) |
| $\mathrm{C}(19)-\mathrm{H}(19 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(20)-\mathrm{C}(21)$ | 1.392(7) |
| $\mathrm{C}(20)-\mathrm{H}(20 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(21)-\mathrm{C}(22)$ | 1.369(7) |
| $\mathrm{C}(22)-\mathrm{C}(23)$ | 1.379(7) |
| $\mathrm{C}(22)-\mathrm{H}(22 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(23)-\mathrm{H}(23 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(24)-\mathrm{H}(24 \mathrm{~A})$ | 0.9800 |
| $\mathrm{C}(24)-\mathrm{H}(24 \mathrm{~B})$ | 0.9800 |


| $\mathrm{C}(24)-\mathrm{H}(24 \mathrm{C})$ | 0.9800 |
| :---: | :---: |
| $\mathrm{C}(25)-\mathrm{C}(26)$ | 1.364(7) |
| $\mathrm{C}(25)-\mathrm{C}(30)$ | 1.488(7) |
| C (26)-C(27) | 1.409(7) |
| $\mathrm{C}(26)-\mathrm{H}(26 \mathrm{~A})$ | 0.9500 |
| C(28)-C(29) | 1.522(7) |
| C(28)-H(28A) | 0.9900 |
| $\mathrm{C}(28)-\mathrm{H}(28 \mathrm{~B})$ | 0.9900 |
| $\mathrm{C}(29)-\mathrm{H}(29 \mathrm{~A})$ | 0.9900 |
| $\mathrm{C}(29)-\mathrm{H}(29 \mathrm{~B})$ | 0.9900 |
| $\mathrm{C}(30)-\mathrm{C}(35)$ | 1.397(7) |
| $\mathrm{C}(30)-\mathrm{C}(31)$ | 1.399 (7) |
| $\mathrm{C}(31)-\mathrm{C}(32)$ | 1.382(7) |
| $\mathrm{C}(31)-\mathrm{H}(31 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(32)-\mathrm{C}(33)$ | 1.386(8) |
| $\mathrm{C}(32)-\mathrm{H}(32 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(33)-\mathrm{C}(34)$ | $1.395(7)$ |
| $\mathrm{C}(34)-\mathrm{C}(35)$ | 1.374(7) |
| $\mathrm{C}(34)-\mathrm{H}(34 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(35)-\mathrm{H}(35 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(36)-\mathrm{H}(36 \mathrm{~A})$ | 0.9800 |
| $\mathrm{C}(36)-\mathrm{H}(36 \mathrm{~B})$ | 0.9800 |
| $\mathrm{C}(36)-\mathrm{H}(36 \mathrm{C})$ | 0.9800 |
| $\mathrm{O}(1 \mathrm{~W})-\mathrm{H}(1 \mathrm{WA})$ | 0.8420 |
| $\mathrm{O}(1 \mathrm{~W})-\mathrm{H}(1 \mathrm{WB})$ | 0.8477 |
| $\mathrm{N}(3)-\mathrm{Co}(1)-\mathrm{O}(4)$ | 91.27(16) |
| $\mathrm{N}(3)-\mathrm{Co}(1)-\mathrm{O}(7)$ | 93.73(16) |
| $\mathrm{O}(4)-\mathrm{Co}(1)-\mathrm{O}(7)$ | 173.77(14) |
| $\mathrm{N}(3)-\mathrm{Co}(1)-\mathrm{N}(2)$ | 89.22(17) |
| $\mathrm{O}(4)-\mathrm{Co}(1)-\mathrm{N}(2)$ | 93.58(16) |
| $\mathrm{O}(7)-\mathrm{Co}(1)-\mathrm{N}(2)$ | 90.21(16) |
| $\mathrm{N}(3)-\mathrm{Co}(1)-\mathrm{O}(1)$ | 176.07(16) |
| $\mathrm{O}(4)-\mathrm{Co}(1)-\mathrm{O}(1)$ | 87.13(15) |
| $\mathrm{O}(7)-\mathrm{Co}(1)-\mathrm{O}(1)$ | 88.11(14) |
| $\mathrm{N}(2)-\mathrm{Co}(1)-\mathrm{O}(1)$ | 87.30(16) |


| $\mathrm{N}(3)-\mathrm{Co}(1)-\mathrm{N}(1)$ | 90.92(17) |
| :---: | :---: |
| $\mathrm{O}(4)-\mathrm{Co}(1)-\mathrm{N}(1)$ | 87.06(16) |
| $\mathrm{O}(7)-\mathrm{Co}(1)-\mathrm{N}(1)$ | 89.14(16) |
| $\mathrm{N}(2)-\mathrm{Co}(1)-\mathrm{N}(1)$ | 179.35(18) |
| $\mathrm{O}(1)-\mathrm{Co}(1)-\mathrm{N}(1)$ | 92.58(16) |
| $\mathrm{C}(1)-\mathrm{O}(1)-\mathrm{Co}(1)$ | 124.9(3) |
| $\mathrm{C}(3)-\mathrm{O}(2)-\mathrm{C}(4)$ | 106.4(4) |
| $\mathrm{C}(9)-\mathrm{O}(3)-\mathrm{C}(12)$ | 117.3(4) |
| $\mathrm{C}(13)-\mathrm{O}(4)-\mathrm{Co}(1)$ | 126.4(3) |
| $\mathrm{C}(15)-\mathrm{O}(5)-\mathrm{C}(16)$ | 107.0(4) |
| $\mathrm{C}(21)-\mathrm{O}(6)-\mathrm{C}(24)$ | 118.4(4) |
| $\mathrm{C}(25)-\mathrm{O}(7)-\mathrm{Co}(1)$ | 126.3(3) |
| $\mathrm{C}(27)-\mathrm{O}(8)-\mathrm{C}(28)$ | 107.3(4) |
| $\mathrm{C}(33)-\mathrm{O}(9)-\mathrm{C}(36)$ | 117.1(5) |
| $\mathrm{C}(3)-\mathrm{N}(1)-\mathrm{C}(5)$ | 108.4(4) |
| $\mathrm{C}(3)-\mathrm{N}(1)-\mathrm{Co}(1)$ | 123.6(3) |
| $\mathrm{C}(5)-\mathrm{N}(1)-\mathrm{Co}(1)$ | 127.9(3) |
| $\mathrm{C}(15)-\mathrm{N}(2)-\mathrm{C}(17)$ | 108.8(4) |
| $\mathrm{C}(15)-\mathrm{N}(2)-\mathrm{Co}(1)$ | 124.8(4) |
| $\mathrm{C}(17)-\mathrm{N}(2)-\mathrm{Co}(1)$ | 126.4(3) |
| $\mathrm{C}(27)-\mathrm{N}(3)-\mathrm{C}(29)$ | 109.6(4) |
| $\mathrm{C}(27)-\mathrm{N}(3)-\mathrm{Co}(1)$ | 124.6(4) |
| $\mathrm{C}(29)-\mathrm{N}(3)-\mathrm{Co}(1)$ | 125.7(3) |
| $\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(2)$ | 125.9(5) |
| $\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(6)$ | 113.8(4) |
| $\mathrm{C}(2)-\mathrm{C}(1)-\mathrm{C}(6)$ | 120.3(4) |
| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)$ | 121.5(5) |
| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{H}(2 \mathrm{~A})$ | 119.2 |
| $\mathrm{C}(3)-\mathrm{C}(2)-\mathrm{H}(2 \mathrm{~A})$ | 119.2 |
| $\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{O}(2)$ | 115.6(4) |
| $\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{C}(2)$ | 127.0(5) |
| $\mathrm{O}(2)-\mathrm{C}(3)-\mathrm{C}(2)$ | 117.4(4) |
| $\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{C}(5)$ | 105.9(4) |
| $\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~A})$ | 110.6 |
| $\mathrm{C}(5)-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~A})$ | 110.6 |
| $\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~B})$ | 110.6 |


| $\mathrm{C}(5)-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~B})$ | 110.6 |
| :---: | :---: |
| $\mathrm{H}(4 \mathrm{~A})-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~B})$ | 108.7 |
| $\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(4)$ | 103.6(4) |
| $\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{H}(5 \mathrm{~A})$ | 111.0 |
| $\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{H}(5 \mathrm{~A})$ | 111.0 |
| $\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{H}(5 \mathrm{~B})$ | 111.0 |
| $\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{H}(5 \mathrm{~B})$ | 111.0 |
| $\mathrm{H}(5 \mathrm{~A})-\mathrm{C}(5)-\mathrm{H}(5 \mathrm{~B})$ | 109.0 |
| $\mathrm{C}(7)-\mathrm{C}(6)-\mathrm{C}(11)$ | 118.6(5) |
| $\mathrm{C}(7)-\mathrm{C}(6)-\mathrm{C}(1)$ | 119.9(5) |
| $\mathrm{C}(11)-\mathrm{C}(6)-\mathrm{C}(1)$ | 121.5(5) |
| $\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{C}(8)$ | 121.5(5) |
| $\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{H}(7 \mathrm{~A})$ | 119.2 |
| $\mathrm{C}(8)-\mathrm{C}(7)-\mathrm{H}(7 \mathrm{~A})$ | 119.2 |
| $\mathrm{C}(9)-\mathrm{C}(8)-\mathrm{C}(7)$ | 119.2(5) |
| $\mathrm{C}(9)-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~A})$ | 120.4 |
| $\mathrm{C}(7)-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~A})$ | 120.4 |
| $\mathrm{O}(3)-\mathrm{C}(9)-\mathrm{C}(8)$ | 124.3(5) |
| $\mathrm{O}(3)-\mathrm{C}(9)-\mathrm{C}(10)$ | 115.2(5) |
| $\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{C}(10)$ | 120.5(5) |
| $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(11)$ | 119.5(5) |
| $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{H}(10 \mathrm{~A})$ | 120.3 |
| $\mathrm{C}(11)-\mathrm{C}(10)-\mathrm{H}(10 \mathrm{~A})$ | 120.3 |
| $\mathrm{C}(10)-\mathrm{C}(11)-\mathrm{C}(6)$ | 120.6(5) |
| $\mathrm{C}(10)-\mathrm{C}(11)-\mathrm{H}(11 \mathrm{~A})$ | 119.7 |
| $\mathrm{C}(6)-\mathrm{C}(11)-\mathrm{H}(11 \mathrm{~A})$ | 119.7 |
| $\mathrm{O}(3)-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~A})$ | 109.5 |
| $\mathrm{O}(3)-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~B})$ | 109.5 |
| $\mathrm{H}(12 \mathrm{~A})-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~B})$ | 109.5 |
| $\mathrm{O}(3)-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(12 \mathrm{~A})-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(12 \mathrm{~B})-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{C})$ | 109.5 |
| $\mathrm{O}(4)-\mathrm{C}(13)-\mathrm{C}(14)$ | 126.0(5) |
| $\mathrm{O}(4)-\mathrm{C}(13)-\mathrm{C}(18)$ | 113.3(4) |
| $\mathrm{C}(14)-\mathrm{C}(13)-\mathrm{C}(18)$ | 120.7(4) |
| $\mathrm{C}(13)-\mathrm{C}(14)-\mathrm{C}(15)$ | 122.1(5) |


| $\mathrm{C}(13)-\mathrm{C}(14)-\mathrm{H}(14 \mathrm{~A})$ | 118.9 |
| :---: | :---: |
| $\mathrm{C}(15)-\mathrm{C}(14)-\mathrm{H}(14 \mathrm{~A})$ | 118.9 |
| $\mathrm{N}(2)-\mathrm{C}(15)-\mathrm{O}(5)$ | 115.4(4) |
| $\mathrm{N}(2)-\mathrm{C}(15)-\mathrm{C}(14)$ | 126.7(5) |
| $\mathrm{O}(5)-\mathrm{C}(15)-\mathrm{C}(14)$ | 117.8(4) |
| $\mathrm{O}(5)-\mathrm{C}(16)-\mathrm{C}(17)$ | 104.9(4) |
| $\mathrm{O}(5)-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~A})$ | 110.8 |
| $\mathrm{C}(17)-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~A})$ | 110.8 |
| $\mathrm{O}(5)-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~B})$ | 110.8 |
| $\mathrm{C}(17)-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~B})$ | 110.8 |
| $\mathrm{H}(16 \mathrm{~A})-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~B})$ | 108.8 |
| $\mathrm{N}(2)-\mathrm{C}(17)-\mathrm{C}(16)$ | 103.5(4) |
| $\mathrm{N}(2)-\mathrm{C}(17)-\mathrm{H}(17 \mathrm{~A})$ | 111.1 |
| $\mathrm{C}(16)-\mathrm{C}(17)-\mathrm{H}(17 \mathrm{~A})$ | 111.1 |
| $\mathrm{N}(2)-\mathrm{C}(17)-\mathrm{H}(17 \mathrm{~B})$ | 111.1 |
| $\mathrm{C}(16)-\mathrm{C}(17)-\mathrm{H}(17 \mathrm{~B})$ | 111.1 |
| $\mathrm{H}(17 \mathrm{~A})-\mathrm{C}(17)-\mathrm{H}(17 \mathrm{~B})$ | 109.0 |
| $\mathrm{C}(19)-\mathrm{C}(18)-\mathrm{C}(23)$ | 118.6(5) |
| $\mathrm{C}(19)-\mathrm{C}(18)-\mathrm{C}(13)$ | 119.8(5) |
| $\mathrm{C}(23)-\mathrm{C}(18)-\mathrm{C}(13)$ | 121.7(5) |
| $\mathrm{C}(18)-\mathrm{C}(19)-\mathrm{C}(20)$ | 121.1(5) |
| $\mathrm{C}(18)-\mathrm{C}(19)-\mathrm{H}(19 \mathrm{~A})$ | 119.4 |
| $\mathrm{C}(20)-\mathrm{C}(19)-\mathrm{H}(19 \mathrm{~A})$ | 119.4 |
| $\mathrm{C}(21)-\mathrm{C}(20)-\mathrm{C}(19)$ | 119.2(5) |
| $\mathrm{C}(21)-\mathrm{C}(20)-\mathrm{H}(20 \mathrm{~A})$ | 120.4 |
| $\mathrm{C}(19)-\mathrm{C}(20)-\mathrm{H}(20 \mathrm{~A})$ | 120.4 |
| $\mathrm{C}(22)-\mathrm{C}(21)-\mathrm{O}(6)$ | 116.3(5) |
| $\mathrm{C}(22)-\mathrm{C}(21)-\mathrm{C}(20)$ | 120.2(5) |
| $\mathrm{O}(6)-\mathrm{C}(21)-\mathrm{C}(20)$ | 123.4(5) |
| $\mathrm{C}(21)-\mathrm{C}(22)-\mathrm{C}(23)$ | 121.0(5) |
| $\mathrm{C}(21)-\mathrm{C}(22)-\mathrm{H}(22 \mathrm{~A})$ | 119.5 |
| $\mathrm{C}(23)-\mathrm{C}(22)-\mathrm{H}(22 \mathrm{~A})$ | 119.5 |
| $\mathrm{C}(22)-\mathrm{C}(23)-\mathrm{C}(18)$ | 119.9(5) |
| $\mathrm{C}(22)-\mathrm{C}(23)-\mathrm{H}(23 \mathrm{~A})$ | 120.0 |
| $\mathrm{C}(18)-\mathrm{C}(23)-\mathrm{H}(23 \mathrm{~A})$ | 120.0 |
| $\mathrm{O}(6)-\mathrm{C}(24)-\mathrm{H}(24 \mathrm{~A})$ | 109.5 |


| $\mathrm{O}(6)-\mathrm{C}(24)-\mathrm{H}(24 \mathrm{~B})$ | 109.5 |
| :---: | :---: |
| $\mathrm{H}(24 \mathrm{~A})-\mathrm{C}(24)-\mathrm{H}(24 \mathrm{~B})$ | 109.5 |
| $\mathrm{O}(6)-\mathrm{C}(24)-\mathrm{H}(24 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(24 \mathrm{~A})-\mathrm{C}(24)-\mathrm{H}(24 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(24 \mathrm{~B})-\mathrm{C}(24)-\mathrm{H}(24 \mathrm{C})$ | 109.5 |
| $\mathrm{O}(7)-\mathrm{C}(25)-\mathrm{C}(26)$ | 126.1(5) |
| $\mathrm{O}(7)-\mathrm{C}(25)-\mathrm{C}(30)$ | 113.2(4) |
| $\mathrm{C}(26)-\mathrm{C}(25)-\mathrm{C}(30)$ | 120.6(4) |
| $\mathrm{C}(25)-\mathrm{C}(26)-\mathrm{C}(27)$ | 121.5(5) |
| $\mathrm{C}(25)-\mathrm{C}(26)-\mathrm{H}(26 \mathrm{~A})$ | 119.2 |
| $\mathrm{C}(27)-\mathrm{C}(26)-\mathrm{H}(26 \mathrm{~A})$ | 119.2 |
| $\mathrm{N}(3)-\mathrm{C}(27)-\mathrm{O}(8)$ | 114.4(4) |
| $\mathrm{N}(3)-\mathrm{C}(27)-\mathrm{C}(26)$ | 127.6(5) |
| $\mathrm{O}(8)-\mathrm{C}(27)-\mathrm{C}(26)$ | 118.0(4) |
| $\mathrm{O}(8)-\mathrm{C}(28)-\mathrm{C}(29)$ | 105.3(4) |
| $\mathrm{O}(8)-\mathrm{C}(28)-\mathrm{H}(28 \mathrm{~A})$ | 110.7 |
| $\mathrm{C}(29)-\mathrm{C}(28)-\mathrm{H}(28 \mathrm{~A})$ | 110.7 |
| $\mathrm{O}(8)-\mathrm{C}(28)-\mathrm{H}(28 \mathrm{~B})$ | 110.7 |
| $\mathrm{C}(29)-\mathrm{C}(28)-\mathrm{H}(28 \mathrm{~B})$ | 110.7 |
| $\mathrm{H}(28 \mathrm{~A})-\mathrm{C}(28)-\mathrm{H}(28 \mathrm{~B})$ | 108.8 |
| $\mathrm{N}(3)-\mathrm{C}(29)-\mathrm{C}(28)$ | 103.3(4) |
| $\mathrm{N}(3)-\mathrm{C}(29)-\mathrm{H}(29 \mathrm{~A})$ | 111.1 |
| $\mathrm{C}(28)-\mathrm{C}(29)-\mathrm{H}(29 \mathrm{~A})$ | 111.1 |
| $\mathrm{N}(3)-\mathrm{C}(29)-\mathrm{H}(29 \mathrm{~B})$ | 111.1 |
| $\mathrm{C}(28)-\mathrm{C}(29)-\mathrm{H}(29 \mathrm{~B})$ | 111.1 |
| $\mathrm{H}(29 \mathrm{~A})-\mathrm{C}(29)-\mathrm{H}(29 \mathrm{~B})$ | 109.1 |
| $\mathrm{C}(35)-\mathrm{C}(30)-\mathrm{C}(31)$ | 117.4(5) |
| $\mathrm{C}(35)-\mathrm{C}(30)-\mathrm{C}(25)$ | 120.3(4) |
| $\mathrm{C}(31)-\mathrm{C}(30)-\mathrm{C}(25)$ | 122.3(5) |
| $\mathrm{C}(32)-\mathrm{C}(31)-\mathrm{C}(30)$ | 121.7(5) |
| $\mathrm{C}(32)-\mathrm{C}(31)-\mathrm{H}(31 \mathrm{~A})$ | 119.2 |
| $\mathrm{C}(30)-\mathrm{C}(31)-\mathrm{H}(31 \mathrm{~A})$ | 119.2 |
| $\mathrm{C}(31)-\mathrm{C}(32)-\mathrm{C}(33)$ | 119.3(5) |
| $\mathrm{C}(31)-\mathrm{C}(32)-\mathrm{H}(32 \mathrm{~A})$ | 120.3 |
| $\mathrm{C}(33)-\mathrm{C}(32)-\mathrm{H}(32 \mathrm{~A})$ | 120.3 |
| $\mathrm{O}(9)-\mathrm{C}(33)-\mathrm{C}(32)$ | 124.9(5) |


| $\mathrm{O}(9)-\mathrm{C}(33)-\mathrm{C}(34)$ | $114.6(5)$ |
| :--- | :--- |
| $\mathrm{C}(32)-\mathrm{C}(33)-\mathrm{C}(34)$ | $120.3(5)$ |
| $\mathrm{C}(35)-\mathrm{C}(34)-\mathrm{C}(33)$ | $119.4(5)$ |
| $\mathrm{C}(35)-\mathrm{C}(34)-\mathrm{H}(34 \mathrm{~A})$ | 120.3 |
| $\mathrm{C}(33)-\mathrm{C}(34)-\mathrm{H}(34 \mathrm{~A})$ | 120.3 |
| $\mathrm{C}(34)-\mathrm{C}(35)-\mathrm{C}(30)$ | $121.8(5)$ |
| $\mathrm{C}(34)-\mathrm{C}(35)-\mathrm{H}(35 \mathrm{~A})$ | 119.1 |
| $\mathrm{C}(30)-\mathrm{C}(35)-\mathrm{H}(35 \mathrm{~A})$ | 119.1 |
| $\mathrm{O}(9)-\mathrm{C}(36)-\mathrm{H}(36 \mathrm{~A})$ | 109.5 |
| $\mathrm{O}(9)-\mathrm{C}(36)-\mathrm{H}(36 \mathrm{~B})$ | 109.5 |
| $\mathrm{H}(36 \mathrm{~A})-\mathrm{C}(36)-\mathrm{H}(36 \mathrm{~B})$ | 109.5 |
| $\mathrm{O}(9)-\mathrm{C}(36)-\mathrm{H}(36 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(36 \mathrm{~A})-\mathrm{C}(36)-\mathrm{H}(36 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(36 \mathrm{~B})-\mathrm{C}(36)-\mathrm{H}(36 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(1 \mathrm{WA})-\mathrm{O}(1 \mathrm{~W})-\mathrm{H}(1 \mathrm{WB})$ | 106.5 |

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters $\left(\approx^{2} \times 10^{3}\right)$ for d1842_a. The anisotropic displacement factor exponent takes the form: $-2 \pi^{2}\left[h^{2} a^{* 2} U^{11}+\ldots+2 h k a^{*} b^{*} U^{12}\right]$

|  | $\mathrm{U}^{11}$ | $\mathrm{U}^{22}$ | $\mathrm{U}^{33}$ | $\mathrm{U}^{23}$ | $\mathrm{U}^{13}$ | $\mathrm{U}^{12}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{Co}(1)$ | 17(1) | 37(1) | 27(1) | -1(1) | 4(1) | -1(1) |
| $\mathrm{O}(1)$ | 24(2) | 42(2) | 27(2) | 2(2) | 1(2) | -2(2) |
| $\mathrm{O}(2)$ | 32(2) | 61(3) | 30(2) | -1(2) | 9(2) | -14(2) |
| $\mathrm{O}(3)$ | 24(2) | 51(2) | 45(2) | -2(2) | -2(2) | -7(2) |
| $\mathrm{O}(4)$ | 19(2) | 44(2) | 28(2) | 1(2) | 8(2) | 1(2) |
| $\mathrm{O}(5)$ | 29(2) | 47(2) | 34(2) | 7(2) | 11(2) | 4(2) |
| $\mathrm{O}(6)$ | 56(3) | 61(3) | 38(2) | 7(2) | 2(2) | 26(2) |
| $\mathrm{O}(7)$ | 19(2) | 40(2) | 29(2) | 0(2) | 2(1) | -1(2) |
| $\mathrm{O}(8)$ | 23(2) | 38(2) | 32(2) | -7(2) | 2(2) | -1(2) |
| $\mathrm{O}(9)$ | 41(2) | 44(3) | 97(4) | -2(2) | -8(2) | 13(2) |
| N(1) | 20(2) | 33(2) | 32(2) | -5(2) | 4(2) | -2(2) |
| N(2) | 21(2) | 36(2) | 36(3) | 1(2) | 1(2) | -1(2) |
| N(3) | 23(2) | 33(2) | 28(2) | 0(2) | 6(2) | 2(2) |
| $\mathrm{C}(1)$ | 19(2) | 46(3) | 23(3) | -4(2) | 1(2) | 3(2) |
| C(2) | 17(2) | 50(3) | 23(3) | -5(2) | 1(2) | -4(2) |
| C(3) | 24(3) | 41(3) | 26(3) | -5(2) | 8(2) | 2(2) |
| C(4) | 38(3) | 70(4) | 36(3) | -3(3) | 4(3) | -22(3) |
| C(5) | 30(3) | 57(4) | 36(3) | -2(3) | 11(2) | -10(3) |
| C(6) | 21(3) | 38(3) | 33(3) | 2(2) | -1(2) | -2(2) |
| C(7) | 30(3) | 46(3) | 32(3) | -7(3) | 4(2) | -6(3) |
| C(8) | 23(3) | 50(3) | 40(3) | 0(3) | 6(2) | -1(2) |
| C(9) | 21(3) | 39(3) | 35(3) | 3(2) | -6(2) | -8(2) |
| C(10) | 33(3) | 50(4) | 35(3) | -9(3) | 0(3) | -2(3) |
| $\mathrm{C}(11)$ | 25(3) | 57(4) | 40(3) | -8(3) | 5(2) | -4(3) |
| C(12) | 23(3) | 52(4) | 53(4) | 2(3) | 2(3) | -9(3) |
| C(13) | 18(2) | 40(3) | 25(3) | -4(2) | -1(2) | -2(2) |
| C(14) | 19(2) | 44(3) | 31(3) | 2(2) | 9(2) | 3(2) |
| C(15) | 22(2) | 36(3) | 27(3) | -2(2) | 1(2) | -6(2) |
| C(16) | 31(3) | 53(4) | 37(3) | 10(3) | 5(2) | 4(3) |
| C(17) | 33(3) | 50(3) | 30(3) | 6(3) | 6(2) | -3(3) |
| C(18) | 14(2) | 38(3) | 34(3) | 2(2) | 3(2) | -2(2) |


| $\mathrm{C}(19)$ | $22(3)$ | $49(3)$ | $31(3)$ | $-1(2)$ | $7(2)$ | $3(2)$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $\mathrm{C}(20)$ | $30(3)$ | $43(3)$ | $29(3)$ | $2(2)$ | $-1(2)$ | $3(2)$ |
| $\mathrm{C}(21)$ | $32(3)$ | $39(3)$ | $41(3)$ | $2(3)$ | $4(3)$ | $7(2)$ |
| $\mathrm{C}(22)$ | $36(3)$ | $49(4)$ | $34(3)$ | $2(3)$ | $7(3)$ | $9(3)$ |
| $\mathrm{C}(23)$ | $26(3)$ | $47(3)$ | $30(3)$ | $-1(2)$ | $5(2)$ | $2(2)$ |
| $\mathrm{C}(24)$ | $64(4)$ | $63(4)$ | $41(4)$ | $9(3)$ | $0(3)$ | $18(3)$ |
| $\mathrm{C}(25)$ | $19(2)$ | $34(3)$ | $32(3)$ | $-1(2)$ | $7(2)$ | $0(2)$ |
| $\mathrm{C}(26)$ | $21(3)$ | $36(3)$ | $33(3)$ | $-4(2)$ | $-2(2)$ | $1(2)$ |
| $\mathrm{C}(27)$ | $22(3)$ | $38(3)$ | $25(3)$ | $-1(2)$ | $3(2)$ | $-4(2)$ |
| $\mathrm{C}(28)$ | $27(3)$ | $34(3)$ | $49(4)$ | $-6(3)$ | $5(3)$ | $3(2)$ |
| $\mathrm{C}(29)$ | $27(3)$ | $34(3)$ | $43(3)$ | $-6(2)$ | $3(2)$ | $0(2)$ |
| $\mathrm{C}(30)$ | $24(3)$ | $35(3)$ | $28(3)$ | $-2(2)$ | $1(2)$ | $1(2)$ |
| $\mathrm{C}(31)$ | $24(3)$ | $38(3)$ | $47(3)$ | $-2(3)$ | $-1(2)$ | $0(2)$ |
| $\mathrm{C}(32)$ | $30(3)$ | $44(3)$ | $62(4)$ | $-2(3)$ | $-1(3)$ | $9(3)$ |
| $\mathrm{C}(33)$ | $42(3)$ | $37(3)$ | $48(4)$ | $-1(3)$ | $1(3)$ | $9(3)$ |
| $\mathrm{C}(34)$ | $39(3)$ | $36(3)$ | $35(3)$ | $1(2)$ | $1(3)$ | $1(2)$ |
| $\mathrm{C}(35)$ | $29(3)$ | $42(3)$ | $31(3)$ | $1(2)$ | $6(2)$ | $0(2)$ |
| $\mathrm{C}(36)$ | $43(4)$ | $54(4)$ | $140(8)$ | $-3(5)$ | $-7(4)$ | $20(3)$ |
| $\mathrm{O}(1 \mathrm{~W})$ | $77(4)$ | $78(4)$ | $148(6)$ | $18(4)$ | $8(4)$ | $0(3)$ |
|  |  |  |  |  |  |  |

Table 5. Hydrogen coordinates ( $\times 10^{4}$ ) and isotropic displacement parameters $\left(\approx^{2} \times 10^{3}\right)$ for d1842_a.

|  | x | y | z | $\mathrm{U}(\mathrm{eq})$ |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{H}(2 \mathrm{~A})$ | 5733 | 6945 | 4327 | 36 |
| H(4A) | 9777 | 8051 | 4726 | 58 |
| H(4B) | 10618 | 7469 | 4740 | 58 |
| H(5A) | 10470 | 7415 | 6067 | 48 |
| H(5B) | 9564 | 7987 | 6046 | 48 |
| H(7A) | 2829 | 6631 | 6122 | 43 |
| H(8A) | 480 | 6218 | 5706 | 45 |
| H(10A) | 2324 | 5551 | 3793 | 47 |
| H(11A) | 4604 | 6021 | 4161 | 49 |
| H(12A) | -2247 | 5386 | 4640 | 64 |
| H(12B) | -1713 | 5983 | 4932 | 64 |
| H(12C) | -1102 | 5463 | 5450 | 64 |
| H(14A) | 3372 | 7715 | 7854 | 37 |
| H(16A) | 5232 | 6177 | 9055 | 48 |
| H(16B) | 6312 | 6636 | 9510 | 48 |
| H(17A) | 7911 | 6545 | 8554 | 45 |
| H(17B) | 6749 | 6129 | 8054 | 45 |
| H(19A) | 4118 | 8030 | 5334 | 40 |
| H(20A) | 2484 | 8656 | 4618 | 41 |
| H(22A) | 1017 | 9158 | 6727 | 47 |
| H(23A) | 2602 | 8530 | 7446 | 41 |
| H(24A) | -325 | 9654 | 4210 | 85 |
| H(24B) | 198 | 9034 | 4140 | 85 |
| H(24C) | 1454 | 9508 | 4229 | 85 |
| H(26A) | 11544 | 6935 | 8146 | 36 |
| H(28A) | 10035 | 8688 | 7967 | 44 |
| H(28B) | 9215 | 8466 | 8728 | 44 |
| H(29A) | 7201 | 8214 | 7880 | 42 |
| $\mathrm{H}(29 \mathrm{~B})$ | 8055 | 8412 | 7114 | 42 |
| H(31A) | 12930 | 6283 | 7700 | 44 |


| $\mathrm{H}(32 \mathrm{~A})$ | 14141 | 5441 | 7720 | 54 |
| :--- | ---: | ---: | ---: | ---: |
| $\mathrm{H}(34 \mathrm{~A})$ | 10014 | 4711 | 7174 | 44 |
| $\mathrm{H}(35 \mathrm{~A})$ | 8831 | 5554 | 7139 | 40 |
| $\mathrm{H}(36 \mathrm{~A})$ | 14678 | 4033 | 7589 | 120 |
| $\mathrm{H}(36 \mathrm{~B})$ | 14670 | 4532 | 8209 | 120 |
| $\mathrm{H}(36 \mathrm{C})$ | 14946 | 4640 | 7282 | 120 |
| $\mathrm{H}(1 \mathrm{WA})$ | 5934 | 5808 | 6281 | 152 |
| $\mathrm{H}(1 \mathrm{WB})$ | 5620 | 5270 | 6213 | 152 |

Table 6. Torsion angles [ $\infty$ ] for d1842_a.

| $\mathrm{N}(3)-\mathrm{Co}(1)-\mathrm{O}(4)-\mathrm{C}(13)$ | -94.3(4) |
| :---: | :---: |
| $\mathrm{N}(2)-\mathrm{Co}(1)-\mathrm{O}(4)-\mathrm{C}(13)$ | $-5.0(4)$ |
| $\mathrm{O}(1)-\mathrm{Co}(1)-\mathrm{O}(4)-\mathrm{C}(13)$ | 82.1(4) |
| $\mathrm{N}(1)-\mathrm{Co}(1)-\mathrm{O}(4)-\mathrm{C}(13)$ | $174.8(4)$ |
| $\mathrm{O}(4)-\mathrm{Co}(1)-\mathrm{N}(3)-\mathrm{C}(27)$ | -178.4(4) |
| $\mathrm{O}(7)-\mathrm{Co}(1)-\mathrm{N}(3)-\mathrm{C}(27)$ | $-2.1(4)$ |
| $\mathrm{N}(2)-\mathrm{Co}(1)-\mathrm{N}(3)-\mathrm{C}(27)$ | 88.0(4) |
| $\mathrm{N}(1)-\mathrm{Co}(1)-\mathrm{N}(3)-\mathrm{C}(27)$ | -91.3(4) |
| $\mathrm{O}(4)-\mathrm{Co}(1)-\mathrm{N}(3)-\mathrm{C}(29)$ | $5.4(4)$ |
| $\mathrm{O}(7)-\mathrm{Co}(1)-\mathrm{N}(3)-\mathrm{C}(29)$ | -178.3(4) |
| $\mathrm{N}(2)-\mathrm{Co}(1)-\mathrm{N}(3)-\mathrm{C}(29)$ | -88.2(4) |
| $\mathrm{N}(1)-\mathrm{Co}(1)-\mathrm{N}(3)-\mathrm{C}(29)$ | 92.5(4) |
| $\mathrm{Co}(1)-\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(2)$ | 18.6(7) |
| $\mathrm{Co}(1)-\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(6)$ | -160.6(3) |
| $\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)$ | $0.9(8)$ |
| $\mathrm{C}(6)-\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)$ | -179.9(4) |
| $\mathrm{C}(5)-\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{O}(2)$ | $-1.5(6)$ |
| $\mathrm{Co}(1)-\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{O}(2)$ | 177.1(3) |
| $\mathrm{C}(5)-\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{C}(2)$ | 178.8(5) |
| $\mathrm{Co}(1)-\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{C}(2)$ | -2.6(7) |
| $\mathrm{C}(4)-\mathrm{O}(2)-\mathrm{C}(3)-\mathrm{N}(1)$ | $3.0(6)$ |
| $\mathrm{C}(4)-\mathrm{O}(2)-\mathrm{C}(3)-\mathrm{C}(2)$ | -177.3(5) |
| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)-\mathrm{N}(1)$ | -9.5(8) |
| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)-\mathrm{O}(2)$ | 170.7(5) |
| $\mathrm{C}(3)-\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{C}(5)$ | -3.1(6) |
| $\mathrm{C}(3)-\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(4)$ | -0.6(6) |
| $\mathrm{Co}(1)-\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(4)$ | -179.1(4) |
| $\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{N}(1)$ | 2.2(6) |
| $\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(6)-\mathrm{C}(7)$ | 43.1(7) |
| $\mathrm{C}(2)-\mathrm{C}(1)-\mathrm{C}(6)-\mathrm{C}(7)$ | -136.2(5) |
| $\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(6)-\mathrm{C}(11)$ | -136.7(5) |
| $\mathrm{C}(2)-\mathrm{C}(1)-\mathrm{C}(6)-\mathrm{C}(11)$ | 44.0(7) |
| $\mathrm{C}(11)-\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{C}(8)$ | -2.3(8) |
| $\mathrm{C}(1)-\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{C}(8)$ | 177.9(5) |
|  |  |


| $\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{C}(8)-\mathrm{C}(9)$ | 3.5(8) |
| :---: | :---: |
| $\mathrm{C}(12)-\mathrm{O}(3)-\mathrm{C}(9)-\mathrm{C}(8)$ | -2.9(7) |
| $\mathrm{C}(12)-\mathrm{O}(3)-\mathrm{C}(9)-\mathrm{C}(10)$ | 178.1(5) |
| $\mathrm{C}(7)-\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{O}(3)$ | 179.2(5) |
| $\mathrm{C}(7)-\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{C}(10)$ | -1.8(8) |
| $\mathrm{O}(3)-\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(11)$ | 178.2(5) |
| $\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(11)$ | -0.8(8) |
| $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(11)-\mathrm{C}(6)$ | 1.9(8) |
| $\mathrm{C}(7)-\mathrm{C}(6)-\mathrm{C}(11)-\mathrm{C}(10)$ | -0.4(8) |
| $\mathrm{C}(1)-\mathrm{C}(6)-\mathrm{C}(11)-\mathrm{C}(10)$ | 179.4(5) |
| $\mathrm{Co}(1)-\mathrm{O}(4)-\mathrm{C}(13)-\mathrm{C}(14)$ | 8.3(7) |
| $\mathrm{Co}(1)-\mathrm{O}(4)-\mathrm{C}(13)-\mathrm{C}(18)$ | -170.8(3) |
| $\mathrm{O}(4)-\mathrm{C}(13)-\mathrm{C}(14)-\mathrm{C}(15)$ | -5.3(8) |
| $\mathrm{C}(18)-\mathrm{C}(13)-\mathrm{C}(14)-\mathrm{C}(15)$ | 173.7(5) |
| $\mathrm{C}(17)-\mathrm{N}(2)-\mathrm{C}(15)-\mathrm{O}(5)$ | -0.3(6) |
| $\mathrm{Co}(1)-\mathrm{N}(2)-\mathrm{C}(15)-\mathrm{O}(5)$ | 179.4(3) |
| $\mathrm{C}(17)-\mathrm{N}(2)-\mathrm{C}(15)-\mathrm{C}(14)$ | -177.2(5) |
| $\mathrm{Co}(1)-\mathrm{N}(2)-\mathrm{C}(15)-\mathrm{C}(14)$ | 2.4(7) |
| $\mathrm{C}(16)-\mathrm{O}(5)-\mathrm{C}(15)-\mathrm{N}(2)$ | 3.8(6) |
| $\mathrm{C}(16)-\mathrm{O}(5)-\mathrm{C}(15)-\mathrm{C}(14)$ | -179.0(4) |
| $\mathrm{C}(13)-\mathrm{C}(14)-\mathrm{C}(15)-\mathrm{N}(2)$ | -0.4(8) |
| $\mathrm{C}(13)-\mathrm{C}(14)-\mathrm{C}(15)-\mathrm{O}(5)$ | -177.3(5) |
| $\mathrm{C}(15)-\mathrm{O}(5)-\mathrm{C}(16)-\mathrm{C}(17)$ | -5.4(5) |
| $\mathrm{C}(15)-\mathrm{N}(2)-\mathrm{C}(17)-\mathrm{C}(16)$ | -3.1(6) |
| $\mathrm{Co}(1)-\mathrm{N}(2)-\mathrm{C}(17)-\mathrm{C}(16)$ | 177.2(3) |
| $\mathrm{O}(5)-\mathrm{C}(16)-\mathrm{C}(17)-\mathrm{N}(2)$ | 5.1(5) |
| $\mathrm{O}(4)-\mathrm{C}(13)-\mathrm{C}(18)-\mathrm{C}(19)$ | 27.4(6) |
| $\mathrm{C}(14)-\mathrm{C}(13)-\mathrm{C}(18)-\mathrm{C}(19)$ | -151.7(5) |
| $\mathrm{O}(4)-\mathrm{C}(13)-\mathrm{C}(18)-\mathrm{C}(23)$ | -152.5(4) |
| $\mathrm{C}(14)-\mathrm{C}(13)-\mathrm{C}(18)-\mathrm{C}(23)$ | 28.4(7) |
| $\mathrm{C}(23)-\mathrm{C}(18)-\mathrm{C}(19)-\mathrm{C}(20)$ | -0.4(7) |
| $\mathrm{C}(13)-\mathrm{C}(18)-\mathrm{C}(19)-\mathrm{C}(20)$ | 179.7(4) |
| $\mathrm{C}(18)-\mathrm{C}(19)-\mathrm{C}(20)-\mathrm{C}(21)$ | 0.3(8) |
| $\mathrm{C}(24)-\mathrm{O}(6)-\mathrm{C}(21)-\mathrm{C}(22)$ | -179.5(5) |
| $\mathrm{C}(24)-\mathrm{O}(6)-\mathrm{C}(21)-\mathrm{C}(20)$ | -0.7(8) |
| $\mathrm{C}(19)-\mathrm{C}(20)-\mathrm{C}(21)-\mathrm{C}(22)$ | 0.3(8) |


| $\mathrm{C}(19)-\mathrm{C}(20)-\mathrm{C}(21)-\mathrm{O}(6)$ | -178.5(5) |
| :---: | :---: |
| $\mathrm{O}(6)-\mathrm{C}(21)-\mathrm{C}(22)-\mathrm{C}(23)$ | 178.0(5) |
| $\mathrm{C}(20)-\mathrm{C}(21)-\mathrm{C}(22)-\mathrm{C}(23)$ | -0.8(8) |
| $\mathrm{C}(21)-\mathrm{C}(22)-\mathrm{C}(23)-\mathrm{C}(18)$ | 0.7(8) |
| $\mathrm{C}(19)-\mathrm{C}(18)-\mathrm{C}(23)-\mathrm{C}(22)$ | -0.1(8) |
| $\mathrm{C}(13)-\mathrm{C}(18)-\mathrm{C}(23)-\mathrm{C}(22)$ | 179.8(5) |
| $\mathrm{Co}(1)-\mathrm{O}(7)-\mathrm{C}(25)-\mathrm{C}(26)$ | -0.4(7) |
| $\mathrm{Co}(1)-\mathrm{O}(7)-\mathrm{C}(25)-\mathrm{C}(30)$ | 177.7(3) |
| $\mathrm{O}(7)-\mathrm{C}(25)-\mathrm{C}(26)-\mathrm{C}(27)$ | -1.7(8) |
| $\mathrm{C}(30)-\mathrm{C}(25)-\mathrm{C}(26)-\mathrm{C}(27)$ | -179.7(5) |
| $\mathrm{C}(29)-\mathrm{N}(3)-\mathrm{C}(27)-\mathrm{O}(8)$ | -1.6(6) |
| $\mathrm{Co}(1)-\mathrm{N}(3)-\mathrm{C}(27)-\mathrm{O}(8)$ | -178.3(3) |
| $\mathrm{C}(29)-\mathrm{N}(3)-\mathrm{C}(27)-\mathrm{C}(26)$ | 177.6(5) |
| $\mathrm{Co}(1)-\mathrm{N}(3)-\mathrm{C}(27)-\mathrm{C}(26)$ | 0.9(7) |
| $\mathrm{C}(28)-\mathrm{O}(8)-\mathrm{C}(27)-\mathrm{N}(3)$ | 3.3(5) |
| $\mathrm{C}(28)-\mathrm{O}(8)-\mathrm{C}(27)-\mathrm{C}(26)$ | -176.0(4) |
| $\mathrm{C}(25)-\mathrm{C}(26)-\mathrm{C}(27)-\mathrm{N}(3)$ | 1.5(8) |
| $\mathrm{C}(25)-\mathrm{C}(26)-\mathrm{C}(27)-\mathrm{O}(8)$ | -179.3(5) |
| $\mathrm{C}(27)-\mathrm{O}(8)-\mathrm{C}(28)-\mathrm{C}(29)$ | -3.4(5) |
| $\mathrm{C}(27)-\mathrm{N}(3)-\mathrm{C}(29)-\mathrm{C}(28)$ | -0.7(5) |
| $\mathrm{Co}(1)-\mathrm{N}(3)-\mathrm{C}(29)-\mathrm{C}(28)$ | 176.0(3) |
| $\mathrm{O}(8)-\mathrm{C}(28)-\mathrm{C}(29)-\mathrm{N}(3)$ | $2.5(5)$ |
| $\mathrm{O}(7)-\mathrm{C}(25)-\mathrm{C}(30)-\mathrm{C}(35)$ | -22.5(7) |
| $\mathrm{C}(26)-\mathrm{C}(25)-\mathrm{C}(30)-\mathrm{C}(35)$ | 155.8(5) |
| $\mathrm{O}(7)-\mathrm{C}(25)-\mathrm{C}(30)-\mathrm{C}(31)$ | 155.9(5) |
| $\mathrm{C}(26)-\mathrm{C}(25)-\mathrm{C}(30)-\mathrm{C}(31)$ | -25.8(8) |
| $\mathrm{C}(35)-\mathrm{C}(30)-\mathrm{C}(31)-\mathrm{C}(32)$ | -1.0(8) |
| $\mathrm{C}(25)-\mathrm{C}(30)-\mathrm{C}(31)-\mathrm{C}(32)$ | -179.4(5) |
| $\mathrm{C}(30)-\mathrm{C}(31)-\mathrm{C}(32)-\mathrm{C}(33)$ | -0.6(9) |
| $\mathrm{C}(36)-\mathrm{O}(9)-\mathrm{C}(33)-\mathrm{C}(32)$ | 5.3(9) |
| $\mathrm{C}(36)-\mathrm{O}(9)-\mathrm{C}(33)-\mathrm{C}(34)$ | -178.2(6) |
| $\mathrm{C}(31)-\mathrm{C}(32)-\mathrm{C}(33)-\mathrm{O}(9)$ | 178.1(6) |
| $\mathrm{C}(31)-\mathrm{C}(32)-\mathrm{C}(33)-\mathrm{C}(34)$ | 1.7(9) |
| $\mathrm{O}(9)-\mathrm{C}(33)-\mathrm{C}(34)-\mathrm{C}(35)$ | -177.9(5) |
| $\mathrm{C}(32)-\mathrm{C}(33)-\mathrm{C}(34)-\mathrm{C}(35)$ | -1.2(9) |
| $\mathrm{C}(33)-\mathrm{C}(34)-\mathrm{C}(35)-\mathrm{C}(30)$ | -0.4(8) |


| $\mathrm{C}(31)-\mathrm{C}(30)-\mathrm{C}(35)-\mathrm{C}(34)$ | $1.5(8)$ |
| :--- | :---: |
| $\mathrm{C}(25)-\mathrm{C}(30)-\mathrm{C}(35)-\mathrm{C}(34)$ | $180.0(5)$ |

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for d1842_a [ $\approx$ and $\infty$ ].

| D-H...A | $d(D-H)$ | $d(H \ldots A)$ | $d(D \ldots A)$ | $<(D H A)$ |
| :--- | :---: | :---: | :---: | :---: |
| $O(1 W)-H(1 W A) \ldots O(1)$ | 0.84 | 2.07 | $2.853(6)$ | 155.6 |

Symmetry transformations used to generate equivalent atoms:


F4: Crystal data and structure refinement for d1870ra_b (9j).

Identification code
Empirical formula
Formula weight
Temperature
Wavelength
Crystal system
Space group
Unit cell dimensions

Volume

Z

Density (calculated)
Absorption coefficient
F(000)
Crystal size
Theta range for data collection
Index ranges
Reflections collected
Independent reflections
Completeness to theta $=25.242^{\circ}$
Absorption correction
Max. and min. transmission
Refinement method
d1870ra_b (9j)
C16 H24 Co N2 O4
367.30

150(2) K
$0.71073 \AA$
Orthorhombic
Pca2 1
$a=10.6455(5) \AA \quad a=90^{\circ}$.
$b=14.6865(9) \AA \quad b=90^{\circ}$.
$\mathrm{c}=11.3187(6) \AA \quad \mathrm{g}=90^{\circ}$.
1769.62(17) $\AA^{3}$

4
$1.379 \mathrm{Mg} / \mathrm{m}^{3}$
$0.990 \mathrm{~mm}^{-1}$
772
$0.190 \times 0.190 \times 0.100 \mathrm{~mm}^{3}$
2.363 to $27.547^{\circ}$.
$-13<=\mathrm{h}<=12,-19<=\mathrm{k}<=18,-14<=\mathrm{l}<=14$
18782
$4071[\mathrm{R}(\mathrm{int})=0.0458]$
99.9 \%

Semi-empirical from equivalents
0.7456 and 0.6801

Full-matrix least-squares on $\mathrm{F}^{2}$

Data / restraints / parameters
Goodness-of-fit on $\mathrm{F}^{2}$
Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ]
R indices (all data)
Absolute structure parameter
Extinction coefficient
Largest diff. peak and hole

4071 / $1 / 214$
1.035
$\mathrm{R} 1=0.0323, \mathrm{wR} 2=0.0637$
$\mathrm{R} 1=0.0701, \mathrm{wR} 2=0.0763$
0.023(11)
n/a
0.297 and -0.405 e. $\AA^{-3}$

Table 2. Atomic coordinates $\left(\times 10^{4}\right)$ and equivalent isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for d1870ra_b. $\mathrm{U}(\mathrm{eq})$ is defined as one third of the trace of the orthogonalized $\mathrm{U}^{\mathrm{ij}}$ tensor.

|  | x | y | z | $\mathrm{U}(\mathrm{eq})$ |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{Co}(1)$ | 4978(1) | 2528(1) | 4394(1) | 17(1) |
| $\mathrm{O}(1)$ | 5491(2) | 1478(2) | 3465(2) | 23(1) |
| $\mathrm{O}(2)$ | 2345(3) | 724(2) | 5598(3) | 42(1) |
| $\mathrm{O}(3)$ | 4592(2) | 3653(2) | 3580(2) | 25(1) |
| $\mathrm{O}(4)$ | 7672(3) | 4134(2) | 5934(2) | 38(1) |
| N(1) | 3510(3) | 1932(2) | 5092(2) | 23(1) |
| $\mathrm{N}(2)$ | 6347(3) | 3034(2) | 5342(2) | 19(1) |
| C(1) | 3353(3) | 1059(3) | 4995(3) | 27(1) |
| $\mathrm{C}(2)$ | 4077(3) | 422(2) | 4347(4) | 27(1) |
| C(3) | 5070(4) | 660(3) | 3626(3) | 23(1) |
| C(4) | 1886(4) | 1472(4) | 6329(4) | 50(2) |
| C(5) | 2440(4) | 2322(3) | 5751(4) | 31(1) |
| C(6) | 5743(4) | -66(3) | 2936(4) | 35(1) |
| C(7) | 2900(4) | 3030(4) | 6646(4) | 56(2) |
| C(8) | 1536(4) | 2767(3) | 4892(4) | 35(1) |
| C(9) | 5153(4) | 4424(3) | 3755(4) | 25(1) |
| $\mathrm{C}(10)$ | 6134(3) | 4566(3) | 4528(4) | 30(1) |
| $\mathrm{C}(11)$ | 6671(3) | 3889(3) | 5245(3) | 24(1) |
| $\mathrm{C}(12)$ | 7953(4) | 3363(3) | 6689(4) | 40(1) |
| $\mathrm{C}(13)$ | 7221(3) | 2563(3) | 6154(4) | 25(1) |
| $\mathrm{C}(14)$ | 4656(5) | 5197(3) | 3032(4) | 45(1) |
| $\mathrm{C}(15)$ | 6501(4) | 2023(4) | 7075(4) | 49(1) |
| $\mathrm{C}(16)$ | 8066(4) | 1933(3) | 5460(4) | 35(1) |

Table 3. Bond lengths $\left[\AA\right.$ ] and angles [ ${ }^{\circ}$ ] for d1870ra_b.

| $\mathrm{Co}(1)-\mathrm{O}(3)$ | 1.935(3) |
| :---: | :---: |
| $\mathrm{Co}(1)-\mathrm{O}(1)$ | 1.944(3) |
| $\mathrm{Co}(1)-\mathrm{N}(2)$ | 1.957(3) |
| $\mathrm{Co}(1)-\mathrm{N}(1)$ | 1.958(3) |
| $\mathrm{O}(1)-\mathrm{C}(3)$ | 1.295(4) |
| $\mathrm{O}(2)-\mathrm{C}(1)$ | 1.364(4) |
| $\mathrm{O}(2)-\mathrm{C}(4)$ | 1.459(6) |
| $\mathrm{O}(3)-\mathrm{C}(9)$ | $1.296(5)$ |
| $\mathrm{O}(4)-\mathrm{C}(11)$ | 1.368(4) |
| $\mathrm{O}(4)-\mathrm{C}(12)$ | 1.450(5) |
| $\mathrm{N}(1)-\mathrm{C}(1)$ | 1.297(5) |
| $\mathrm{N}(1)-\mathrm{C}(5)$ | $1.478(5)$ |
| $\mathrm{N}(2)-\mathrm{C}(11)$ | 1.307(5) |
| $\mathrm{N}(2)-\mathrm{C}(13)$ | 1.480(5) |
| $\mathrm{C}(1)-\mathrm{C}(2)$ | 1.417(6) |
| $\mathrm{C}(2)-\mathrm{C}(3)$ | $1.380(5)$ |
| $\mathrm{C}(2)-\mathrm{H}(2 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(3)-\mathrm{C}(6)$ | 1.503(5) |
| $\mathrm{C}(4)-\mathrm{C}(5)$ | 1.529(6) |
| $\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~A})$ | 0.9900 |
| $\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~B})$ | 0.9900 |
| $\mathrm{C}(5)-\mathrm{C}(8)$ | 1.516(5) |
| $\mathrm{C}(5)-\mathrm{C}(7)$ | 1.532(6) |
| $\mathrm{C}(6)-\mathrm{H}(6 \mathrm{~A})$ | 0.9800 |
| $\mathrm{C}(6)-\mathrm{H}(6 \mathrm{~B})$ | 0.9800 |
| $\mathrm{C}(6)-\mathrm{H}(6 \mathrm{C})$ | 0.9800 |
| $\mathrm{C}(7)-\mathrm{H}(7 \mathrm{~A})$ | 0.9800 |
| $\mathrm{C}(7)-\mathrm{H}(7 \mathrm{~B})$ | 0.9800 |
| $\mathrm{C}(7)-\mathrm{H}(7 \mathrm{C})$ | 0.9800 |
| $\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~A})$ | 0.9800 |
| $\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~B})$ | 0.9800 |
| $\mathrm{C}(8)-\mathrm{H}(8 \mathrm{C})$ | 0.9800 |
| $\mathrm{C}(9)-\mathrm{C}(10)$ | 1.378(5) |
| $\mathrm{C}(9)-\mathrm{C}(14)$ | 1.497(6) |


| $\mathrm{C}(10)-\mathrm{C}(11)$ | $1.405(6)$ |
| :---: | :---: |
| $\mathrm{C}(10)-\mathrm{H}(10 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(12)-\mathrm{C}(13)$ | 1.535(6) |
| $\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~A})$ | 0.9900 |
| $\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~B})$ | 0.9900 |
| $\mathrm{C}(13)-\mathrm{C}(16)$ | 1.510(6) |
| $\mathrm{C}(13)-\mathrm{C}(15)$ | 1.517(6) |
| $\mathrm{C}(14)-\mathrm{H}(14 \mathrm{~A})$ | 0.9800 |
| $\mathrm{C}(14)-\mathrm{H}(14 \mathrm{~B})$ | 0.9800 |
| $\mathrm{C}(14)-\mathrm{H}(14 \mathrm{C})$ | 0.9800 |
| $\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~A})$ | 0.9800 |
| $\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~B})$ | 0.9800 |
| $\mathrm{C}(15)-\mathrm{H}(15 \mathrm{C})$ | 0.9800 |
| $\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~A})$ | 0.9800 |
| $\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~B})$ | 0.9800 |
| $\mathrm{C}(16)-\mathrm{H}(16 \mathrm{C})$ | 0.9800 |
| $\mathrm{O}(3)-\mathrm{Co}(1)-\mathrm{O}(1)$ | 118.64(13) |
| $\mathrm{O}(3)-\mathrm{Co}(1)-\mathrm{N}(2)$ | 95.42(13) |
| $\mathrm{O}(1)-\mathrm{Co}(1)-\mathrm{N}(2)$ | 112.90(11) |
| $\mathrm{O}(3)-\mathrm{Co}(1)-\mathrm{N}(1)$ | 113.84(12) |
| $\mathrm{O}(1)-\mathrm{Co}(1)-\mathrm{N}(1)$ | 95.03(13) |
| $\mathrm{N}(2)-\mathrm{Co}(1)-\mathrm{N}(1)$ | 122.89(16) |
| $\mathrm{C}(3)-\mathrm{O}(1)-\mathrm{Co}(1)$ | 124.2(2) |
| $\mathrm{C}(1)-\mathrm{O}(2)-\mathrm{C}(4)$ | 106.0(3) |
| $\mathrm{C}(9)-\mathrm{O}(3)-\mathrm{Co}(1)$ | 125.2(2) |
| $\mathrm{C}(11)-\mathrm{O}(4)-\mathrm{C}(12)$ | 107.0(3) |
| $\mathrm{C}(1)-\mathrm{N}(1)-\mathrm{C}(5)$ | 109.0(3) |
| $\mathrm{C}(1)-\mathrm{N}(1)-\mathrm{Co}(1)$ | 120.7(3) |
| $\mathrm{C}(5)-\mathrm{N}(1)-\mathrm{Co}(1)$ | 130.2(3) |
| $\mathrm{C}(11)-\mathrm{N}(2)-\mathrm{C}(13)$ | 109.7(3) |
| $\mathrm{C}(11)-\mathrm{N}(2)-\mathrm{Co}(1)$ | 121.0(3) |
| $\mathrm{C}(13)-\mathrm{N}(2)-\mathrm{Co}(1)$ | 129.1(3) |
| $\mathrm{N}(1)-\mathrm{C}(1)-\mathrm{O}(2)$ | 114.6(4) |
| $\mathrm{N}(1)-\mathrm{C}(1)-\mathrm{C}(2)$ | 128.7(3) |
| $\mathrm{O}(2)-\mathrm{C}(1)-\mathrm{C}(2)$ | 116.7(4) |


| $\mathrm{C}(3)-\mathrm{C}(2)-\mathrm{C}(1)$ | 123.8(3) |
| :---: | :---: |
| $\mathrm{C}(3)-\mathrm{C}(2)-\mathrm{H}(2 \mathrm{~A})$ | 118.1 |
| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{H}(2 \mathrm{~A})$ | 118.1 |
| $\mathrm{O}(1)-\mathrm{C}(3)-\mathrm{C}(2)$ | 125.7(4) |
| $\mathrm{O}(1)-\mathrm{C}(3)-\mathrm{C}(6)$ | 114.8(4) |
| $\mathrm{C}(2)-\mathrm{C}(3)-\mathrm{C}(6)$ | 119.5(4) |
| $\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{C}(5)$ | 104.1(3) |
| $\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~A})$ | 110.9 |
| $\mathrm{C}(5)-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~A})$ | 110.9 |
| $\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~B})$ | 110.9 |
| $\mathrm{C}(5)-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~B})$ | 110.9 |
| $\mathrm{H}(4 \mathrm{~A})-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~B})$ | 109.0 |
| $\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(8)$ | 109.5(3) |
| $\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(4)$ | 101.4(3) |
| $\mathrm{C}(8)-\mathrm{C}(5)-\mathrm{C}(4)$ | 112.4(3) |
| $\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(7)$ | 110.5(3) |
| $\mathrm{C}(8)-\mathrm{C}(5)-\mathrm{C}(7)$ | 109.5(4) |
| $\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{C}(7)$ | 113.3(4) |
| $\mathrm{C}(3)-\mathrm{C}(6)-\mathrm{H}(6 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(3)-\mathrm{C}(6)-\mathrm{H}(6 \mathrm{~B})$ | 109.5 |
| $\mathrm{H}(6 \mathrm{~A})-\mathrm{C}(6)-\mathrm{H}(6 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(3)-\mathrm{C}(6)-\mathrm{H}(6 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(6 \mathrm{~A})-\mathrm{C}(6)-\mathrm{H}(6 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(6 \mathrm{~B})-\mathrm{C}(6)-\mathrm{H}(6 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(5)-\mathrm{C}(7)-\mathrm{H}(7 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(5)-\mathrm{C}(7)-\mathrm{H}(7 \mathrm{~B})$ | 109.5 |
| $\mathrm{H}(7 \mathrm{~A})-\mathrm{C}(7)-\mathrm{H}(7 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(5)-\mathrm{C}(7)-\mathrm{H}(7 \mathrm{C})$ | 109.5 |
| H(7A)-C(7)-H(7C) | 109.5 |
| $\mathrm{H}(7 \mathrm{~B})-\mathrm{C}(7)-\mathrm{H}(7 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(5)-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(5)-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~B})$ | 109.5 |
| $\mathrm{H}(8 \mathrm{~A})-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(5)-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(8 \mathrm{~A})-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(8 \mathrm{~B})-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{C})$ | 109.5 |


| $\mathrm{O}(3)-\mathrm{C}(9)-\mathrm{C}(10)$ | 125.4(4) |
| :---: | :---: |
| $\mathrm{O}(3)-\mathrm{C}(9)-\mathrm{C}(14)$ | 114.6(4) |
| $\mathrm{C}(10)-\mathrm{C}(9)-\mathrm{C}(14)$ | 120.0(4) |
| $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(11)$ | 124.6(4) |
| $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{H}(10 \mathrm{~A})$ | 117.7 |
| $\mathrm{C}(11)-\mathrm{C}(10)-\mathrm{H}(10 \mathrm{~A})$ | 117.7 |
| $\mathrm{N}(2)-\mathrm{C}(11)-\mathrm{O}(4)$ | 114.2(4) |
| $\mathrm{N}(2)-\mathrm{C}(11)-\mathrm{C}(10)$ | 128.4(4) |
| $\mathrm{O}(4)-\mathrm{C}(11)-\mathrm{C}(10)$ | 117.4(4) |
| $\mathrm{O}(4)-\mathrm{C}(12)-\mathrm{C}(13)$ | 105.1(3) |
| $\mathrm{O}(4)-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~A})$ | 110.7 |
| $\mathrm{C}(13)-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~A})$ | 110.7 |
| $\mathrm{O}(4)-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~B})$ | 110.7 |
| $\mathrm{C}(13)-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~B})$ | 110.7 |
| $\mathrm{H}(12 \mathrm{~A})-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~B})$ | 108.8 |
| $\mathrm{N}(2)-\mathrm{C}(13)-\mathrm{C}(16)$ | 109.7(3) |
| $\mathrm{N}(2)-\mathrm{C}(13)-\mathrm{C}(15)$ | 110.7(3) |
| $\mathrm{C}(16)-\mathrm{C}(13)-\mathrm{C}(15)$ | 109.8(4) |
| $\mathrm{N}(2)-\mathrm{C}(13)-\mathrm{C}(12)$ | 101.9(3) |
| $\mathrm{C}(16)-\mathrm{C}(13)-\mathrm{C}(12)$ | 111.8(3) |
| $\mathrm{C}(15)-\mathrm{C}(13)-\mathrm{C}(12)$ | 112.7(4) |
| $\mathrm{C}(9)-\mathrm{C}(14)-\mathrm{H}(14 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(9)-\mathrm{C}(14)-\mathrm{H}(14 \mathrm{~B})$ | 109.5 |
| $\mathrm{H}(14 \mathrm{~A})-\mathrm{C}(14)-\mathrm{H}(14 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(9)-\mathrm{C}(14)-\mathrm{H}(14 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(14 \mathrm{~A})-\mathrm{C}(14)-\mathrm{H}(14 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(14 \mathrm{~B})-\mathrm{C}(14)-\mathrm{H}(14 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(13)-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(13)-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~B})$ | 109.5 |
| $\mathrm{H}(15 \mathrm{~A})-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(13)-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(15 \mathrm{~A})-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(15 \mathrm{~B})-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(13)-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(13)-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~B})$ | 109.5 |
| $\mathrm{H}(16 \mathrm{~A})-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~B})$ | 109.5 |


| $\mathrm{C}(13)-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{C})$ | 109.5 |
| :--- | :--- |
| $\mathrm{H}(16 \mathrm{~A})-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(16 \mathrm{~B})-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{C})$ | 109.5 |

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for d1870ra_b. The anisotropic displacement factor exponent takes the form: $-2 p^{2}\left[h^{2} a^{* 2} U^{11}+\ldots+2 h k a^{*} b^{*} U^{12}\right]$

|  | $\mathrm{U}^{11}$ | $\mathrm{U}^{22}$ | $\mathrm{U}^{33}$ | $\mathrm{U}^{23}$ | $\mathrm{U}^{13}$ | $\mathrm{U}^{12}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{Co}(1)$ | 15(1) | 19(1) | 16(1) | -1(1) | $0(1)$ | -1(1) |
| $\mathrm{O}(1)$ | 22(1) | 22(2) | 24(2) | -4(1) | 2(1) | -4(1) |
| $\mathrm{O}(2)$ | 27(2) | 46(2) | 52(2) | 25(2) | 9(2) | -7(1) |
| $\mathrm{O}(3)$ | 24(1) | 23(2) | 27(2) | 4(1) | -2(1) | $0(1)$ |
| $\mathrm{O}(4)$ | 34(2) | 37(2) | 42(2) | -11(2) | -11(2) | -11(1) |
| $\mathrm{N}(1)$ | 19(2) | 32(2) | 18(2) | 5(2) | 2(1) | 0(2) |
| $\mathrm{N}(2)$ | 19(2) | 25(2) | 14(2) | -4(2) | -1(1) | 3(1) |
| $\mathrm{C}(1)$ | 18(2) | 38(3) | 25(2) | 17(2) | -2(2) | -5(2) |
| $\mathrm{C}(2)$ | 28(2) | 19(2) | 35(2) | 5(2) | -5(2) | -7(2) |
| $\mathrm{C}(3)$ | 27(2) | 18(2) | 25(2) | -3(2) | -12(2) | -2(2) |
| C(4) | 29(2) | 69(4) | 52(3) | 32(3) | 21(2) | 15(2) |
| $\mathrm{C}(5)$ | 22(2) | 49(3) | 22(2) | 7(2) | 10(2) | 4(2) |
| C (6) | 41(3) | 25(3) | 40(3) | -6(2) | -7(2) | 4(2) |
| $\mathrm{C}(7)$ | 39(3) | 96(5) | 33(3) | -23(3) | 5(2) | 9(3) |
| C(8) | 26(2) | 38(3) | 41(3) | 6(2) | 4(2) | 5(2) |
| C(9) | 31(2) | 19(2) | 25(2) | 1(2) | 8(2) | 6(2) |
| C(10) | 37(2) | 16(2) | 36(2) | -5(2) | 1(2) | -3(2) |
| $\mathrm{C}(11)$ | 27(2) | 25(2) | 22(2) | -11(2) | 2(2) | -2(2) |
| $\mathrm{C}(12)$ | 35(2) | 46(3) | 38(3) | -19(2) | -16(2) | 9(2) |
| C(13) | 22(2) | 34(2) | 19(2) | -1(2) | -7(2) | 3(2) |
| C(14) | 50(3) | 29(3) | 55(3) | 14(2) | -9(3) | 2(2) |
| C(15) | 38(3) | 80(4) | 31(3) | 20(3) | -6(2) | 1(3) |
| C(16) | 30(2) | 38(3) | 37(3) | -7(2) | -10(2) | 13(2) |

Table 5. Hydrogen coordinates ( $\times 10^{4}$ ) and isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for d1870ra_b.

|  | x | y | z | $\mathrm{U}(\mathrm{eq})$ |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{H}(2 \mathrm{~A})$ | 3866 | -204 | 4411 | 33 |
| H(4A) | 2182 | 1408 | 7154 | 60 |
| H(4B) | 956 | 1494 | 6326 | 60 |
| H(6A) | 5480 | -667 | 3218 | 53 |
| H(6B) | 6651 | 2 | 3043 | 53 |
| H(6C) | 5535 | -5 | 2096 | 53 |
| H(7A) | 2199 | 3217 | 7152 | 84 |
| H(7B) | 3229 | 3562 | 6224 | 84 |
| H(7C) | 3566 | 2764 | 7133 | 84 |
| H(8A) | 861 | 3068 | 5333 | 53 |
| H(8B) | 1175 | 2302 | 4372 | 53 |
| H(8C) | 1986 | 3218 | 4416 | 53 |
| H(10A) | 6470 | 5164 | 4581 | 35 |
| H(12A) | 7677 | 3482 | 7510 | 48 |
| $\mathrm{H}(12 \mathrm{~B})$ | 8866 | 3235 | 6692 | 48 |
| H(14A) | 5095 | 5760 | 3249 | 67 |
| H(14B) | 3754 | 5269 | 3181 | 67 |
| H(14C) | 4793 | 5070 | 2191 | 67 |
| H(15A) | 7095 | 1738 | 7624 | 74 |
| H(15B) | 6003 | 1550 | 6683 | 74 |
| H(15C) | 5941 | 2432 | 7511 | 74 |
| H(16A) | 8638 | 1618 | 6002 | 53 |
| H(16B) | 8555 | 2288 | 4889 | 53 |
| H(16C) | 7553 | 1484 | 5039 | 53 |

Table 6. Torsion angles [ ${ }^{\circ}$ ] for d1870ra_b.

| $\mathrm{C}(5)-\mathrm{N}(1)-\mathrm{C}(1)-\mathrm{O}(2)$ | -5.8(4) |
| :---: | :---: |
| $\mathrm{Co}(1)-\mathrm{N}(1)-\mathrm{C}(1)-\mathrm{O}(2)$ | 175.2(2) |
| $\mathrm{C}(5)-\mathrm{N}(1)-\mathrm{C}(1)-\mathrm{C}(2)$ | 173.7(4) |
| $\mathrm{Co}(1)-\mathrm{N}(1)-\mathrm{C}(1)-\mathrm{C}(2)$ | -5.3(5) |
| $\mathrm{C}(4)-\mathrm{O}(2)-\mathrm{C}(1)-\mathrm{N}(1)$ | -9.2(4) |
| $\mathrm{C}(4)-\mathrm{O}(2)-\mathrm{C}(1)-\mathrm{C}(2)$ | 171.3(3) |
| $\mathrm{N}(1)-\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)$ | -4.2(6) |
| $\mathrm{O}(2)-\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)$ | 175.3(4) |
| $\mathrm{Co}(1)-\mathrm{O}(1)-\mathrm{C}(3)-\mathrm{C}(2)$ | 10.0(5) |
| $\mathrm{Co}(1)-\mathrm{O}(1)-\mathrm{C}(3)-\mathrm{C}(6)$ | -170.9(2) |
| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)-\mathrm{O}(1)$ | 1.6(6) |
| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)-\mathrm{C}(6)$ | -177.4(4) |
| $\mathrm{C}(1)-\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{C}(5)$ | 19.3(4) |
| $\mathrm{C}(1)-\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(8)$ | -101.7(4) |
| $\mathrm{Co}(1)-\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(8)$ | 77.2(4) |
| $\mathrm{C}(1)-\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(4)$ | 17.2(4) |
| $\mathrm{Co}(1)-\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(4)$ | -163.9(3) |
| $\mathrm{C}(1)-\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(7)$ | 137.6(4) |
| $\mathrm{Co}(1)-\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(7)$ | -43.6(5) |
| $\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{N}(1)$ | -21.6(4) |
| $\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{C}(8)$ | 95.2(4) |
| $\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{C}(7)$ | -140.0(4) |
| $\mathrm{Co}(1)-\mathrm{O}(3)-\mathrm{C}(9)-\mathrm{C}(10)$ | 1.5(6) |
| $\mathrm{Co}(1)-\mathrm{O}(3)-\mathrm{C}(9)-\mathrm{C}(14)$ | -178.6(3) |
| $\mathrm{O}(3)-\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(11)$ | 0.0(7) |
| $C(14)-C(9)-C(10)-C(11)$ | -179.9(4) |
| $\mathrm{C}(13)-\mathrm{N}(2)-\mathrm{C}(11)-\mathrm{O}(4)$ | -2.5(4) |
| $\mathrm{Co}(1)-\mathrm{N}(2)-\mathrm{C}(11)-\mathrm{O}(4)$ | -177.8(2) |
| $\mathrm{C}(13)-\mathrm{N}(2)-\mathrm{C}(11)-\mathrm{C}(10)$ | 176.9(4) |
| $\mathrm{Co}(1)-\mathrm{N}(2)-\mathrm{C}(11)-\mathrm{C}(10)$ | 1.6(5) |
| $\mathrm{C}(12)-\mathrm{O}(4)-\mathrm{C}(11)-\mathrm{N}(2)$ | -7.5(4) |
| $\mathrm{C}(12)-\mathrm{O}(4)-\mathrm{C}(11)-\mathrm{C}(10)$ | 173.0(3) |
| $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(11)-\mathrm{N}(2)$ | -1.8(7) |
| $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(11)-\mathrm{O}(4)$ | 177.6(4) |


| $\mathrm{C}(11)-\mathrm{O}(4)-\mathrm{C}(12)-\mathrm{C}(13)$ | $13.6(4)$ |
| :--- | :---: |
| $\mathrm{C}(11)-\mathrm{N}(2)-\mathrm{C}(13)-\mathrm{C}(16)$ | $-108.0(4)$ |
| $\mathrm{Co}(1)-\mathrm{N}(2)-\mathrm{C}(13)-\mathrm{C}(16)$ | $66.8(4)$ |
| $\mathrm{C}(11)-\mathrm{N}(2)-\mathrm{C}(13)-\mathrm{C}(15)$ | $130.6(4)$ |
| $\mathrm{Co}(1)-\mathrm{N}(2)-\mathrm{C}(13)-\mathrm{C}(15)$ | $-54.5(5)$ |
| $\mathrm{C}(11)-\mathrm{N}(2)-\mathrm{C}(13)-\mathrm{C}(12)$ | $10.6(4)$ |
| $\mathrm{Co}(1)-\mathrm{N}(2)-\mathrm{C}(13)-\mathrm{C}(12)$ | $-174.6(3)$ |
| $\mathrm{O}(4)-\mathrm{C}(12)-\mathrm{C}(13)-\mathrm{N}(2)$ | $-14.4(4)$ |
| $\mathrm{O}(4)-\mathrm{C}(12)-\mathrm{C}(13)-\mathrm{C}(16)$ | $102.8(4)$ |
| $\mathrm{O}(4)-\mathrm{C}(12)-\mathrm{C}(13)-\mathrm{C}(15)$ | $-133.0(4)$ |
|  |  |

Symmetry transformations used to generate equivalent atoms:


F5: Crystal data and structure refinement for d1867_a (9k).

| Identification code | d1867_a (9k) |
| :---: | :---: |
| Empirical formula | C16 H18 Co F6 N2 O4 |
| Formula weight | 475.25 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 A |
| Crystal system | Orthorhombic |
| Space group | Pbca |
| Unit cell dimensions | $a=11.3622(5) \AA \quad a=90^{\circ}$. |
|  | $\mathrm{b}=18.1752(10) \AA \quad \mathrm{b}=90^{\circ}$. |
|  | $\mathrm{c}=18.9609(9) \AA \quad \mathrm{g}=90^{\circ}$. |
| Volume | 3915.6(3) $\AA^{3}$ |
| Z | 8 |
| Density (calculated) | $1.612 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.957 \mathrm{~mm}^{-1}$ |
| F(000) | 1928 |
| Crystal size | $0.270 \times 0.190 \times 0.060 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 2.148 to $27.520^{\circ}$. |
| Index ranges | $-14<=\mathrm{h}<=8,-17<=\mathrm{k}<=23,-24<=\mathrm{l}<=17$ |
| Reflections collected | 18516 |
| Independent reflections | $4500[\mathrm{R}(\mathrm{int})=0.0536]$ |
| Completeness to theta $=25.242^{\circ}$ | 100.0 \% |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.7456 and 0.6827 |

Refinement method
Data / restraints / parameters
Goodness-of-fit on $\mathrm{F}^{2}$
Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ]
R indices (all data)
Extinction coefficient
Largest diff. peak and hole

Full-matrix least-squares on $\mathrm{F}^{2}$
4500 / 0 / 266
1.015
$\mathrm{R} 1=0.0415, \mathrm{wR} 2=0.0833$
$\mathrm{R} 1=0.0795, \mathrm{wR} 2=0.0981$
n/a
0.557 and -0.406 e. $\AA^{-3}$

Table 2. Atomic coordinates ( $\times 10^{4}$ ) and equivalent isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for $\mathrm{d} 1867 \_\mathrm{a}$. $\mathrm{U}(\mathrm{eq})$ is defined as one third of the trace of the orthogonalized $\mathrm{U}^{\mathrm{ij}}$ tensor.

|  | X | y | z | U(eq) |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{Co}(1)$ | 3872(1) | 3396(1) | 6266(1) | 20(1) |
| F(1) | 2850(2) | 1072(1) | 6924(1) | 59(1) |
| F(2) | 1374(2) | 1696(1) | 7303(1) | 60(1) |
| F(3) | 2673(2) | 1297(1) | 8021(1) | 46(1) |
| F(4) | 2658(2) | 5652(1) | 5310(2) | 110(1) |
| $F(5)$ | 2049(3) | 5169(2) | 4391(1) | 99(1) |
| F(6) | 1170(2) | 4987(1) | 5331(1) | 72(1) |
| $\mathrm{O}(1)$ | 3063(2) | 2543(1) | 6632(1) | 31(1) |
| $\mathrm{O}(2)$ | 4921(2) | 3547(1) | 8328(1) | 41(1) |
| O(3) | 2897(2) | 4166(1) | 5858(1) | 30(1) |
| $\mathrm{O}(4)$ | 5094(2) | 3306(1) | 4232(1) | 36(1) |
| N(1) | 4576(2) | 3673(1) | 7174(1) | 23(1) |
| $\mathrm{N}(2)$ | 4715(2) | 3181(1) | 5385(1) | 24(1) |
| C(1) | 3198(2) | 2297(2) | 7261(2) | 25(1) |
| C(2) | 3815(2) | 2596(2) | 7802(2) | 28(1) |
| C(3) | 4433(2) | 3277(2) | 7738(1) | 26(1) |
| C(4) | 5338(3) | 4280(2) | 8161(2) | 48(1) |
| C(5) | 5319(2) | 4314(2) | 7357(2) | 26(1) |
| C(6) | 2523(3) | 1589(2) | 7383(2) | 32(1) |
| C(7) | 6533(3) | 4206(2) | 7041(2) | 52(1) |
| C(8) | 4758(3) | 5025(2) | 7091(2) | 43(1) |
| C(9) | 2997(2) | 4392(2) | 5225(2) | 26(1) |
| C(10) | 3706(2) | 4131(2) | 4704(2) | 30(1) |
| $\mathrm{C}(11)$ | 4505(2) | 3533(2) | 4802(1) | 26(1) |
| $\mathrm{C}(12)$ | 5950(3) | 2770(2) | 4479(2) | 36(1) |
| C(13) | 5525(2) | 2557(2) | 5215(2) | 27(1) |
| C(14) | 2220(3) | 5046(2) | 5063(2) | 35(1) |
| C(15) | 6513(3) | 2524(2) | 5750(2) | 46(1) |
| C(16) | 4809(3) | 1844(2) | 5205(2) | 46(1) |

Table 3. Bond lengths [ $\AA$ ] and angles [ ${ }^{\circ}$ ] for d1867_a.

| $\mathrm{Co}(1)-\mathrm{O}(1)$ | $1.9315(19)$ |
| :---: | :---: |
| $\mathrm{Co}(1)-\mathrm{O}(3)$ | 1.9449(19) |
| $\mathrm{Co}(1)-\mathrm{N}(1)$ | 1.964(2) |
| $\mathrm{Co}(1)-\mathrm{N}(2)$ | 1.964(2) |
| $\mathrm{F}(1)-\mathrm{C}(6)$ | 1.334(3) |
| $\mathrm{F}(2)-\mathrm{C}(6)$ | 1.329(3) |
| $\mathrm{F}(3)-\mathrm{C}(6)$ | 1.331(3) |
| $\mathrm{F}(4)-\mathrm{C}(14)$ | 1.296(4) |
| $F(5)-C(14)$ | 1.308(4) |
| $F(6)-C(14)$ | 1.301(4) |
| $\mathrm{O}(1)-\mathrm{C}(1)$ | 1.283(3) |
| $\mathrm{O}(2)-\mathrm{C}(3)$ | 1.342(3) |
| $\mathrm{O}(2)-\mathrm{C}(4)$ | 1.449(4) |
| $\mathrm{O}(3)-\mathrm{C}(9)$ | $1.275(3)$ |
| $\mathrm{O}(4)-\mathrm{C}(11)$ | 1.337(3) |
| $\mathrm{O}(4)-\mathrm{C}(12)$ | $1.455(4)$ |
| $\mathrm{N}(1)-\mathrm{C}(3)$ | 1.300(3) |
| $\mathrm{N}(1)-\mathrm{C}(5)$ | 1.480(3) |
| $\mathrm{N}(2)-\mathrm{C}(11)$ | 1.299(3) |
| $\mathrm{N}(2)-\mathrm{C}(13)$ | 1.494(3) |
| $\mathrm{C}(1)-\mathrm{C}(2)$ | 1.357(4) |
| $\mathrm{C}(1)-\mathrm{C}(6)$ | 1.516(4) |
| $\mathrm{C}(2)$-C(3) | 1.427(4) |
| $\mathrm{C}(2)-\mathrm{H}(2 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(4)-\mathrm{C}(5)$ | 1.525(4) |
| $\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~A})$ | 0.9900 |
| $\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~B})$ | 0.9900 |
| $\mathrm{C}(5)-\mathrm{C}(7)$ | 1.517(4) |
| $\mathrm{C}(5)-\mathrm{C}(8)$ | 1.528(4) |
| $\mathrm{C}(7)-\mathrm{H}(7 \mathrm{~A})$ | 0.9800 |
| $\mathrm{C}(7)-\mathrm{H}(7 \mathrm{~B})$ | 0.9800 |
| $\mathrm{C}(7)-\mathrm{H}(7 \mathrm{C})$ | 0.9800 |
| $\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~A})$ | 0.9800 |
| $\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~B})$ | 0.9800 |


| $\mathrm{C}(8)-\mathrm{H}(8 \mathrm{C})$ | 0.9800 |
| :---: | :---: |
| $\mathrm{C}(9)-\mathrm{C}(10)$ | 1.360(4) |
| $\mathrm{C}(9)-\mathrm{C}(14)$ | 1.512(4) |
| $\mathrm{C}(10)-\mathrm{C}(11)$ | 1.428(4) |
| $\mathrm{C}(10)-\mathrm{H}(10 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(12)-\mathrm{C}(13)$ | 1.528(4) |
| $\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~A})$ | 0.9900 |
| $\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~B})$ | 0.9900 |
| $\mathrm{C}(13)-\mathrm{C}(15)$ | 1.513(4) |
| $\mathrm{C}(13)-\mathrm{C}(16)$ | 1.531(4) |
| $\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~A})$ | 0.9800 |
| $\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~B})$ | 0.9800 |
| $\mathrm{C}(15)-\mathrm{H}(15 \mathrm{C})$ | 0.9800 |
| $\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~A})$ | 0.9800 |
| $\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~B})$ | 0.9800 |
| $\mathrm{C}(16)-\mathrm{H}(16 \mathrm{C})$ | 0.9800 |
| $\mathrm{O}(1)-\mathrm{Co}(1)-\mathrm{O}(3)$ | 116.69(8) |
| $\mathrm{O}(1)-\mathrm{Co}(1)-\mathrm{N}(1)$ | 94.87(9) |
| $\mathrm{O}(3)-\mathrm{Co}(1)-\mathrm{N}(1)$ | 113.29(9) |
| $\mathrm{O}(1)-\mathrm{Co}(1)-\mathrm{N}(2)$ | 112.19(9) |
| $\mathrm{O}(3)-\mathrm{Co}(1)-\mathrm{N}(2)$ | 94.78(9) |
| $\mathrm{N}(1)-\mathrm{Co}(1)-\mathrm{N}(2)$ | 126.71(9) |
| $\mathrm{C}(1)-\mathrm{O}(1)-\mathrm{Co}(1)$ | 123.83(18) |
| $\mathrm{C}(3)-\mathrm{O}(2)-\mathrm{C}(4)$ | 106.8(2) |
| $\mathrm{C}(9)-\mathrm{O}(3)-\mathrm{Co}(1)$ | 123.78(18) |
| $\mathrm{C}(11)-\mathrm{O}(4)-\mathrm{C}(12)$ | 106.3(2) |
| $\mathrm{C}(3)-\mathrm{N}(1)-\mathrm{C}(5)$ | 108.3(2) |
| $\mathrm{C}(3)-\mathrm{N}(1)-\mathrm{Co}(1)$ | 121.86(19) |
| $\mathrm{C}(5)-\mathrm{N}(1)-\mathrm{Co}(1)$ | 129.84(18) |
| $\mathrm{C}(11)-\mathrm{N}(2)-\mathrm{C}(13)$ | 107.7(2) |
| $\mathrm{C}(11)-\mathrm{N}(2)-\mathrm{Co}(1)$ | 122.36(19) |
| $\mathrm{C}(13)-\mathrm{N}(2)-\mathrm{Co}(1)$ | 129.33(18) |
| $\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(2)$ | 128.7(3) |
| $\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(6)$ | 112.2(2) |
| $\mathrm{C}(2)-\mathrm{C}(1)-\mathrm{C}(6)$ | 119.1(3) |


| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)$ | 122.5(3) |
| :---: | :---: |
| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{H}(2 \mathrm{~A})$ | 118.8 |
| $\mathrm{C}(3)-\mathrm{C}(2)-\mathrm{H}(2 \mathrm{~A})$ | 118.8 |
| $\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{O}(2)$ | 115.6(3) |
| $\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{C}(2)$ | 127.8(3) |
| $\mathrm{O}(2)-\mathrm{C}(3)-\mathrm{C}(2)$ | 116.6(2) |
| $\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{C}(5)$ | 104.5(2) |
| $\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~A})$ | 110.8 |
| $\mathrm{C}(5)-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~A})$ | 110.8 |
| $\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~B})$ | 110.8 |
| $\mathrm{C}(5)-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~B})$ | 110.8 |
| $\mathrm{H}(4 \mathrm{~A})-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~B})$ | 108.9 |
| $\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(7)$ | 108.9(2) |
| $\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(4)$ | 102.2(2) |
| $\mathrm{C}(7)-\mathrm{C}(5)-\mathrm{C}(4)$ | 112.2(3) |
| $\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(8)$ | 110.5(2) |
| $\mathrm{C}(7)-\mathrm{C}(5)-\mathrm{C}(8)$ | 111.0(3) |
| $\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{C}(8)$ | 111.7(3) |
| $\mathrm{F}(2)-\mathrm{C}(6)-\mathrm{F}(3)$ | 106.7(2) |
| $\mathrm{F}(2)-\mathrm{C}(6)-\mathrm{F}(1)$ | 107.6(3) |
| $\mathrm{F}(3)-\mathrm{C}(6)-\mathrm{F}(1)$ | 106.1(2) |
| $\mathrm{F}(2)-\mathrm{C}(6)-\mathrm{C}(1)$ | 110.8(2) |
| $\mathrm{F}(3)-\mathrm{C}(6)-\mathrm{C}(1)$ | 114.4(2) |
| $\mathrm{F}(1)-\mathrm{C}(6)-\mathrm{C}(1)$ | 111.0(2) |
| $\mathrm{C}(5)-\mathrm{C}(7)-\mathrm{H}(7 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(5)-\mathrm{C}(7)-\mathrm{H}(7 \mathrm{~B})$ | 109.5 |
| $\mathrm{H}(7 \mathrm{~A})-\mathrm{C}(7)-\mathrm{H}(7 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(5)-\mathrm{C}(7)-\mathrm{H}(7 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(7 \mathrm{~A})-\mathrm{C}(7)-\mathrm{H}(7 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(7 \mathrm{~B})-\mathrm{C}(7)-\mathrm{H}(7 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(5)-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(5)-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~B})$ | 109.5 |
| $\mathrm{H}(8 \mathrm{~A})-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(5)-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(8 \mathrm{~A})-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(8 \mathrm{~B})-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{C})$ | 109.5 |


| $\mathrm{O}(3)-\mathrm{C}(9)-\mathrm{C}(10)$ | 128.6(3) |
| :---: | :---: |
| $\mathrm{O}(3)-\mathrm{C}(9)-\mathrm{C}(14)$ | 113.2(3) |
| $\mathrm{C}(10)-\mathrm{C}(9)-\mathrm{C}(14)$ | 118.3(3) |
| $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(11)$ | 123.3(3) |
| $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{H}(10 \mathrm{~A})$ | 118.4 |
| $\mathrm{C}(11)-\mathrm{C}(10)-\mathrm{H}(10 \mathrm{~A})$ | 118.4 |
| $\mathrm{N}(2)-\mathrm{C}(11)-\mathrm{O}(4)$ | 116.4(3) |
| $\mathrm{N}(2)-\mathrm{C}(11)-\mathrm{C}(10)$ | 127.0(3) |
| $\mathrm{O}(4)-\mathrm{C}(11)-\mathrm{C}(10)$ | 116.6(2) |
| $\mathrm{O}(4)-\mathrm{C}(12)-\mathrm{C}(13)$ | 104.6(2) |
| $\mathrm{O}(4)-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~A})$ | 110.8 |
| $\mathrm{C}(13)-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~A})$ | 110.8 |
| $\mathrm{O}(4)-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~B})$ | 110.8 |
| $\mathrm{C}(13)-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~B})$ | 110.8 |
| $\mathrm{H}(12 \mathrm{~A})-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~B})$ | 108.9 |
| $\mathrm{N}(2)-\mathrm{C}(13)-\mathrm{C}(15)$ | 110.0(2) |
| $\mathrm{N}(2)-\mathrm{C}(13)-\mathrm{C}(12)$ | 101.5(2) |
| $\mathrm{C}(15)-\mathrm{C}(13)-\mathrm{C}(12)$ | 112.8(2) |
| $\mathrm{N}(2)-\mathrm{C}(13)-\mathrm{C}(16)$ | 108.6(2) |
| $\mathrm{C}(15)-\mathrm{C}(13)-\mathrm{C}(16)$ | 111.7(3) |
| $\mathrm{C}(12)-\mathrm{C}(13)-\mathrm{C}(16)$ | 111.7(3) |
| $\mathrm{F}(4)-\mathrm{C}(14)-\mathrm{F}(6)$ | 106.3(3) |
| $\mathrm{F}(4)-\mathrm{C}(14)-\mathrm{F}(5)$ | 105.4(3) |
| $\mathrm{F}(6)-\mathrm{C}(14)-\mathrm{F}(5)$ | 105.0(3) |
| $\mathrm{F}(4)-\mathrm{C}(14)-\mathrm{C}(9)$ | 111.7(3) |
| $\mathrm{F}(6)-\mathrm{C}(14)-\mathrm{C}(9)$ | 113.0(3) |
| $\mathrm{F}(5)-\mathrm{C}(14)-\mathrm{C}(9)$ | 114.7(3) |
| $\mathrm{C}(13)-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(13)-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~B})$ | 109.5 |
| $\mathrm{H}(15 \mathrm{~A})-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(13)-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(15 \mathrm{~A})-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(15 \mathrm{~B})-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(13)-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(13)-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~B})$ | 109.5 |
| $\mathrm{H}(16 \mathrm{~A})-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~B})$ | 109.5 |


| $\mathrm{C}(13)-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{C})$ | 109.5 |
| :--- | :--- |
| $\mathrm{H}(16 \mathrm{~A})-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(16 \mathrm{~B})-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{C})$ | 109.5 |

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for d1867_a. The anisotropic displacement factor exponent takes the form: $-2 p^{2}\left[h^{2} a^{* 2} U^{11}+\ldots+2 h k a^{*} b^{*} U^{12}\right]$

|  | $\mathrm{U}^{11}$ | $\mathrm{U}^{22}$ | $\mathrm{U}^{33}$ | $\mathrm{U}^{23}$ | $\mathrm{U}^{13}$ | $\mathrm{U}^{12}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{Co}(1)$ | 19(1) | 25(1) | 15(1) | 2(1) | -1(1) | 1(1) |
| $\mathrm{F}(1)$ | 88(2) | 36(1) | 52(1) | -11(1) | 16(1) | -16(1) |
| F(2) | 31(1) | 54(1) | 94(2) | 29(1) | -7(1) | -14(1) |
| F(3) | 60(1) | 39(1) | 40(1) | 20(1) | 2(1) | -5(1) |
| F(4) | 82(2) | 31(1) | 216(4) | -13(2) | -59(2) | 10(1) |
| $F(5)$ | 124(2) | 127(2) | 47(1) | 40(2) | 8(1) | 78(2) |
| F(6) | 41(1) | 76(2) | 98(2) | 45(1) | 15(1) | 28(1) |
| $\mathrm{O}(1)$ | 32(1) | 36(1) | 23(1) | 9(1) | -8(1) | -10(1) |
| $\mathrm{O}(2)$ | 60(1) | 39(1) | 24(1) | -1(1) | -16(1) | -7(1) |
| $\mathrm{O}(3)$ | 28(1) | 39(1) | 21(1) | 8(1) | 1(1) | 8(1) |
| $\mathrm{O}(4)$ | 39(1) | 49(1) | 20(1) | -4(1) | 6(1) | 3(1) |
| N(1) | 22(1) | 26(1) | 22(1) | $0(1)$ | $0(1)$ | $0(1)$ |
| N(2) | 24(1) | 27(1) | 22(1) | -2(1) | $0(1)$ | -1(1) |
| C(1) | 21(1) | 29(2) | 27(2) | 4(1) | 2(1) | 2(1) |
| C(2) | 35(2) | 27(2) | 21(1) | 7(1) | -1(1) | 3(1) |
| C(3) | 26(1) | 32(2) | 19(1) | -2(1) | -4(1) | 5(1) |
| C(4) | 64(2) | 43(2) | 38(2) | -5(2) | -12(2) | -11(2) |
| C(5) | 22(1) | 27(2) | 30(2) | -6(1) | -3(1) | -2(1) |
| C(6) | 34(2) | 31(2) | 33(2) | 3(2) | 1(1) | -3(1) |
| C(7) | 23(2) | 52(2) | 81(3) | -23(2) | 3(2) | -9(2) |
| C(8) | 32(2) | 31(2) | 66(2) | 2(2) | -6(2) | 1(1) |
| C(9) | 25(1) | 28(2) | 25(2) | 6(1) | -5(1) | -4(1) |
| C(10) | 37(2) | 34(2) | 20(1) | 8(1) | -1(1) | -5(1) |
| C(11) | 30(2) | 33(2) | 16(1) | -3(1) | 3(1) | -8(1) |
| C(12) | 35(2) | 41(2) | 33(2) | -11(2) | 6(1) | $0(2)$ |
| C(13) | 25(1) | 30(2) | 27(2) | -6(1) | 4(1) | 3(1) |
| C(14) | 38(2) | 33(2) | 34(2) | 12(1) | -5(1) | 2(1) |
| C(15) | 40(2) | 58(2) | 41(2) | -9(2) | -4(2) | 22(2) |
| C(16) | 53(2) | 30(2) | 56(2) | -6(2) | 12(2) | -1(2) |

Table 5. Hydrogen coordinates ( $\times 10^{4}$ ) and isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for d1867_a.

|  | x | y | z | $\mathrm{U}(\mathrm{eq})$ |
| :---: | :---: | :---: | :---: | :---: |
| H(2A) | 3836 | 2344 | 8241 | 33 |
| H(4A) | 6145 | 4357 | 8343 | 58 |
| H(4B) | 4812 | 4658 | 8366 | 58 |
| H(7A) | 6888 | 3758 | 7235 | 78 |
| H(7B) | 7029 | 4631 | 7156 | 78 |
| H(7C) | 6466 | 4160 | 6528 | 78 |
| H(8A) | 4708 | 5012 | 6575 | 64 |
| H(8B) | 5241 | 5446 | 7237 | 64 |
| H(8C) | 3966 | 5075 | 7290 | 64 |
| H(10A) | 3669 | 4357 | 4253 | 36 |
| H(12A) | 6747 | 2988 | 4499 | 44 |
| H(12B) | 5968 | 2335 | 4164 | 44 |
| H(15A) | 6937 | 2994 | 5752 | 69 |
| H(15B) | 7056 | 2127 | 5624 | 69 |
| H(15C) | 6185 | 2432 | 6219 | 69 |
| H(16A) | 4456 | 1762 | 5670 | 69 |
| H(16B) | 5327 | 1430 | 5088 | 69 |
| H(16C) | 4185 | 1882 | 4849 | 69 |

Table 6. Torsion angles [ ${ }^{\circ}$ ] for d1867_a.

| $\mathrm{Co}(1)-\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(2)$ | 6.3(4) |
| :---: | :---: |
| $\mathrm{Co}(1)-\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(6)$ | -175.66(17) |
| $\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)$ | 0.5(5) |
| $\mathrm{C}(6)-\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)$ | -177.4(3) |
| $\mathrm{C}(5)-\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{O}(2)$ | 2.9(3) |
| $\mathrm{Co}(1)-\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{O}(2)$ | -177.28(18) |
| $\mathrm{C}(5)-\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{C}(2)$ | -177.7(3) |
| $\mathrm{Co}(1)-\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{C}(2)$ | 2.2(4) |
| $\mathrm{C}(4)-\mathrm{O}(2)-\mathrm{C}(3)-\mathrm{N}(1)$ | 7.9(3) |
| $\mathrm{C}(4)-\mathrm{O}(2)-\mathrm{C}(3)-\mathrm{C}(2)$ | -171.6(3) |
| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)-\mathrm{N}(1)$ | -5.3(5) |
| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)-\mathrm{O}(2)$ | 174.2(3) |
| $\mathrm{C}(3)-\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{C}(5)$ | -14.6(3) |
| $\mathrm{C}(3)-\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(7)$ | 107.2(3) |
| $\mathrm{Co}(1)-\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(7)$ | -72.6(3) |
| $\mathrm{C}(3)-\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(4)$ | -11.6(3) |
| $\mathrm{Co}(1)-\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(4)$ | 168.6(2) |
| $\mathrm{C}(3)-\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(8)$ | -130.7(3) |
| $\mathrm{Co}(1)-\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(8)$ | 49.5(3) |
| $\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{N}(1)$ | 15.6(3) |
| $\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{C}(7)$ | -100.9(3) |
| $\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{C}(8)$ | 133.7(3) |
| $\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(6)-\mathrm{F}(2)$ | -61.9(3) |
| $\mathrm{C}(2)-\mathrm{C}(1)-\mathrm{C}(6)-\mathrm{F}(2)$ | 116.4(3) |
| $\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(6)-\mathrm{F}(3)$ | 177.5(2) |
| $\mathrm{C}(2)-\mathrm{C}(1)-\mathrm{C}(6)-\mathrm{F}(3)$ | -4.2(4) |
| $\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(6)-\mathrm{F}(1)$ | 57.6(3) |
| $\mathrm{C}(2)-\mathrm{C}(1)-\mathrm{C}(6)-\mathrm{F}(1)$ | -124.2(3) |
| $\mathrm{Co}(1)-\mathrm{O}(3)-\mathrm{C}(9)-\mathrm{C}(10)$ | 4.7(4) |
| $\mathrm{Co}(1)-\mathrm{O}(3)-\mathrm{C}(9)-\mathrm{C}(14)$ | -174.11(18) |
| $\mathrm{O}(3)-\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(11)$ | -1.0(5) |
| $\mathrm{C}(14)-\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(11)$ | 177.8(3) |
| $\mathrm{C}(13)-\mathrm{N}(2)-\mathrm{C}(11)-\mathrm{O}(4)$ | -4.7(3) |
| $\mathrm{Co}(1)-\mathrm{N}(2)-\mathrm{C}(11)-\mathrm{O}(4)$ | -176.49(18) |


| $\mathrm{C}(13)-\mathrm{N}(2)-\mathrm{C}(11)-\mathrm{C}(10)$ | $174.7(3)$ |
| :--- | :---: |
| $\mathrm{Co}(1)-\mathrm{N}(2)-\mathrm{C}(11)-\mathrm{C}(10)$ | $2.9(4)$ |
| $\mathrm{C}(12)-\mathrm{O}(4)-\mathrm{C}(11)-\mathrm{N}(2)$ | $-7.9(3)$ |
| $\mathrm{C}(12)-\mathrm{O}(4)-\mathrm{C}(11)-\mathrm{C}(10)$ | $172.7(2)$ |
| $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(11)-\mathrm{N}(2)$ | $-3.4(5)$ |
| $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(11)-\mathrm{O}(4)$ | $176.0(3)$ |
| $\mathrm{C}(11)-\mathrm{O}(4)-\mathrm{C}(12)-\mathrm{C}(13)$ | $16.4(3)$ |
| $\mathrm{C}(11)-\mathrm{N}(2)-\mathrm{C}(13)-\mathrm{C}(15)$ | $133.9(3)$ |
| $\mathrm{Co}(1)-\mathrm{N}(2)-\mathrm{C}(13)-\mathrm{C}(15)$ | $-55.0(3)$ |
| $\mathrm{C}(11)-\mathrm{N}(2)-\mathrm{C}(13)-\mathrm{C}(12)$ | $14.3(3)$ |
| $\mathrm{Co}(1)-\mathrm{N}(2)-\mathrm{C}(13)-\mathrm{C}(12)$ | $-174.70(18)$ |
| $\mathrm{C}(11)-\mathrm{N}(2)-\mathrm{C}(13)-\mathrm{C}(16)$ | $-103.6(3)$ |
| $\mathrm{Co}(1)-\mathrm{N}(2)-\mathrm{C}(13)-\mathrm{C}(16)$ | $67.5(3)$ |
| $\mathrm{O}(4)-\mathrm{C}(12)-\mathrm{C}(13)-\mathrm{N}(2)$ | $-18.2(3)$ |
| $\mathrm{O}(4)-\mathrm{C}(12)-\mathrm{C}(13)-\mathrm{C}(15)$ | $-135.8(3)$ |
| $\mathrm{O}(4)-\mathrm{C}(12)-\mathrm{C}(13)-\mathrm{C}(16)$ | $97.4(3)$ |
| $\mathrm{O}(3)-\mathrm{C}(9)-\mathrm{C}(14)-\mathrm{F}(4)$ | $78.0(4)$ |
| $\mathrm{C}(10)-\mathrm{C}(9)-\mathrm{C}(14)-\mathrm{F}(4)$ | $-101.0(4)$ |
| $\mathrm{O}(3)-\mathrm{C}(9)-\mathrm{C}(14)-\mathrm{F}(6)$ | $-41.9(4)$ |
| $\mathrm{C}(10)-\mathrm{C}(9)-\mathrm{C}(14)-\mathrm{F}(6)$ | $139.1(3)$ |
| $\mathrm{O}(3)-\mathrm{C}(9)-\mathrm{C}(14)-\mathrm{F}(5)$ | $-162.2(3)$ |
| $\mathrm{C}(10)-\mathrm{C}(9)-\mathrm{C}(14)-\mathrm{F}(5)$ | $18.8(4)$ |
|  |  |

Symmetry transformations used to generate equivalent atoms:


F6: Crystal data and structure refinement for d1889a_a (91).

| Identification code | d1889a_a (91) |
| :---: | :---: |
| Empirical formula | C16 H18 Co Cl6 N2 O4 |
| Formula weight | 573.95 |
| Temperature | 150(2) K |
| Wavelength | $0.71073 \AA$ |
| Crystal system | Orthorhombic |
| Space group | Pna21 |
| Unit cell dimensions | $a=32.2380(14) \AA \quad a=90^{\circ}$. |
|  | $\mathrm{b}=8.4769(4) \AA \quad \mathrm{b}=90^{\circ}$. |
|  | $\mathrm{c}=8.3149(3) \AA \quad \mathrm{g}=90^{\circ}$. |
| Volume | 2272.28(17) $\AA^{3}$ |
| Z | 4 |
| Density (calculated) | $1.678 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $1.486 \mathrm{~mm}^{-1}$ |
| F(000) | 1156 |
| Crystal size | $0.21 \times 0.060 \times 0.020 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 2.484 to $27.551^{\circ}$. |
| Index ranges | $-30<=\mathrm{h}<=41,-10<=\mathrm{k}<=11,-7<=\mathrm{l}<=10$ |
| Reflections collected | 11915 |
| Independent reflections | $4617[\mathrm{R}(\mathrm{int})=0.0419]$ |
| Completeness to theta $=25.242^{\circ}$ | 99.8 \% |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.7456 and 0.6777 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
|  | 418 |

Data / restraints / parameters
Goodness-of-fit on $\mathrm{F}^{2}$
Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ]
R indices (all data)
Extinction coefficient
Largest diff. peak and hole

4617 / 1 / 266
1.021
$\mathrm{R} 1=0.0378, \mathrm{wR} 2=0.0677$
$R 1=0.0532, w R 2=0.0716$
n/a
0.445 and $-0.482 \mathrm{e} . \AA^{-3}$

Table 2. Atomic coordinates ( $\times 10^{4}$ ) and equivalent isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for $\mathrm{d} 1867 \_\mathrm{a}$. $\mathrm{U}(\mathrm{eq})$ is defined as one third of the trace of the orthogonalized $\mathrm{U}^{\mathrm{ij}}$ tensor.

|  | X | y | Z | U(eq) |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{Co}(1)$ | 6271(1) | 5501(1) | 4559(1) | 20(1) |
| $\mathrm{Cl}(1)$ | 5248(1) | 7932(2) | 1365(2) | 58(1) |
| $\mathrm{Cl}(2)$ | 4752(1) | 5513(2) | 3129(3) | 69(1) |
| $\mathrm{Cl}(3)$ | 7709(1) | 8768(2) | 4032(2) | 51(1) |
| $\mathrm{Cl}(4)$ | 7791(1) | 5629(2) | 786(2) | 34(1) |
| $\mathrm{Cl}(5)$ | 7309(1) | 6452(2) | 4142(1) | 32(1) |
| $\mathrm{Cl}(6)$ | 5759() | 8400(2) | 1987(2) | 33(1) |
| O(1) | 5759(1) | 6270(4) | 3612(4) | 27(1) |
| $\mathrm{O}(2)$ | 5812(1) | 7957(5) | 8414(4) | 36(1) |
| O(3) | 6785(1) | 6312(4) | 3684(4) | 27(1) |
| $\mathrm{O}(4)$ | 6726(1) | 1408(4) | 2606(4) | 25(1) |
| N(1) | 6156(1) | 6409(5) | 6684(4) | 19(1) |
| N(2) | 6381(1) | 3309(5) | 3909(5) | 20(1) |
| C(1) | 5482(1) | 7066(5) | 4342(6) | 18(1) |
| C(2) | 5496(1) | 7615(6) | 5890(6) | 21(1) |
| C(3) | 5834(2) | 7276(6) | 6943(5) | 20(1) |
| C(4) | 6188(2) | 7519(10) | 9241(7) | 72(3) |
| C(5) | 6415(2) | 6373(6) | 8169(6) | 24(1) |
| C(6) | 5097(1) | 7336(6) | 3311(6) | 25(1) |
| C(7) | 6849(2) | 6919(11) | 7773(8) | 70(3) |
| C(8) | 6413(3) | 4755(9) | 8849(9) | 84(3) |
| C(9) | 7058(1) | 5481(5) | 2954(5) | 17(1) |
| C(10) | 7044(1) | 3920(6) | 2632(6) | 19(1) |
| C(11) | 6708(1) | 2925(5) | 3091(5) | 18(1) |
| $\mathrm{C}(12)$ | 6368(2) | 616(7) | 3258(8) | 40(1) |
| C(13) | 6103(1) | 1909(6) | 4066(6) | 26(1) |
| C(14) | 7444(1) | 6444(6) | 2458(6) | 21(1) |
| C(15) | 5703(1) | 2218(8) | 3182(10) | 64(2) |
| C(16) | 6030(1) | 1559(8) | 5811(8) | 55(2) |

Table 3. Bond lengths [ $\AA$ ] and angles [ ${ }^{\circ}$ ] for d1867_a.

| $\mathrm{Co}(1)-\mathrm{O}(3)$ | 1.936(3) |
| :---: | :---: |
| $\mathrm{Co}(1)-\mathrm{O}(1)$ | 1.940(3) |
| $\mathrm{Co}(1)-\mathrm{N}(1)$ | 1.963(4) |
| $\mathrm{Co}(1)-\mathrm{N}(2)$ | 1.968(4) |
| $\mathrm{Cl}(1)-\mathrm{C}(6)$ | 1.764(5) |
| $\mathrm{Cl}(2)-\mathrm{C}(6)$ | $1.767(5)$ |
| $\mathrm{Cl}(3)-\mathrm{C}(6)$ | 1.752(5) |
| C;(4)-C(14) | $1.772(5)$ |
| $\mathrm{Cl}(5)-\mathrm{C}(14)$ | 1.791(5) |
| $\mathrm{Cl}(6)-\mathrm{C}(14)$ | 1.758(5) |
| $\mathrm{O}(1)-\mathrm{C}(1)$ | 1.274(5) |
| $\mathrm{O}(2)-\mathrm{C}(3)$ | 1.354(6) |
| $\mathrm{O}(2)-\mathrm{C}(4)$ | 1.443 (6) |
| $\mathrm{O}(3)-\mathrm{C}(9)$ | 1.280(5) |
| $\mathrm{O}(4)-\mathrm{C}(11)$ | 1.349(5) |
| $\mathrm{O}(4)-\mathrm{C}(12)$ | 1.441(6) |
| $\mathrm{N}(1)-\mathrm{C}(3)$ | 1.290(6) |
| $\mathrm{N}(1)-\mathrm{C}(5)$ | 1.490(6) |
| $\mathrm{N}(2)-\mathrm{C}(11)$ | 1.294(6) |
| $\mathrm{N}(2)-\mathrm{C}(13)$ | 1.493(6) |
| $\mathrm{C}(1)-\mathrm{C}(2)$ | 1.370(6) |
| $\mathrm{C}(1)-\mathrm{C}(6)$ | 1.526(6) |
| $\mathrm{C}(2)-\mathrm{C}(3)$ | 1.427(6) |
| $\mathrm{C}(2)-\mathrm{H}(2 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(4)-\mathrm{C}(5)$ | 1.508(7) |
| $\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~A})$ | 0.9900 |
| $\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~B})$ | 0.9900 |
| $\mathrm{C}(5)-\mathrm{C}(7)$ | 1.483(8) |
| $\mathrm{C}(5)-\mathrm{C}(8)$ | 1.510(8) |
| $\mathrm{C}(7)-\mathrm{H}(7 \mathrm{~A})$ | 0.9800 |
| $\mathrm{C}(7)-\mathrm{H}(7 \mathrm{~B})$ | 0.9800 |
| $\mathrm{C}(7)-\mathrm{H}(7 \mathrm{C})$ | 0.9800 |
| $\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~A})$ | 0.9800 |
| $\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~B})$ | 0.9800 |


| $\mathrm{C}(8)-\mathrm{H}(8 \mathrm{C})$ | 0.9800 |
| :---: | :---: |
| $\mathrm{C}(9)-\mathrm{C}(10)$ | 1.351(6) |
| $\mathrm{C}(9)-\mathrm{C}(14)$ | 1.546(6) |
| $\mathrm{C}(10)-\mathrm{C}(11)$ | 1.427(6) |
| $\mathrm{C}(10)-\mathrm{H}(10 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(12)-\mathrm{C}(13)$ | 1.542(7) |
| $\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~A})$ | 0.9900 |
| $\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~B})$ | 0.9900 |
| $\mathrm{C}(13)-\mathrm{C}(15)$ | 1.508(8) |
| $\mathrm{C}(13)-\mathrm{C}(16)$ | $1.500(8)$ |
| $\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~A})$ | 0.9800 |
| $\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~B})$ | 0.9800 |
| $\mathrm{C}(15)-\mathrm{H}(15 \mathrm{C})$ | 0.9800 |
| $\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~A})$ | 0.9800 |
| $\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~B})$ | 0.9800 |
| $\mathrm{C}(16)-\mathrm{H}(16 \mathrm{C})$ | 0.9800 |
| $\mathrm{O}(1)-\mathrm{Co}(1)-\mathrm{O}(3)$ | 117.13(15) |
| $\mathrm{O}(3)-\mathrm{Co}(1)-\mathrm{N}(1)$ | 111.12(15) |
| $\mathrm{O}(1)-\mathrm{Co}(1)-\mathrm{N}(1)$ | 94.21(14) |
| $\mathrm{O}(3)-\mathrm{Co}(1)-\mathrm{N}(2)$ | 94.42(15) |
| $\mathrm{O}(1)-\mathrm{Co}(1)-\mathrm{N}(2)$ | 111.09(15) |
| $\mathrm{N}(1)-\mathrm{Co}(1)-\mathrm{N}(2)$ | 130.67(17) |
| $\mathrm{C}(1)-\mathrm{O}(1)-\mathrm{Co}(1)$ | 125.6(3) |
| $\mathrm{C}(3)-\mathrm{O}(2)-\mathrm{C}(4)$ | 160.0(4) |
| $\mathrm{C}(9)-\mathrm{O}(3)-\mathrm{Co}(1)$ | 124.8(3) |
| $\mathrm{C}(11)-\mathrm{O}(4)-\mathrm{C}(12)$ | 107.3(4) |
| $\mathrm{C}(3)-\mathrm{N}(1)-\mathrm{C}(5)$ | 108.9(4) |
| $\mathrm{C}(3)-\mathrm{N}(1)-\mathrm{Co}(1)$ | 121.7(3) |
| $\mathrm{C}(5)-\mathrm{N}(1)-\mathrm{Co}(1)$ | 129.2(3) |
| $\mathrm{C}(11)-\mathrm{N}(2)-\mathrm{C}(13)$ | 109.5(4) |
| $\mathrm{C}(11)-\mathrm{N}(2)-\mathrm{Co}(1)$ | 121.9(3) |
| $\mathrm{C}(13)-\mathrm{N}(2)-\mathrm{Co}(1)$ | 1128.2(3) |
| $\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(2)$ | 127.1(4) |
| $\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(6)$ | 112.5(4) |
| $\mathrm{C}(2)-\mathrm{C}(1)-\mathrm{C}(6)$ | 120.3(4) |


| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)$ | 122.3(4) |
| :---: | :---: |
| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{H}(2 \mathrm{~A})$ | 118.8 |
| $\mathrm{C}(3)-\mathrm{C}(2)-\mathrm{H}(2 \mathrm{~A})$ | 118.8 |
| $\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{O}(2)$ | 115.8(4) |
| $\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{C}(2)$ | 128.8(4) |
| $\mathrm{O}(2)-\mathrm{C}(3)-\mathrm{C}(2)$ | 115.3(4) |
| $\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{C}(5)$ | 107.0(4) |
| $\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~A})$ | 110.3 |
| $\mathrm{C}(5)-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~A})$ | 110.3 |
| $\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~B})$ | 110.3 |
| $\mathrm{C}(5)-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~B})$ | 110.3 |
| $\mathrm{H}(4 \mathrm{~A})-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~B})$ | 108.6 |
| $\mathrm{C}(8)-\mathrm{C}(5)-\mathrm{N}(1)$ | 109.4( |
| $\mathrm{C}(8)-\mathrm{C}(5)-\mathrm{C}(4)$ | 111.7(6) |
| $\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(4)$ | 101.8(4) |
| $\mathrm{C}(8)-\mathrm{C}(5)-\mathrm{C}(7)$ | 111.7(6) |
| $\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(7)$ | 109.3(4) |
| $\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{C}(7)$ | 112.4(6) |
| $\mathrm{C}(1)-\mathrm{C}(6)-\mathrm{Cl}(3)$ | 115.3(3) |
| $\mathrm{C}(1)-\mathrm{C}(6)-\mathrm{Cl}(1)$ | 109.4(3) |
| $\mathrm{Cl}(1)-\mathrm{C}(6)-\mathrm{Cl}(3)$ | 106.9(3) |
| $\mathrm{Cl}(2)-\mathrm{C}(6)-\mathrm{C}(1)$ | 107.8(3) |
| $\mathrm{Cl}(3)-\mathrm{C}(6)-\mathrm{C}(2)$ | 109.5(3) |
| $\mathrm{Cl}(1)-\mathrm{C}(6)-\mathrm{Cl}(2)$ | 107.7(3) |
| $\mathrm{C}(5)-\mathrm{C}(7)-\mathrm{H}(7 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(5)-\mathrm{C}(7)-\mathrm{H}(7 \mathrm{~B})$ | 109.5 |
| $\mathrm{H}(7 \mathrm{~A})-\mathrm{C}(7)-\mathrm{H}(7 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(5)-\mathrm{C}(7)-\mathrm{H}(7 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(7 \mathrm{~A})-\mathrm{C}(7)-\mathrm{H}(7 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(7 \mathrm{~B})-\mathrm{C}(7)-\mathrm{H}(7 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(5)-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(5)-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~B})$ | 109.5 |
| $\mathrm{H}(8 \mathrm{~A})-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(5)-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(8 \mathrm{~A})-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(8 \mathrm{~B})-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{C})$ | 109.5 |


| $\mathrm{O}(3)-\mathrm{C}(9)-\mathrm{C}(10)$ | 127.7(4) |
| :---: | :---: |
| $\mathrm{O}(3)-\mathrm{C}(9)-\mathrm{C}(14)$ | 112.9(4) |
| $\mathrm{C}(10)-\mathrm{C}(9)-\mathrm{C}(14)$ | 119.3(4) |
| $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(11)$ | 123.4(4) |
| $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{H}(10 \mathrm{~A})$ | 118.3 |
| $\mathrm{C}(11)-\mathrm{C}(10)-\mathrm{H}(10 \mathrm{~A})$ | 118.3 |
| $\mathrm{N}(2)-\mathrm{C}(11)-\mathrm{O}(4)$ | 115.6(4) |
| $\mathrm{N}(2)-\mathrm{C}(11)-\mathrm{C}(10)$ | 127.6(4) |
| $\mathrm{O}(4)-\mathrm{C}(11)-\mathrm{C}(10)$ | 116.8(4) |
| $\mathrm{O}(4)-\mathrm{C}(12)-\mathrm{C}(13)$ | 106.0(4) |
| $\mathrm{O}(4)-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~A})$ | 110.5 |
| $\mathrm{C}(13)-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~A})$ | 110.5 |
| $\mathrm{O}(4)-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~B})$ | 110.5 |
| $\mathrm{C}(13)-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~B})$ | 110.5 |
| $\mathrm{H}(12 \mathrm{~A})-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~B})$ | 108.7 |
| $\mathrm{N}(2)-\mathrm{C}(13)-\mathrm{C}(16)$ | 109.4(4) |
| $\mathrm{N}(2)-\mathrm{C}(13)-\mathrm{C}(15)$ | 109.4(4) |
| $\mathrm{C}(16)-\mathrm{C}(13)-\mathrm{C}(15)$ | 111.8(5) |
| $\mathrm{C}(12)-\mathrm{C}(13)-\mathrm{C}(16)$ | 101.2(4) |
| $\mathrm{C}(15)-\mathrm{C}(13)-\mathrm{C}(12)$ | 111.6(5) |
| $\mathrm{C}(9)-\mathrm{C}(14)-\mathrm{Cl}(6)$ | 112.6(5) |
| $\mathrm{C}(9)-\mathrm{C}(14)-\mathrm{Cl}(4)$ | 111.0(3) |
| $\mathrm{Cl}(6)-\mathrm{C}(14)-\mathrm{Cl}(4)$ | 108.2(3) |
| $\mathrm{C}(9)-\mathrm{C}(14)-\mathrm{Cl}(5)$ | 107.2(3) |
| $\mathrm{Cl}(6)-\mathrm{C}(14)-\mathrm{Cl}(5)$ | 108.9(3) |
| $\mathrm{Cl}(4)-\mathrm{C}(14)-\mathrm{Cl}(5)$ | 108.3(3) |
| $\mathrm{C}(13)-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(13)-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~B})$ | 109.5 |
| $\mathrm{H}(15 \mathrm{~A})-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(13)-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(15 \mathrm{~A})-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(15 \mathrm{~B})-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(13)-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(13)-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~B})$ | 109.5 |
| $\mathrm{H}(16 \mathrm{~A})-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(13)-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{C})$ | 109.5 |


| $H(16 A)-C(16)-H(16 C)$ | 109.5 |
| :--- | :--- |
| $H(16 B)-C(16)-H(16 C)$ | 109.5 |

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for d1867_a. The anisotropic displacement factor exponent takes the form: $-2 p^{2}\left[h^{2} a^{* 2} U^{11}+\ldots+2 h k a^{*} b^{*} U^{12}\right]$

|  | $\mathrm{U}^{11}$ | $\mathrm{U}^{22}$ | $\mathrm{U}^{33}$ | $\mathrm{U}^{23}$ | $\mathrm{U}^{13}$ | $\mathrm{U}^{12}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{Co}(1)$ | 16(1) | 19(1) | 24(1) | -5(1) | 2(1) | 2(1) |
| $\mathrm{Cl}(1)$ | 47(1) | 96(2) | 29(1) | 18(1) | -8(1) | $8(1)$ |
| $\mathrm{Cl}(2)$ | 40(1) | 32(1) | 135(2) | 8(1) | -41(1) | -13(1) |
| $\mathrm{Cl}(3)$ | 42(1) | 64(1) | 46(1) | -18(1) | -18(1) | 34(1) |
| $\mathrm{Cl}(4)$ | 34(1) | 37(1) | 31(1) | -5(1) | 15(1) | -5(1) |
| $\mathrm{Cl}(5)$ | 27(1) | 38(1) | 30(1) | 2(1) | -8(1) | -8(2) |
| $\mathrm{Cl}(6)$ | 38(1) | 22(1) | 38(1) | 8(1) | 3(1) | -1(1) |
| $\mathrm{O}(1)$ | 25(2) | 31(2) | 24(2) | -6(2) | -3(1) | 9(2) |
| $\mathrm{O}(2)$ | 34(2) | 55(3) | 19(2) | -10(2) | -4(2) | 21(2) |
| $\mathrm{O}(3)$ | 22(2) | 21(2) | 38(2) | -7(2) | 10(1) | -2(1) |
| $\mathrm{O}(4)$ | 26(2) | 14(2) | 36(2) | -9(2) | 6(2) | $0(1)$ |
| N(1) | 16(2) | 22(2) | 20(2) | -2(2) | -2(2) | 4(2) |
| N(2) | 15(2) | 15(2) | 29(2) | -3(2) | 4(2) | $0(2)$ |
| C(1) | 14(2) | 17(2) | 24(3) | 2(2) | 4(2) | $0(2)$ |
| C(2) | 20(2) | 21(3) | 23(3) | 0 (2) | 2(2) | 6 (2) |
| C(3) | 26(3) | 17(2) | 15(2) | 4(2) | 4(2) | 2(2) |
| C(4) | 57(4) | 125(7) | 34(4) | -33(4) | -24(3) | 61(4) |
| C(5) | 24(2) | 32(3) | 18(3) | -3(2) | -7(2) | 5(2) |
| C(6) | 24(3) | 21(3) | 31(3) | -2(2) | -2(2) | 3(2) |
| C(7) | 42(4) | 126(8) | 42(4) | -20(5) | -11(3) | -31(4) |
| C(8) | 129(7) | 45(5) | 78(6) | 26(4) | -78(5) | -10(4) |
| C(9) | 20(2) | 18(2) | 14(2) | -1(2) | -2(2) | $0(2)$ |
| $\mathrm{C}(10)$ | 18(2) | 19(2) | 19(3) | -3(2) | 5(2) | 1(2) |
| $\mathrm{C}(11)$ | 20(2) | 16(3) | 19(3) | -4(2) | -9(2) | 5(2) |
| $\mathrm{C}(12)$ | 36(3) | 25(3) | 60(4) | -16(3) | 13(3) | $0(2)$ |
| C(13) | 17(2) | 18(3) | 44(3) | -4(2) | 3(2) | 3(1) |
| $\mathrm{C}(14)$ | 20(2) | 22(3) | 22(3) | -3(2) | 5(2) | $0(2)$ |
| C(15) | 37(4) | 35(4) | 120(7) | -15(4) | -28(4) | -11(3) |
| C(16) | 76(5) | 33(4) | 58(4) | -4(3) | 26(4) | -25(3) |

Table 5. Hydrogen coordinates ( $\times 10^{4}$ ) and isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for d1867_a.

|  | x | y | z | U(eq) |
| :---: | :---: | :---: | :---: | :---: |
| H(2A) | 5274 | 8244 | 6277 | 25 |
| H(4A) | 6122 | 7020 | 10286 | 86 |
| H(4B) | 6362 | 8463 | 9443 | 86 |
| H(7A) | 7023 | 6854 | 8738 | 105 |
| H(7B) | 6840 | 8013 | 7393 | 105 |
| H(7C) | 6966 | 9244 | 6930 | 105 |
| H(8A) | 6576 | 4739 | 9845 | 126 |
| H(8B) | 6536 | 4022 | 8071 | 126 |
| H(8C) | 6127 | 4436 | 9081 | 126 |
| H(10A) | 7271 | 3461 | 2071 | 23 |
| H(12A) | 6452 | -188 | 4055 | 48 |
| H(12B) | 6209 | 91 | 2392 | 48 |
| H(15A) | 5522 | 1295 | 3274 | 96 |
| H(15B) | 5763 | 2422 | 2045 | 96 |
| H(15C) | 5565 | 3139 | 3651 | 96 |
| H(16A) | 5871 | 578 | 5913 | 83 |
| H(16B) | 5874 | 2428 | 6300 | 83 |
| H(16C) | 6297 | 1443 | 6361 | 83 |



F7: Crystal data and structure refinement for d1825_a (7g).

Identification code
Empirical formula
Formula weight
Temperature
Wavelength
Crystal system
Space group
Unit cell dimensions

Volume

Z

Density (calculated)
Absorption coefficient
F(000)
Crystal size
Theta range for data collection
Index ranges
Reflections collected
Independent reflections
Completeness to theta $=25.242 \infty$
Absorption correction
Max. and min. transmission
Refinement method
Data / restraints / parameters
d1825_a (7g)
C34 H32 Cu N2 O4
596.15

150(2) K
$0.71073 \approx$
Triclinic
P-1
$\mathrm{a}=5.6548(4) \approx \quad \alpha=86.961(2) \infty$.
$b=10.2976(8) \approx \quad \beta=83.937(2) \infty$.
$\mathrm{c}=12.5388(10) \approx \quad \gamma=79.616(2) \infty$.
713.74(9) $\approx^{3}$

1
$1.387 \mathrm{Mg} / \mathrm{m}^{3}$
$0.807 \mathrm{~mm}^{-1}$
311
$0.230 \times 0.200 \times 0.040 \mathrm{~mm}^{3}$
1.634 to $27.595 \infty$.
$-7<=\mathrm{h}<=7,-13<=\mathrm{k}<=13,-16<=1<=16$
21074
$3316[\mathrm{R}(\mathrm{int})=0.0263]$
100.0 \%

Semi-empirical from equivalents
0.7456 and 0.6988

Full-matrix least-squares on $\mathrm{F}^{2}$
3316 / 0 / 189

Goodness-of-fit on $\mathrm{F}^{2}$
Final R indices [I>2sigma(I)]
R indices (all data)
Extinction coefficient
Largest diff. peak and hole
1.070
$R 1=0.0266, w R 2=0.0648$
$R 1=0.0312, w R 2=0.0669$
n/a
0.350 and -0.260 e. $\approx^{-3}$

Table 2. Atomic coordinates ( $\times 10^{4}$ ) and equivalent isotropic displacement parameters $\left(\approx^{2} \times 10^{3}\right)$ for $\mathrm{d} 1825 \_$a. $\mathrm{U}(\mathrm{eq})$ is defined as one third of the trace of the orthogonalized $\mathrm{U}^{\mathrm{ij}}$ tensor.

|  | x | y | z | U(eq) |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{Cu}(1)$ | 5000 | 5000 | 5000 | 15(1) |
| $\mathrm{O}(1)$ | 3401(2) | 6165(1) | 6093(1) | 24(1) |
| $\mathrm{O}(2)$ | 7068(2) | 8552(1) | 3929(1) | 26(1) |
| N(1) | 6552(2) | 6439(1) | 4247(1) | 16(1) |
| C(1) | 8365(3) | 6416(1) | 3276(1) | 18(1) |
| C(2) | 9076(3) | 7778(2) | 3311(1) | 27(1) |
| C(3) | 5889(3) | 7668(1) | 4512(1) | 18(1) |
| C(4) | 4117(3) | 8218(1) | 5321(1) | 22(1) |
| C(5) | 3028(3) | 7445(1) | 6063(1) | 18(1) |
| C(6) | 1260(3) | 8096(1) | 6933(1) | 19(1) |
| C(7) | -790(3) | 8925(2) | 6661(1) | 24(1) |
| C(8) | -2554(3) | 9522(2) | 7455(1) | 29(1) |
| C(9) | -2220(3) | 9289(2) | 8512(1) | 31(1) |
| C(10) | -115(3) | 8457(2) | 8836(1) | 25(1) |
| C(11) | 275(4) | 8216(2) | 9932(1) | 37(1) |
| C(12) | 2320(4) | 7431(2) | 10224(1) | 40(1) |
| C(13) | 4105(3) | 6851(2) | 9441(1) | 34(1) |
| C(14) | 3802(3) | 7051(2) | 8373(1) | 25(1) |
| C(15) | 1662(3) | 7846(1) | 8039(1) | 21(1) |
| C(16) | 10577(3) | 5342(2) | 3347(2) | 32(1) |
| C(17) | 7101(3) | 6302(2) | 2281(1) | 27(1) |

Table 3. Bond lengths [ $\approx]$ and angles [ $\infty$ ] for d1825_a.

| $\mathrm{Cu}(1)-\mathrm{O}(1) \# 1$ | 1.9122(10) |
| :---: | :---: |
| $\mathrm{Cu}(1)-\mathrm{O}(1)$ | 1.9122(10) |
| $\mathrm{Cu}(1)-\mathrm{N}(1)$ | 2.0007(11) |
| $\mathrm{Cu}(1)-\mathrm{N}(1) \# 1$ | 2.0007(11) |
| $\mathrm{O}(1)-\mathrm{C}(5)$ | 1.2959(17) |
| $\mathrm{O}(2)-\mathrm{C}(3)$ | 1.3607(17) |
| $\mathrm{O}(2)-\mathrm{C}(2)$ | 1.4416(18) |
| $\mathrm{N}(1)-\mathrm{C}(3)$ | 1.3045(18) |
| $\mathrm{N}(1)-\mathrm{C}(1)$ | 1.5044(17) |
| $\mathrm{C}(1)-\mathrm{C}(16)$ | 1.520(2) |
| $\mathrm{C}(1)-\mathrm{C}(17)$ | 1.522(2) |
| $\mathrm{C}(1)-\mathrm{C}(2)$ | 1.531(2) |
| $\mathrm{C}(2)-\mathrm{H}(2 \mathrm{~A})$ | 0.9900 |
| $\mathrm{C}(2)-\mathrm{H}(2 \mathrm{~B})$ | 0.9900 |
| $\mathrm{C}(3)-\mathrm{C}(4)$ | 1.413(2) |
| $\mathrm{C}(4)-\mathrm{C}(5)$ | 1.363(2) |
| $\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(5)-\mathrm{C}(6)$ | 1.4984(19) |
| $\mathrm{C}(6)-\mathrm{C}(7)$ | 1.373(2) |
| C(6)-C(15) | 1.431(2) |
| $\mathrm{C}(7)-\mathrm{C}(8)$ | 1.413(2) |
| $\mathrm{C}(7)-\mathrm{H}(7 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(8)-\mathrm{C}(9)$ | 1.362(2) |
| $\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(9)-\mathrm{C}(10)$ | 1.419(2) |
| $\mathrm{C}(9)-\mathrm{H}(9 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(10)-\mathrm{C}(11)$ | 1.416(2) |
| $\mathrm{C}(10)-\mathrm{C}(15)$ | 1.425(2) |
| $\mathrm{C}(11)-\mathrm{C}(12)$ | 1.358(3) |
| $\mathrm{C}(11)-\mathrm{H}(11 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(12)-\mathrm{C}(13)$ | 1.405(3) |
| $\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(13)-\mathrm{C}(14)$ | 1.368(2) |
| $\mathrm{C}(13)-\mathrm{H}(13 \mathrm{~A})$ | 0.9500 |


| $\mathrm{C}(14)-\mathrm{C}(15)$ | 1.423(2) |
| :---: | :---: |
| $\mathrm{C}(14)-\mathrm{H}(14 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~A})$ | 0.9800 |
| $\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~B})$ | 0.9800 |
| $\mathrm{C}(16)-\mathrm{H}(16 \mathrm{C})$ | 0.9800 |
| $\mathrm{C}(17)-\mathrm{H}(17 \mathrm{~A})$ | 0.9800 |
| $\mathrm{C}(17)-\mathrm{H}(17 \mathrm{~B})$ | 0.9800 |
| $\mathrm{C}(17)-\mathrm{H}(17 \mathrm{C})$ | 0.9800 |
| $\mathrm{O}(1) \# 1-\mathrm{Cu}(1)-\mathrm{O}(1)$ | 180.0 |
| $\mathrm{O}(1) \# 1-\mathrm{Cu}(1)-\mathrm{N}(1)$ | 88.54(5) |
| $\mathrm{O}(1)-\mathrm{Cu}(1)-\mathrm{N}(1)$ | 91.46(5) |
| $\mathrm{O}(1) \# 1-\mathrm{Cu}(1)-\mathrm{N}(1) \# 1$ | 91.46(5) |
| $\mathrm{O}(1)-\mathrm{Cu}(1)-\mathrm{N}(1) \# 1$ | 88.54(5) |
| $\mathrm{N}(1)-\mathrm{Cu}(1)-\mathrm{N}(1) \# 1$ | 180.0 |
| $\mathrm{C}(5)-\mathrm{O}(1)-\mathrm{Cu}(1)$ | 128.02(9) |
| $\mathrm{C}(3)-\mathrm{O}(2)-\mathrm{C}(2)$ | 105.98(11) |
| $\mathrm{C}(3)-\mathrm{N}(1)-\mathrm{C}(1)$ | 107.21(11) |
| $\mathrm{C}(3)-\mathrm{N}(1)-\mathrm{Cu}(1)$ | 121.52(10) |
| $\mathrm{C}(1)-\mathrm{N}(1)-\mathrm{Cu}(1)$ | 131.00(9) |
| $\mathrm{N}(1)-\mathrm{C}(1)-\mathrm{C}(16)$ | 113.46(12) |
| $\mathrm{N}(1)-\mathrm{C}(1)-\mathrm{C}(17)$ | 108.77(12) |
| $\mathrm{C}(16)-\mathrm{C}(1)-\mathrm{C}(17)$ | 111.78(13) |
| $\mathrm{N}(1)-\mathrm{C}(1)-\mathrm{C}(2)$ | 101.17(11) |
| $\mathrm{C}(16)-\mathrm{C}(1)-\mathrm{C}(2)$ | 109.96(13) |
| $\mathrm{C}(17)-\mathrm{C}(1)-\mathrm{C}(2)$ | 111.25(13) |
| $\mathrm{O}(2)-\mathrm{C}(2)-\mathrm{C}(1)$ | 104.51(12) |
| $\mathrm{O}(2)-\mathrm{C}(2)-\mathrm{H}(2 \mathrm{~A})$ | 110.8 |
| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{H}(2 \mathrm{~A})$ | 110.8 |
| $\mathrm{O}(2)-\mathrm{C}(2)-\mathrm{H}(2 \mathrm{~B})$ | 110.8 |
| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{H}(2 \mathrm{~B})$ | 110.8 |
| $\mathrm{H}(2 \mathrm{~A})-\mathrm{C}(2)-\mathrm{H}(2 \mathrm{~B})$ | 108.9 |
| $\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{O}(2)$ | 115.67(13) |
| $\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{C}(4)$ | 129.24(13) |
| $\mathrm{O}(2)-\mathrm{C}(3)-\mathrm{C}(4)$ | 115.08(12) |
| $\mathrm{C}(5)-\mathrm{C}(4)-\mathrm{C}(3)$ | 121.69(13) |


| $\mathrm{C}(5)-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~A})$ | 119.2 |
| :---: | :---: |
| $\mathrm{C}(3)-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~A})$ | 119.2 |
| $\mathrm{O}(1)-\mathrm{C}(5)-\mathrm{C}(4)$ | 125.40(13) |
| $\mathrm{O}(1)-\mathrm{C}(5)-\mathrm{C}(6)$ | 115.83(12) |
| $\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{C}(6)$ | 118.77(12) |
| $\mathrm{C}(7)-\mathrm{C}(6)-\mathrm{C}(15)$ | 119.89(14) |
| $\mathrm{C}(7)-\mathrm{C}(6)-\mathrm{C}(5)$ | 119.24(13) |
| $\mathrm{C}(15)-\mathrm{C}(6)-\mathrm{C}(5)$ | 120.86(13) |
| $\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{C}(8)$ | 121.24(15) |
| $\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{H}(7 \mathrm{~A})$ | 119.4 |
| $\mathrm{C}(8)-\mathrm{C}(7)-\mathrm{H}(7 \mathrm{~A})$ | 119.4 |
| $\mathrm{C}(9)-\mathrm{C}(8)-\mathrm{C}(7)$ | 119.91(15) |
| $\mathrm{C}(9)-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~A})$ | 120.0 |
| $\mathrm{C}(7)-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~A})$ | 120.0 |
| $\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{C}(10)$ | 121.08(15) |
| $\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{H}(9 \mathrm{~A})$ | 119.5 |
| $\mathrm{C}(10)-\mathrm{C}(9)-\mathrm{H}(9 \mathrm{~A})$ | 119.5 |
| $\mathrm{C}(11)-\mathrm{C}(10)-\mathrm{C}(9)$ | 121.85(15) |
| $\mathrm{C}(11)-\mathrm{C}(10)-\mathrm{C}(15)$ | 118.89(15) |
| $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(15)$ | 119.26(14) |
| $\mathrm{C}(12)-\mathrm{C}(11)-\mathrm{C}(10)$ | 120.90(17) |
| $\mathrm{C}(12)-\mathrm{C}(11)-\mathrm{H}(11 \mathrm{~A})$ | 119.5 |
| $\mathrm{C}(10)-\mathrm{C}(11)-\mathrm{H}(11 \mathrm{~A})$ | 119.5 |
| $\mathrm{C}(11)-\mathrm{C}(12)-\mathrm{C}(13)$ | 120.48(16) |
| $\mathrm{C}(11)-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~A})$ | 119.8 |
| $\mathrm{C}(13)-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~A})$ | 119.8 |
| $\mathrm{C}(14)-\mathrm{C}(13)-\mathrm{C}(12)$ | 120.70(17) |
| $\mathrm{C}(14)-\mathrm{C}(13)-\mathrm{H}(13 \mathrm{~A})$ | 119.6 |
| $\mathrm{C}(12)-\mathrm{C}(13)-\mathrm{H}(13 \mathrm{~A})$ | 119.6 |
| $\mathrm{C}(13)-\mathrm{C}(14)-\mathrm{C}(15)$ | 120.34(15) |
| $\mathrm{C}(13)-\mathrm{C}(14)-\mathrm{H}(14 \mathrm{~A})$ | 119.8 |
| $\mathrm{C}(15)-\mathrm{C}(14)-\mathrm{H}(14 \mathrm{~A})$ | 119.8 |
| $\mathrm{C}(14)-\mathrm{C}(15)-\mathrm{C}(10)$ | 118.66(14) |
| $\mathrm{C}(14)-\mathrm{C}(15)-\mathrm{C}(6)$ | 122.69(14) |
| $\mathrm{C}(10)-\mathrm{C}(15)-\mathrm{C}(6)$ | 118.61(14) |
| $\mathrm{C}(1)-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~A})$ | 109.5 |


| $\mathrm{C}(1)-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~B})$ | 109.5 |
| :--- | :--- |
| $\mathrm{H}(16 \mathrm{~A})-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(1)-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(16 \mathrm{~A})-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(16 \mathrm{~B})-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(1)-\mathrm{C}(17)-\mathrm{H}(17 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(1)-\mathrm{C}(17)-\mathrm{H}(17 \mathrm{~B})$ | 109.5 |
| $\mathrm{H}(17 \mathrm{~A})-\mathrm{C}(17)-\mathrm{H}(17 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(1)-\mathrm{C}(17)-\mathrm{H}(17 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(17 \mathrm{~A})-\mathrm{C}(17)-\mathrm{H}(17 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(17 \mathrm{~B})-\mathrm{C}(17)-\mathrm{H}(17 \mathrm{C})$ | 109.5 |

Symmetry transformations used to generate equivalent atoms:
\#1-x+1,-y+1,-z+1

Table 4. Anisotropic displacement parameters $\left(\approx^{2} \times 10^{3}\right)$ for d1825_a. The anisotropic displacement factor exponent takes the form: $-2 \pi^{2}\left[h^{2} a^{* 2} U^{11}+\ldots+2 h k a^{*} b^{*} U^{12}\right]$

|  | $\mathrm{U}^{11}$ | $\mathrm{U}^{22}$ | $\mathrm{U}^{33}$ | $\mathrm{U}^{23}$ | $\mathrm{U}^{13}$ | $\mathrm{U}^{12}$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
|  |  |  |  |  |  |  |
| $\mathrm{Cu}(1)$ | $18(1)$ | $12(1)$ | $16(1)$ | $-1(1)$ | $1(1)$ | $-3(1)$ |
| $\mathrm{O}(1)$ | $34(1)$ | $13(1)$ | $23(1)$ | $-2(1)$ | $8(1)$ | $-6(1)$ |
| $\mathrm{O}(2)$ | $35(1)$ | $16(1)$ | $28(1)$ | $-1(1)$ | $8(1)$ | $-10(1)$ |
| $\mathrm{N}(1)$ | $17(1)$ | $15(1)$ | $16(1)$ | $-1(1)$ | $0(1)$ | $-4(1)$ |
| $\mathrm{C}(1)$ | $18(1)$ | $18(1)$ | $17(1)$ | $0(1)$ | $1(1)$ | $-6(1)$ |
| $\mathrm{C}(2)$ | $31(1)$ | $24(1)$ | $28(1)$ | $-5(1)$ | $8(1)$ | $-14(1)$ |
| $\mathrm{C}(3)$ | $22(1)$ | $15(1)$ | $19(1)$ | $2(1)$ | $-2(1)$ | $-7(1)$ |
| $\mathrm{C}(4)$ | $28(1)$ | $12(1)$ | $24(1)$ | $-3(1)$ | $2(1)$ | $-4(1)$ |
| $\mathrm{C}(5)$ | $20(1)$ | $16(1)$ | $18(1)$ | $-2(1)$ | $-2(1)$ | $-4(1)$ |
| $\mathrm{C}(6)$ | $23(1)$ | $14(1)$ | $21(1)$ | $-2(1)$ | $1(1)$ | $-6(1)$ |
| $\mathrm{C}(7)$ | $27(1)$ | $20(1)$ | $26(1)$ | $-1(1)$ | $-2(1)$ | $-4(1)$ |
| $\mathrm{C}(8)$ | $25(1)$ | $22(1)$ | $38(1)$ | $-2(1)$ | $2(1)$ | $0(1)$ |
| $\mathrm{C}(9)$ | $30(1)$ | $27(1)$ | $32(1)$ | $-8(1)$ | $11(1)$ | $-5(1)$ |
| $\mathrm{C}(10)$ | $31(1)$ | $23(1)$ | $23(1)$ | $-4(1)$ | $5(1)$ | $-10(1)$ |
| $\mathrm{C}(11)$ | $49(1)$ | $41(1)$ | $21(1)$ | $-6(1)$ | $5(1)$ | $-13(1)$ |
| $\mathrm{C}(12)$ | $54(1)$ | $49(1)$ | $21(1)$ | $1(1)$ | $-6(1)$ | $-18(1)$ |
| $\mathrm{C}(13)$ | $39(1)$ | $36(1)$ | $31(1)$ | $4(1)$ | $-12(1)$ | $-11(1)$ |
| $\mathrm{C}(14)$ | $29(1)$ | $22(1)$ | $25(1)$ | $-2(1)$ | $-2(1)$ | $-8(1)$ |
| $\mathrm{C}(15)$ | $26(1)$ | $17(1)$ | $21(1)$ | $-2(1)$ | $0(1)$ | $-10(1)$ |
| $\mathrm{C}(16)$ | $19(1)$ | $34(1)$ | $39(1)$ | $6(1)$ | $5(1)$ | $-1(1)$ |
| $\mathrm{C}(17)$ | $33(1)$ | $33(1)$ | $18(1)$ | $2(1)$ | $-2(1)$ | $-14(1)$ |
|  |  |  |  |  |  |  |

Table 5. Hydrogen coordinates ( $\times 10^{4}$ ) and isotropic displacement parameters $\left(\approx^{2} \times 10^{3}\right)$ for d1825_a.

|  | x | y | z | $\mathrm{U}(\mathrm{eq})$ |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{H}(2 \mathrm{~A})$ | 10582 | 7717 | 3662 | 33 |
| $\mathrm{H}(2 \mathrm{~B})$ | 9315 | 8171 | 2578 | 33 |
| H(4A) | 3673 | 9152 | 5348 | 26 |
| H(7A) | -1028 | 9101 | 5925 | 29 |
| H(8A) | -3971 | 10084 | 7251 | 35 |
| H(9A) | -3415 | 9691 | 9042 | 37 |
| H(11A) | -909 | 8608 | 10470 | 44 |
| H(12A) | 2544 | 7273 | 10963 | 48 |
| H(13A) | 5537 | 6315 | 9656 | 41 |
| H(14A) | 5027 | 6656 | 7852 | 30 |
| H(16A) | 10157 | 4484 | 3224 | 48 |
| H(16B) | 11140 | 5327 | 4061 | 48 |
| H(16C) | 11862 | 5524 | 2802 | 48 |
| H(17A) | 6444 | 5480 | 2334 | 41 |
| H(17B) | 8262 | 6296 | 1642 | 41 |
| H(17C) | 5782 | 7057 | 2225 | 41 |

Table 6. Torsion angles [ $\infty$ ] for d1825_a.

| $\mathrm{C}(3)-\mathrm{N}(1)-\mathrm{C}(1)-\mathrm{C}(16)$ | 134.57(14) |
| :---: | :---: |
| $\mathrm{Cu}(1)-\mathrm{N}(1)-\mathrm{C}(1)-\mathrm{C}(16)$ | -51.41(17) |
| $\mathrm{C}(3)-\mathrm{N}(1)-\mathrm{C}(1)-\mathrm{C}(17)$ | $-100.34(14)$ |
| $\mathrm{Cu}(1)-\mathrm{N}(1)-\mathrm{C}(1)-\mathrm{C}(17)$ | 73.67(15) |
| $\mathrm{C}(3)-\mathrm{N}(1)-\mathrm{C}(1)-\mathrm{C}(2)$ | $16.86(15)$ |
| $\mathrm{Cu}(1)-\mathrm{N}(1)-\mathrm{C}(1)-\mathrm{C}(2)$ | $-169.12(10)$ |
| $\mathrm{C}(3)-\mathrm{O}(2)-\mathrm{C}(2)-\mathrm{C}(1)$ | $21.01(16)$ |
| $\mathrm{N}(1)-\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{O}(2)$ | $-22.63(15)$ |
| $\mathrm{C}(16)-\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{O}(2)$ | -142.86(13) |
| $\mathrm{C}(17)-\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{O}(2)$ | 92.75(15) |
| $\mathrm{C}(1)-\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{O}(2)$ | -4.54(17) |
| $\mathrm{Cu}(1)-\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{O}(2)$ | $-179.24(9)$ |
| $\mathrm{C}(1)-\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{C}(4)$ | 175.53(15) |
| $\mathrm{Cu}(1)-\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{C}(4)$ | $0.8(2)$ |
| $\mathrm{C}(2)-\mathrm{O}(2)-\mathrm{C}(3)-\mathrm{N}(1)$ | -11.01(17) |
| $\mathrm{C}(2)-\mathrm{O}(2)-\mathrm{C}(3)-\mathrm{C}(4)$ | 168.93(13) |
| $\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{C}(4)-\mathrm{C}(5)$ | $9.2(3)$ |
| $\mathrm{O}(2)-\mathrm{C}(3)-\mathrm{C}(4)-\mathrm{C}(5)$ | -170.76(14) |
| $\mathrm{Cu}(1)-\mathrm{O}(1)-\mathrm{C}(5)-\mathrm{C}(4)$ | -13.7(2) |
| $\mathrm{Cu}(1)-\mathrm{O}(1)-\mathrm{C}(5)-\mathrm{C}(6)$ | 166.92(10) |
| $\mathrm{C}(3)-\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{O}(1)$ | -2.6(2) |
| $\mathrm{C}(3)-\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{C}(6)$ | 176.79(13) |
| $\mathrm{O}(1)-\mathrm{C}(5)-\mathrm{C}(6)-\mathrm{C}(7)$ | -119.23(15) |
| $\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{C}(6)-\mathrm{C}(7)$ | 61.31(19) |
| $\mathrm{O}(1)-\mathrm{C}(5)-\mathrm{C}(6)-\mathrm{C}(15)$ | 59.56(19) |
| $C(4)-C(5)-C(6)-C(15)$ | -119.89(16) |
| $\mathrm{C}(15)-\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{C}(8)$ | -1.3(2) |
| $\mathrm{C}(5)-\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{C}(8)$ | 177.51(14) |
| $\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{C}(8)-\mathrm{C}(9)$ | 0.8(2) |
| $\mathrm{C}(7)-\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{C}(10)$ | 0.2(3) |
| $\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(11)$ | 179.29(16) |
| $\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(15)$ | -0.6(2) |
| $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(11)-\mathrm{C}(12)$ | -179.02(17) |
| $\mathrm{C}(15)-\mathrm{C}(10)-\mathrm{C}(11)-\mathrm{C}(12)$ | 0.9(3) |
|  |  |


| $\mathrm{C}(10)-\mathrm{C}(11)-\mathrm{C}(12)-\mathrm{C}(13)$ | $0.6(3)$ |
| :--- | :---: |
| $\mathrm{C}(11)-\mathrm{C}(12)-\mathrm{C}(13)-\mathrm{C}(14)$ | $-0.9(3)$ |
| $\mathrm{C}(12)-\mathrm{C}(13)-\mathrm{C}(14)-\mathrm{C}(15)$ | $-0.3(3)$ |
| $\mathrm{C}(13)-\mathrm{C}(14)-\mathrm{C}(15)-\mathrm{C}(10)$ | $1.8(2)$ |
| $\mathrm{C}(13)-\mathrm{C}(14)-\mathrm{C}(15)-\mathrm{C}(6)$ | $179.45(15)$ |
| $\mathrm{C}(11)-\mathrm{C}(10)-\mathrm{C}(15)-\mathrm{C}(14)$ | $-2.1(2)$ |
| $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(15)-\mathrm{C}(14)$ | $177.82(14)$ |
| $\mathrm{C}(11)-\mathrm{C}(10)-\mathrm{C}(15)-\mathrm{C}(6)$ | $-179.80(14)$ |
| $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(15)-\mathrm{C}(6)$ | $0.1(2)$ |
| $\mathrm{C}(7)-\mathrm{C}(6)-\mathrm{C}(15)-\mathrm{C}(14)$ | $-176.78(14)$ |
| $\mathrm{C}(5)-\mathrm{C}(6)-\mathrm{C}(15)-\mathrm{C}(14)$ | $4.4(2)$ |
| $\mathrm{C}(7)-\mathrm{C}(6)-\mathrm{C}(15)-\mathrm{C}(10)$ | $0.8(2)$ |
| $\mathrm{C}(5)-\mathrm{C}(6)-\mathrm{C}(15)-\mathrm{C}(10)$ | $-177.95(13)$ |

Symmetry transformations used to generate equivalent atoms:
\#1-x+1,-y+1,-z+1


Identification code
Empirical formula
Formula weight
Temperature
Wavelength
Crystal system
Space group
Unit cell dimensions

Volume
Z
Density (calculated)
Absorption coefficient
F(000)
Crystal size
Theta range for data collection
Index ranges
Reflections collected
Independent reflections
Completeness to theta $=25.242^{\circ}$
Absorption correction
Max. and min. transmission
d1871_a (7h)
C22 H36 Cu N2 O4
456.07

150(2) K
$0.71073 \AA$
Triclinic
P-1
$a=11.4940(9) \AA \quad a=92.155(3)^{\circ}$.
$b=13.6089(12) \AA \quad b=101.732(2)^{\circ}$.
$\mathrm{c}=15.8322(14) \AA \quad \mathrm{g}=101.890(2)^{\circ}$.
2364.5(3) $\AA^{3}$

4
$1.281 \mathrm{Mg} / \mathrm{m}^{3}$
$0.952 \mathrm{~mm}^{-1}$
972
$0.260 \times 0.100 \times 0.030 \mathrm{~mm}^{3}$
1.534 to $27.568^{\circ}$.
$-14<=\mathrm{h}<=14,-17<=\mathrm{k}<=17,-20<=1<=20$
77128
$10909[\mathrm{R}(\mathrm{int})=0.1093]$
100.0 \%

Semi-empirical from equivalents
0.7456 and 0.6549

Refinement method
Data / restraints / parameters
Goodness-of-fit on $\mathrm{F}^{2}$
Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ]
R indices (all data)
Extinction coefficient
Largest diff. peak and hole

Full-matrix least-squares on $\mathrm{F}^{2}$
10909 / 38 / 567
0.995
$\mathrm{R} 1=0.0468, \mathrm{wR} 2=0.0874$
$\mathrm{R} 1=0.1087, w R 2=0.1078$
n/a
0.496 and -0.696 e. $\AA^{-3}$

Table 2. Atomic coordinates ( $\times 10^{4}$ ) and equivalent isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for $\mathrm{d} 1871 \_$a. $\mathrm{U}(\mathrm{eq})$ is defined as one third of the trace of the orthogonalized $\mathrm{U}^{\mathrm{ij}}$ tensor.

|  | x | y | z | U(eq) |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{Cu}(1 \mathrm{~A})$ | 4074(1) | 7392(1) | 7488(1) | 22(1) |
| $\mathrm{O}(1 \mathrm{~A})$ | 3971(2) | 8787(2) | 7552(1) | 25(1) |
| $\mathrm{O}(2 \mathrm{~A})$ | 4423(2) | 8099(2) | 5046(1) | 38(1) |
| $\mathrm{O}(3 \mathrm{~A})$ | 3163(2) | 6025(2) | 7439(1) | 28(1) |
| $\mathrm{O}(4 \mathrm{~A})$ | 5402(2) | 6673(2) | 9937(1) | 32(1) |
| $\mathrm{N}(1 \mathrm{~A})$ | 4220(2) | 7404(2) | 6286(2) | 26(1) |
| $\mathrm{N}(2 \mathrm{~A})$ | 4888(2) | 7356(2) | 8681(2) | 20(1) |
| C (1A) | 3868(3) | 9372(2) | 6929(2) | 23(1) |
| $\mathrm{C}(2 \mathrm{~A})$ | 3947(3) | 9121(2) | 6101(2) | 27(1) |
| C(3A) | 4180(3) | 8192(2) | 5853(2) | 27(1) |
| C(6A) | 3690(3) | 10425(2) | 7191(2) | 28(1) |
| C(7A) | 4901(3) | 11030(3) | 7739(3) | 51(1) |
| C(8A) | 3273(4) | 10988(3) | 6405(3) | 57(1) |
| C(9A) | 2737(3) | 10310(2) | 7749(2) | 36(1) |
| C(4C) | 4460(12) | 7043(6) | 4878(5) | 45(4) |
| C(5C) | 4555(3) | 6627(2) | 5760(2) | 27(1) |
| C(10C) | 3854(8) | 5528(5) | 5762(6) | 37(2) |
| C(11C) | 5883(6) | 6666(7) | 6195(7) | 39(3) |
| C(4A) | 4977(9) | 7227(6) | 5041(5) | 38(3) |
| C(5A) | 4555(3) | 6627(2) | 5760(2) | 27(1) |
| C(10A) | 3336(5) | 5899(5) | 5368(5) | 38(2) |
| $\mathrm{C}(11 \mathrm{~A})$ | 5533(8) | 6161(7) | 6252(6) | 44(2) |
| C(12A) | 3114(3) | 5440(2) | 8063(2) | 23(1) |
| C(13A) | 3797(3) | 5675(2) | 8887(2) | 25(1) |
| C(14A) | 4673(3) | 6584(2) | 9129(2) | 24(1) |
| C(15A) | 6373(3) | 7549(2) | 9951(2) | 34(1) |
| C(16A) | 5862(3) | 8149(2) | 9229(2) | 23(1) |
| C(17A) | 2253(3) | 4394(2) | 7810(2) | 30(1) |
| C(18A) | 3003(5) | 3613(5) | 7697(5) | 44(1) |
| C(19A) | 1622(7) | 4085(5) | 8582(4) | 44(1) |
| C(20A) | 1258(6) | 4371(6) | 7019(4) | 44(1) |
|  |  | 441 |  |  |


| C(18C) | 2880(6) | 3830(6) | 7218(5) | 44(1) |
| :---: | :---: | :---: | :---: | :---: |
| C(19C) | 1991(8) | 3797(6) | 8539(4) | 44(1) |
| C(20C) | 1100(7) | 4593(7) | 7223(5) | 44(1) |
| C(21A) | 6796(3) | 8607(2) | 8724(2) | 32(1) |
| C(22A) | 5272(3) | 8938(2) | 9580(2) | 32(1) |
| $\mathrm{Cu}(1 \mathrm{~B})$ | 892(1) | 2416(1) | 2423(1) | 21(1) |
| $\mathrm{O}(1 \mathrm{~B})$ | 1260(2) | 1244(2) | 2968(1) | 26(1) |
| $\mathrm{O}(2 \mathrm{~B})$ | -1069(2) | 199(2) | 551(1) | 29(1) |
| $\mathrm{O}(3 \mathrm{~B})$ | 1561(2) | 3603(1) | 1904(1) | 24(1) |
| $\mathrm{O}(4 \mathrm{~B})$ | 894(2) | 4587(2) | 4277(1) | 33(1) |
| N(1B) | -73(2) | 1618(2) | 1377(2) | 19(1) |
| $\mathrm{N}(2 \mathrm{~B})$ | 824(2) | 3192(2) | 3452(2) | 21(1) |
| C(1B) | 1009(3) | 328(2) | 2634(2) | 24(1) |
| C(2B) | 300(3) | -7(2) | 1828(2) | 23(1) |
| C(3B) | -248(3) | 644(2) | 1279(2) | 22(1) |
| C(4B) | -1649(3) | 984(2) | 189(2) | 33(1) |
| C(5B) | -791(3) | 1973(2) | 606(2) | 24(1) |
| C(6B) | 1532(3) | -412(2) | 3237(2) | 31(1) |
| C(7B) | 807(4) | -555(3) | 3946(3) | 67(1) |
| C(8B) | 1466(4) | -1429(3) | 2771(3) | 62(1) |
| C(9B) | 2862(3) | 55(3) | 3645(2) | 42(1) |
| C(10B) | 58(3) | 2393(2) | 17(2) | 34(1) |
| C(11B) | -1478(3) | 2727(3) | 872(2) | 36(1) |
| C(12B) | 1892(3) | 4526(2) | 2243(2) | 22(1) |
| C(13B) | 1721(3) | 4832(2) | 3033(2) | 27(1) |
| C(14B) | 1150(3) | 4167(2) | 3561(2) | 25(1) |
| C(15B) | 76(3) | 3784(3) | 4580(2) | 35(1) |
| C(16B) | 332(3) | 2822(2) | 4212(2) | 25(1) |
| C(17B) | 2476(3) | 5279(2) | 1674(2) | 31(1) |
| C(18B) | 3507(4) | 4897(3) | 1404(3) | 66(1) |
| C(19B) | 2915(5) | 6329(3) | 2089(3) | 91(2) |
| C(20B) | 1528(4) | 5286(4) | 847(3) | 82(2) |
| C(21B) | -812(3) | 2006(3) | 3925(2) | 36(1) |
| C(22B) | 1319(3) | 2463(3) | 4842(2) | 35(1) |

Table 3. Bond lengths $[\AA]$ and angles $\left[{ }^{\circ}\right]$ for d1871_a.

| $\mathrm{Cu}(1 \mathrm{~A})-\mathrm{O}(1 \mathrm{~A})$ | 1.927(2) |
| :---: | :---: |
| $\mathrm{Cu}(1 \mathrm{~A})-\mathrm{O}(3 \mathrm{~A})$ | 1.928(2) |
| $\mathrm{Cu}(1 \mathrm{~A})-\mathrm{N}(2 \mathrm{~A})$ | 1.937(2) |
| $\mathrm{Cu}(1 \mathrm{~A})-\mathrm{N}(1 \mathrm{~A})$ | 1.945(2) |
| $\mathrm{O}(1 \mathrm{~A})-\mathrm{C}(1 \mathrm{~A})$ | 1.293(3) |
| $\mathrm{O}(2 \mathrm{~A})-\mathrm{C}(3 \mathrm{~A})$ | 1.370(3) |
| $\mathrm{O}(2 \mathrm{~A})-\mathrm{C}(4 \mathrm{~A})$ | 1.458(6) |
| $\mathrm{O}(2 \mathrm{~A})-\mathrm{C}(4 \mathrm{C})$ | 1.462(7) |
| $\mathrm{O}(3 \mathrm{~A})-\mathrm{C}(12 \mathrm{~A})$ | 1.294(4) |
| $\mathrm{O}(4 \mathrm{~A})-\mathrm{C}(14 \mathrm{~A})$ | $1.365(3)$ |
| $\mathrm{O}(4 \mathrm{~A})-\mathrm{C}(15 \mathrm{~A})$ | 1.452(4) |
| $\mathrm{N}(1 \mathrm{~A})$-C(3A) | 1.299(4) |
| $\mathrm{N}(1 \mathrm{~A})-\mathrm{C}(5 \mathrm{~A})$ | 1.481(4) |
| $\mathrm{N}(1 \mathrm{~A})-\mathrm{C}(5 \mathrm{C})$ | 1.481(4) |
| $\mathrm{N}(2 \mathrm{~A})-\mathrm{C}(14 \mathrm{~A})$ | 1.300(4) |
| $\mathrm{N}(2 \mathrm{~A})-\mathrm{C}(16 \mathrm{~A})$ | 1.485(3) |
| $\mathrm{C}(1 \mathrm{~A})-\mathrm{C}(2 \mathrm{~A})$ | 1.367(4) |
| $\mathrm{C}(1 \mathrm{~A})-\mathrm{C}(6 \mathrm{~A})$ | 1.542(4) |
| $\mathrm{C}(2 \mathrm{~A})-\mathrm{C}(3 \mathrm{~A})$ | 1.403(4) |
| $\mathrm{C}(2 \mathrm{~A})-\mathrm{H}(2 \mathrm{AA})$ | 0.9500 |
| C(6A)-C(9A) | 1.530(4) |
| $\mathrm{C}(6 \mathrm{~A})-\mathrm{C}(8 \mathrm{~A})$ | 1.530(5) |
| $\mathrm{C}(6 \mathrm{~A})-\mathrm{C}(7 \mathrm{~A})$ | 1.533(4) |
| $\mathrm{C}(7 \mathrm{~A})-\mathrm{H}(7 \mathrm{AA})$ | 0.9800 |
| $\mathrm{C}(7 \mathrm{~A})-\mathrm{H}(7 \mathrm{AB})$ | 0.9800 |
| $\mathrm{C}(7 \mathrm{~A})-\mathrm{H}(7 \mathrm{AC})$ | 0.9800 |
| $\mathrm{C}(8 \mathrm{~A})-\mathrm{H}(8 \mathrm{AA})$ | 0.9800 |
| $\mathrm{C}(8 \mathrm{~A})-\mathrm{H}(8 \mathrm{AB})$ | 0.9800 |
| $\mathrm{C}(8 \mathrm{~A})-\mathrm{H}(8 \mathrm{AC})$ | 0.9800 |
| $\mathrm{C}(9 \mathrm{~A})-\mathrm{H}(9 \mathrm{AA})$ | 0.9800 |
| $\mathrm{C}(9 \mathrm{~A})-\mathrm{H}(9 \mathrm{AB})$ | 0.9800 |
| $\mathrm{C}(9 \mathrm{~A})-\mathrm{H}(9 \mathrm{AC})$ | 0.9800 |
| $\mathrm{C}(4 \mathrm{C})-\mathrm{C}(5 \mathrm{C})$ | 1.519(7) |
| $\mathrm{C}(4 \mathrm{C})-\mathrm{H}(4 \mathrm{AA})$ | 0.9900 |


| $\mathrm{C}(4 \mathrm{C})-\mathrm{H}(4 \mathrm{AB})$ | 0.9900 |
| :---: | :---: |
| $\mathrm{C}(5 \mathrm{C})-\mathrm{C}(11 \mathrm{C})$ | 1.531(7) |
| $\mathrm{C}(5 \mathrm{C})-\mathrm{C}(10 \mathrm{C})$ | 1.545(6) |
| $\mathrm{C}(10 \mathrm{C})-\mathrm{H}(10 \mathrm{~A})$ | 0.9800 |
| $\mathrm{C}(10 \mathrm{C})-\mathrm{H}(10 \mathrm{~B})$ | 0.9800 |
| $\mathrm{C}(10 \mathrm{C})-\mathrm{H}(10 \mathrm{C})$ | 0.9800 |
| $\mathrm{C}(11 \mathrm{C})-\mathrm{H}(11 \mathrm{~A})$ | 0.9800 |
| $\mathrm{C}(11 \mathrm{C})-\mathrm{H}(11 \mathrm{~B})$ | 0.9800 |
| $\mathrm{C}(11 \mathrm{C})-\mathrm{H}(11 \mathrm{C})$ | 0.9800 |
| $\mathrm{C}(4 \mathrm{~A})-\mathrm{C}(5 \mathrm{~A})$ | 1.525(7) |
| $\mathrm{C}(4 \mathrm{~A})-\mathrm{H}(4 \mathrm{CA})$ | 0.9900 |
| $\mathrm{C}(4 \mathrm{~A})-\mathrm{H}(4 \mathrm{CB})$ | 0.9900 |
| $\mathrm{C}(5 \mathrm{~A})-\mathrm{C}(11 \mathrm{~A})$ | 1.499(6) |
| $\mathrm{C}(5 \mathrm{~A})-\mathrm{C}(10 \mathrm{~A})$ | $1.535(5)$ |
| $\mathrm{C}(10 \mathrm{~A})-\mathrm{H}(10 \mathrm{D})$ | 0.9800 |
| $\mathrm{C}(10 \mathrm{~A})-\mathrm{H}(10 \mathrm{E})$ | 0.9800 |
| $\mathrm{C}(10 \mathrm{~A})-\mathrm{H}(10 \mathrm{~F})$ | 0.9800 |
| $\mathrm{C}(11 \mathrm{~A})-\mathrm{H}(11 \mathrm{D})$ | 0.9800 |
| $\mathrm{C}(11 \mathrm{~A})-\mathrm{H}(11 \mathrm{E})$ | 0.9800 |
| $\mathrm{C}(11 \mathrm{~A})-\mathrm{H}(11 \mathrm{~F})$ | 0.9800 |
| $\mathrm{C}(12 \mathrm{~A})-\mathrm{C}(13 \mathrm{~A})$ | 1.367(4) |
| $\mathrm{C}(12 \mathrm{~A})-\mathrm{C}(17 \mathrm{~A})$ | 1.544(4) |
| $\mathrm{C}(13 \mathrm{~A})-\mathrm{C}(14 \mathrm{~A})$ | 1.409(4) |
| $\mathrm{C}(13 \mathrm{~A})-\mathrm{H}(13 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(15 \mathrm{~A})$-C(16A) | 1.521(4) |
| $\mathrm{C}(15 \mathrm{~A})-\mathrm{H}(15 \mathrm{~A})$ | 0.9900 |
| $\mathrm{C}(15 \mathrm{~A})-\mathrm{H}(15 \mathrm{~B})$ | 0.9900 |
| C(16A)-C(21A) | 1.514(4) |
| $\mathrm{C}(16 \mathrm{~A})$ - $\mathrm{C}(22 \mathrm{~A})$ | 1.527(4) |
| C(17A)-C(19C) | 1.482(5) |
| C(17A)-C(20A) | 1.509(5) |
| C(17A)-C(18A) | 1.526(5) |
| $\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(20 \mathrm{C})$ | 1.536(5) |
| C(17A)-C(18C) | 1.559(5) |
| C(17A)-C(19A) | 1.571(5) |
| $\mathrm{C}(18 \mathrm{~A})-\mathrm{H}(18 \mathrm{~A})$ | 0.9800 |


| $\mathrm{C}(18 \mathrm{~A})-\mathrm{H}(18 \mathrm{~B})$ | 0.9800 |
| :---: | :---: |
| $\mathrm{C}(18 \mathrm{~A})-\mathrm{H}(18 \mathrm{C})$ | 0.9800 |
| $\mathrm{C}(19 \mathrm{~A})-\mathrm{H}(19 \mathrm{~A})$ | 0.9800 |
| $\mathrm{C}(19 \mathrm{~A})-\mathrm{H}(19 \mathrm{~B})$ | 0.9800 |
| $\mathrm{C}(19 \mathrm{~A})-\mathrm{H}(19 \mathrm{C})$ | 0.9800 |
| $\mathrm{C}(20 \mathrm{~A})-\mathrm{H}(20 \mathrm{~A})$ | 0.9800 |
| $\mathrm{C}(20 \mathrm{~A})-\mathrm{H}(20 \mathrm{~B})$ | 0.9800 |
| $\mathrm{C}(20 \mathrm{~A})-\mathrm{H}(20 \mathrm{C})$ | 0.9800 |
| C(18C)-H(18G) | 0.9800 |
| $\mathrm{C}(18 \mathrm{C})-\mathrm{H}(18 \mathrm{H})$ | 0.9800 |
| C(18C)-H(18I) | 0.9800 |
| C(19C)-H(19G) | 0.9800 |
| $\mathrm{C}(19 \mathrm{C})-\mathrm{H}(19 \mathrm{H})$ | 0.9800 |
| C(19C)-H(19I) | 0.9800 |
| C(20C)-H(20G) | 0.9800 |
| $\mathrm{C}(20 \mathrm{C})-\mathrm{H}(20 \mathrm{H})$ | 0.9800 |
| $\mathrm{C}(20 \mathrm{C})-\mathrm{H}(20 \mathrm{I})$ | 0.9800 |
| $\mathrm{C}(21 \mathrm{~A})-\mathrm{H}(21 \mathrm{~A})$ | 0.9800 |
| $\mathrm{C}(21 \mathrm{~A})-\mathrm{H}(21 \mathrm{~B})$ | 0.9800 |
| $\mathrm{C}(21 \mathrm{~A})-\mathrm{H}(21 \mathrm{C})$ | 0.9800 |
| $\mathrm{C}(22 \mathrm{~A})-\mathrm{H}(22 \mathrm{~A})$ | 0.9800 |
| $\mathrm{C}(22 \mathrm{~A})-\mathrm{H}(22 \mathrm{~B})$ | 0.9800 |
| $\mathrm{C}(22 \mathrm{~A})-\mathrm{H}(22 \mathrm{C})$ | 0.9800 |
| $\mathrm{Cu}(1 \mathrm{~B})-\mathrm{O}(1 \mathrm{~B})$ | 1.923(2) |
| $\mathrm{Cu}(1 \mathrm{~B})-\mathrm{O}(3 \mathrm{~B})$ | 1.928(2) |
| $\mathrm{Cu}(1 \mathrm{~B})-\mathrm{N}(2 \mathrm{~B})$ | 1.933(2) |
| $\mathrm{Cu}(1 \mathrm{~B})-\mathrm{N}(1 \mathrm{~B})$ | 1.942(2) |
| $\mathrm{O}(1 \mathrm{~B})-\mathrm{C}(1 \mathrm{~B})$ | 1.288(3) |
| $\mathrm{O}(2 \mathrm{~B})-\mathrm{C}(3 \mathrm{~B})$ | 1.363(3) |
| $\mathrm{O}(2 \mathrm{~B})-\mathrm{C}(4 \mathrm{~B})$ | 1.448(4) |
| $\mathrm{O}(3 \mathrm{~B})-\mathrm{C}(12 \mathrm{~B})$ | 1.297(3) |
| $\mathrm{O}(4 \mathrm{~B})-\mathrm{C}(14 \mathrm{~B})$ | 1.362(3) |
| $\mathrm{O}(4 \mathrm{~B})-\mathrm{C}(15 \mathrm{~B})$ | 1.451(4) |
| $\mathrm{N}(1 \mathrm{~B})-\mathrm{C}(3 \mathrm{~B})$ | 1.297(3) |
| $\mathrm{N}(1 \mathrm{~B})-\mathrm{C}(5 \mathrm{~B})$ | 1.484(4) |
| $\mathrm{N}(2 \mathrm{~B})$-C(14B) | 1.296(4) |


| $\mathrm{N}(2 \mathrm{~B})-\mathrm{C}(16 \mathrm{~B})$ | 1.492(4) |
| :---: | :---: |
| $\mathrm{C}(1 \mathrm{~B})-\mathrm{C}(2 \mathrm{~B})$ | 1.373(4) |
| $\mathrm{C}(1 \mathrm{~B})-\mathrm{C}(6 \mathrm{~B})$ | 1.540(4) |
| $\mathrm{C}(2 \mathrm{~B})-\mathrm{C}(3 \mathrm{~B})$ | 1.414(4) |
| $\mathrm{C}(2 \mathrm{~B})-\mathrm{H}(2 \mathrm{BA})$ | 0.9500 |
| $\mathrm{C}(4 \mathrm{~B})-\mathrm{C}(5 \mathrm{~B})$ | 1.531(4) |
| $\mathrm{C}(4 \mathrm{~B})-\mathrm{H}(4 \mathrm{BA})$ | 0.9900 |
| $\mathrm{C}(4 \mathrm{~B})-\mathrm{H}(4 \mathrm{BB})$ | 0.9900 |
| $\mathrm{C}(5 \mathrm{~B})-\mathrm{C}(11 \mathrm{~B})$ | 1.513(4) |
| $\mathrm{C}(5 \mathrm{~B})-\mathrm{C}(10 \mathrm{~B})$ | 1.526(4) |
| $\mathrm{C}(6 \mathrm{~B})-\mathrm{C}(7 \mathrm{~B})$ | 1.524(5) |
| $\mathrm{C}(6 \mathrm{~B})-\mathrm{C}(8 \mathrm{~B})$ | 1.525(5) |
| $\mathrm{C}(6 \mathrm{~B})-\mathrm{C}(9 \mathrm{~B})$ | 1.525(4) |
| $\mathrm{C}(7 \mathrm{~B})-\mathrm{H}(7 \mathrm{BA})$ | 0.9800 |
| $\mathrm{C}(7 \mathrm{~B})-\mathrm{H}(7 \mathrm{BB})$ | 0.9800 |
| $\mathrm{C}(7 \mathrm{~B})-\mathrm{H}(7 \mathrm{BC})$ | 0.9800 |
| $\mathrm{C}(8 \mathrm{~B})-\mathrm{H}(8 \mathrm{BA})$ | 0.9800 |
| $\mathrm{C}(8 \mathrm{~B})-\mathrm{H}(8 \mathrm{BB})$ | 0.9800 |
| $\mathrm{C}(8 \mathrm{~B})-\mathrm{H}(8 \mathrm{BC})$ | 0.9800 |
| $\mathrm{C}(9 \mathrm{~B})-\mathrm{H}(9 \mathrm{BA})$ | 0.9800 |
| $\mathrm{C}(9 \mathrm{~B})-\mathrm{H}(9 \mathrm{BB})$ | 0.9800 |
| $\mathrm{C}(9 \mathrm{~B})-\mathrm{H}(9 \mathrm{BC})$ | 0.9800 |
| $\mathrm{C}(10 \mathrm{~B})-\mathrm{H}(10 \mathrm{G})$ | 0.9800 |
| $\mathrm{C}(10 \mathrm{~B})-\mathrm{H}(10 \mathrm{H})$ | 0.9800 |
| $\mathrm{C}(10 \mathrm{~B})-\mathrm{H}(10 \mathrm{I})$ | 0.9800 |
| $\mathrm{C}(11 \mathrm{~B})-\mathrm{H}(11 \mathrm{G})$ | 0.9800 |
| $\mathrm{C}(11 \mathrm{~B})-\mathrm{H}(11 \mathrm{H})$ | 0.9800 |
| $\mathrm{C}(11 \mathrm{~B})-\mathrm{H}(11 \mathrm{I})$ | 0.9800 |
| $\mathrm{C}(12 \mathrm{~B})-\mathrm{C}(13 \mathrm{~B})$ | 1.368(4) |
| $\mathrm{C}(12 \mathrm{~B})-\mathrm{C}(17 \mathrm{~B})$ | 1.531(4) |
| C(13B)-C(14B) | 1.409(4) |
| $\mathrm{C}(13 \mathrm{~B})-\mathrm{H}(13 \mathrm{~B})$ | 0.9500 |
| $\mathrm{C}(15 \mathrm{~B})-\mathrm{C}(16 \mathrm{~B})$ | 1.520(4) |
| $\mathrm{C}(15 \mathrm{~B})-\mathrm{H}(15 \mathrm{C})$ | 0.9900 |
| $\mathrm{C}(15 \mathrm{~B})-\mathrm{H}(15 \mathrm{D})$ | 0.9900 |
| $\mathrm{C}(16 \mathrm{~B})-\mathrm{C}(21 \mathrm{~B})$ | 1.513(4) |


| C(16B)-C(22B) | 1.525(4) |
| :---: | :---: |
| C(17B)-C(19B) | $1.492(5)$ |
| $\mathrm{C}(17 \mathrm{~B})-\mathrm{C}(18 \mathrm{~B})$ | $1.517(5)$ |
| $\mathrm{C}(17 \mathrm{~B})-\mathrm{C}(20 \mathrm{~B})$ | $1.526(5)$ |
| $\mathrm{C}(18 \mathrm{~B})-\mathrm{H}(18 \mathrm{D})$ | 0.9800 |
| $\mathrm{C}(18 \mathrm{~B})-\mathrm{H}(18 \mathrm{E})$ | 0.9800 |
| $\mathrm{C}(18 \mathrm{~B})-\mathrm{H}(18 \mathrm{~F})$ | 0.9800 |
| C(19B)-H(19D) | 0.9800 |
| C(19B)-H(19E) | 0.9800 |
| $\mathrm{C}(19 \mathrm{~B})-\mathrm{H}(19 \mathrm{~F})$ | 0.9800 |
| $\mathrm{C}(20 \mathrm{~B})-\mathrm{H}(20 \mathrm{D})$ | 0.9800 |
| $\mathrm{C}(20 \mathrm{~B})-\mathrm{H}(20 \mathrm{E})$ | 0.9800 |
| $\mathrm{C}(20 \mathrm{~B})-\mathrm{H}(20 \mathrm{~F})$ | 0.9800 |
| $\mathrm{C}(21 \mathrm{~B})-\mathrm{H}(21 \mathrm{D})$ | 0.9800 |
| $\mathrm{C}(21 \mathrm{~B})-\mathrm{H}(21 \mathrm{E})$ | 0.9800 |
| $\mathrm{C}(21 \mathrm{~B})-\mathrm{H}(21 \mathrm{~F})$ | 0.9800 |
| $\mathrm{C}(22 \mathrm{~B})-\mathrm{H}(22 \mathrm{D})$ | 0.9800 |
| $\mathrm{C}(22 \mathrm{~B})-\mathrm{H}(22 \mathrm{E})$ | 0.9800 |
| $\mathrm{C}(22 \mathrm{~B})-\mathrm{H}(22 \mathrm{~F})$ | 0.9800 |
| $\mathrm{O}(1 \mathrm{~A})-\mathrm{Cu}(1 \mathrm{~A})-\mathrm{O}(3 \mathrm{~A})$ | 144.37(9) |
| $\mathrm{O}(1 \mathrm{~A})-\mathrm{Cu}(1 \mathrm{~A})-\mathrm{N}(2 \mathrm{~A})$ | 97.49(9) |
| $\mathrm{O}(3 \mathrm{~A})-\mathrm{Cu}(1 \mathrm{~A})-\mathrm{N}(2 \mathrm{~A})$ | 92.15(9) |
| $\mathrm{O}(1 \mathrm{~A})-\mathrm{Cu}(1 \mathrm{~A})-\mathrm{N}(1 \mathrm{~A})$ | 92.45(10) |
| $\mathrm{O}(3 \mathrm{~A})-\mathrm{Cu}(1 \mathrm{~A})-\mathrm{N}(1 \mathrm{~A})$ | 98.05(10) |
| $\mathrm{N}(2 \mathrm{~A})-\mathrm{Cu}(1 \mathrm{~A})-\mathrm{N}(1 \mathrm{~A})$ | 146.69(10) |
| $\mathrm{C}(1 \mathrm{~A})-\mathrm{O}(1 \mathrm{~A})-\mathrm{Cu}(1 \mathrm{~A})$ | 128.12(19) |
| $\mathrm{C}(3 \mathrm{~A})-\mathrm{O}(2 \mathrm{~A})-\mathrm{C}(4 \mathrm{~A})$ | 105.4(3) |
| $\mathrm{C}(3 \mathrm{~A})-\mathrm{O}(2 \mathrm{~A})-\mathrm{C}(4 \mathrm{C})$ | 106.6(4) |
| $\mathrm{C}(12 \mathrm{~A})-\mathrm{O}(3 \mathrm{~A})-\mathrm{Cu}(1 \mathrm{~A})$ | 128.24(19) |
| $\mathrm{C}(14 \mathrm{~A})-\mathrm{O}(4 \mathrm{~A})-\mathrm{C}(15 \mathrm{~A})$ | 105.3(2) |
| $\mathrm{C}(3 \mathrm{~A})-\mathrm{N}(1 \mathrm{~A})-\mathrm{C}(5 \mathrm{~A})$ | 109.0(2) |
| $\mathrm{C}(3 \mathrm{~A})-\mathrm{N}(1 \mathrm{~A})-\mathrm{C}(5 \mathrm{C})$ | 109.0(2) |
| $\mathrm{C}(3 \mathrm{~A})-\mathrm{N}(1 \mathrm{~A})-\mathrm{Cu}(1 \mathrm{~A})$ | 122.6(2) |
| $\mathrm{C}(5 \mathrm{~A})-\mathrm{N}(1 \mathrm{~A})-\mathrm{Cu}(1 \mathrm{~A})$ | 127.9(2) |
| $\mathrm{C}(5 \mathrm{C})-\mathrm{N}(1 \mathrm{~A})-\mathrm{Cu}(1 \mathrm{~A})$ | 127.9(2) |


| $\mathrm{C}(14 \mathrm{~A})-\mathrm{N}(2 \mathrm{~A})-\mathrm{C}(16 \mathrm{~A})$ | 108.4(2) |
| :---: | :---: |
| $\mathrm{C}(14 \mathrm{~A})-\mathrm{N}(2 \mathrm{~A})-\mathrm{Cu}(1 \mathrm{~A})$ | 123.7(2) |
| $\mathrm{C}(16 \mathrm{~A})-\mathrm{N}(2 \mathrm{~A})-\mathrm{Cu}(1 \mathrm{~A})$ | 127.88(19) |
| $\mathrm{O}(1 \mathrm{~A})-\mathrm{C}(1 \mathrm{~A})-\mathrm{C}(2 \mathrm{~A})$ | 124.5(3) |
| $\mathrm{O}(1 \mathrm{~A})-\mathrm{C}(1 \mathrm{~A})-\mathrm{C}(6 \mathrm{~A})$ | 114.8(3) |
| $\mathrm{C}(2 \mathrm{~A})-\mathrm{C}(1 \mathrm{~A})-\mathrm{C}(6 \mathrm{~A})$ | 120.7(3) |
| $\mathrm{C}(1 \mathrm{~A})-\mathrm{C}(2 \mathrm{~A})-\mathrm{C}(3 \mathrm{~A})$ | 122.3(3) |
| $\mathrm{C}(1 \mathrm{~A})-\mathrm{C}(2 \mathrm{~A})-\mathrm{H}(2 \mathrm{AA})$ | 118.8 |
| $\mathrm{C}(3 \mathrm{~A})-\mathrm{C}(2 \mathrm{~A})-\mathrm{H}(2 \mathrm{AA})$ | 118.8 |
| $\mathrm{N}(1 \mathrm{~A})-\mathrm{C}(3 \mathrm{~A})-\mathrm{O}(2 \mathrm{~A})$ | 114.6(3) |
| $\mathrm{N}(1 \mathrm{~A})-\mathrm{C}(3 \mathrm{~A})-\mathrm{C}(2 \mathrm{~A})$ | 129.3(3) |
| $\mathrm{O}(2 \mathrm{~A})-\mathrm{C}(3 \mathrm{~A})-\mathrm{C}(2 \mathrm{~A})$ | 116.2(3) |
| $\mathrm{C}(9 \mathrm{~A})-\mathrm{C}(6 \mathrm{~A})-\mathrm{C}(8 \mathrm{~A})$ | 109.0(3) |
| $\mathrm{C}(9 \mathrm{~A})-\mathrm{C}(6 \mathrm{~A})-\mathrm{C}(7 \mathrm{~A})$ | 108.3(3) |
| $\mathrm{C}(8 \mathrm{~A})-\mathrm{C}(6 \mathrm{~A})-\mathrm{C}(7 \mathrm{~A})$ | 110.1(3) |
| $\mathrm{C}(9 \mathrm{~A})-\mathrm{C}(6 \mathrm{~A})-\mathrm{C}(1 \mathrm{~A})$ | 108.9(3) |
| $\mathrm{C}(8 \mathrm{~A})-\mathrm{C}(6 \mathrm{~A})-\mathrm{C}(1 \mathrm{~A})$ | 112.4(3) |
| $\mathrm{C}(7 \mathrm{~A})-\mathrm{C}(6 \mathrm{~A})-\mathrm{C}(1 \mathrm{~A})$ | 108.2(3) |
| $\mathrm{C}(6 \mathrm{~A})-\mathrm{C}(7 \mathrm{~A})-\mathrm{H}(7 \mathrm{AA})$ | 109.5 |
| $\mathrm{C}(6 \mathrm{~A})-\mathrm{C}(7 \mathrm{~A})-\mathrm{H}(7 \mathrm{AB})$ | 109.5 |
| H(7AA)-C(7A)-H(7AB) | 109.5 |
| $\mathrm{C}(6 \mathrm{~A})-\mathrm{C}(7 \mathrm{~A})-\mathrm{H}(7 \mathrm{AC})$ | 109.5 |
| H(7AA)-C(7A)-H(7AC) | 109.5 |
| H(7AB)-C(7A)-H(7AC) | 109.5 |
| $\mathrm{C}(6 \mathrm{~A})-\mathrm{C}(8 \mathrm{~A})-\mathrm{H}(8 \mathrm{AA})$ | 109.5 |
| $\mathrm{C}(6 \mathrm{~A})-\mathrm{C}(8 \mathrm{~A})-\mathrm{H}(8 \mathrm{AB})$ | 109.5 |
| $\mathrm{H}(8 \mathrm{AA})-\mathrm{C}(8 \mathrm{~A})-\mathrm{H}(8 \mathrm{AB})$ | 109.5 |
| $\mathrm{C}(6 \mathrm{~A})-\mathrm{C}(8 \mathrm{~A})-\mathrm{H}(8 \mathrm{AC})$ | 109.5 |
| $\mathrm{H}(8 \mathrm{AA})-\mathrm{C}(8 \mathrm{~A})-\mathrm{H}(8 \mathrm{AC})$ | 109.5 |
| $\mathrm{H}(8 \mathrm{AB})-\mathrm{C}(8 \mathrm{~A})-\mathrm{H}(8 \mathrm{AC})$ | 109.5 |
| $\mathrm{C}(6 \mathrm{~A})-\mathrm{C}(9 \mathrm{~A})-\mathrm{H}(9 \mathrm{AA})$ | 109.5 |
| $\mathrm{C}(6 \mathrm{~A})-\mathrm{C}(9 \mathrm{~A})-\mathrm{H}(9 \mathrm{AB})$ | 109.5 |
| H(9AA)-C(9A)-H(9AB) | 109.5 |
| $\mathrm{C}(6 \mathrm{~A})-\mathrm{C}(9 \mathrm{~A})-\mathrm{H}(9 \mathrm{AC})$ | 109.5 |
| H(9AA)-C(9A)-H(9AC) | 109.5 |
| $\mathrm{H}(9 \mathrm{AB})-\mathrm{C}(9 \mathrm{~A})-\mathrm{H}(9 \mathrm{AC})$ | 109.5 |


| $\mathrm{O}(2 \mathrm{~A})-\mathrm{C}(4 \mathrm{C})-\mathrm{C}(5 \mathrm{C})$ | 104.3(5) |
| :---: | :---: |
| $\mathrm{O}(2 \mathrm{~A})-\mathrm{C}(4 \mathrm{C})-\mathrm{H}(4 \mathrm{AA})$ | 110.9 |
| $\mathrm{C}(5 \mathrm{C})-\mathrm{C}(4 \mathrm{C})-\mathrm{H}(4 \mathrm{AA})$ | 110.9 |
| $\mathrm{O}(2 \mathrm{~A})-\mathrm{C}(4 \mathrm{C})-\mathrm{H}(4 \mathrm{AB})$ | 110.9 |
| $\mathrm{C}(5 \mathrm{C})-\mathrm{C}(4 \mathrm{C})-\mathrm{H}(4 \mathrm{AB})$ | 110.9 |
| $\mathrm{H}(4 \mathrm{AA})-\mathrm{C}(4 \mathrm{C})-\mathrm{H}(4 \mathrm{AB})$ | 108.9 |
| $\mathrm{N}(1 \mathrm{~A})-\mathrm{C}(5 \mathrm{C})-\mathrm{C}(4 \mathrm{C})$ | 103.0(4) |
| $\mathrm{N}(1 \mathrm{~A})-\mathrm{C}(5 \mathrm{C})-\mathrm{C}(11 \mathrm{C})$ | 103.3(5) |
| $\mathrm{C}(4 \mathrm{C})-\mathrm{C}(5 \mathrm{C})-\mathrm{C}(11 \mathrm{C})$ | 111.1(7) |
| $\mathrm{N}(1 \mathrm{~A})-\mathrm{C}(5 \mathrm{C})-\mathrm{C}(10 \mathrm{C})$ | 116.7(4) |
| $\mathrm{C}(4 \mathrm{C})-\mathrm{C}(5 \mathrm{C})-\mathrm{C}(10 \mathrm{C})$ | 115.5(5) |
| $\mathrm{C}(11 \mathrm{C})-\mathrm{C}(5 \mathrm{C})-\mathrm{C}(10 \mathrm{C})$ | 106.6(5) |
| $\mathrm{C}(5 \mathrm{C})-\mathrm{C}(10 \mathrm{C})-\mathrm{H}(10 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(5 \mathrm{C})-\mathrm{C}(10 \mathrm{C})-\mathrm{H}(10 \mathrm{~B})$ | 109.5 |
| $\mathrm{H}(10 \mathrm{~A})-\mathrm{C}(10 \mathrm{C})-\mathrm{H}(10 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(5 \mathrm{C})-\mathrm{C}(10 \mathrm{C})-\mathrm{H}(10 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(10 \mathrm{~A})-\mathrm{C}(10 \mathrm{C})-\mathrm{H}(10 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(10 \mathrm{~B})-\mathrm{C}(10 \mathrm{C})-\mathrm{H}(10 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(5 \mathrm{C})-\mathrm{C}(11 \mathrm{C})-\mathrm{H}(11 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(5 \mathrm{C})-\mathrm{C}(11 \mathrm{C})-\mathrm{H}(11 \mathrm{~B})$ | 109.5 |
| $\mathrm{H}(11 \mathrm{~A})-\mathrm{C}(11 \mathrm{C})-\mathrm{H}(11 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(5 \mathrm{C})-\mathrm{C}(11 \mathrm{C})-\mathrm{H}(11 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(11 \mathrm{~A})-\mathrm{C}(11 \mathrm{C})-\mathrm{H}(11 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(11 \mathrm{~B})-\mathrm{C}(11 \mathrm{C})-\mathrm{H}(11 \mathrm{C})$ | 109.5 |
| $\mathrm{O}(2 \mathrm{~A})-\mathrm{C}(4 \mathrm{~A})-\mathrm{C}(5 \mathrm{~A})$ | 104.2(4) |
| $\mathrm{O}(2 \mathrm{~A})-\mathrm{C}(4 \mathrm{~A})-\mathrm{H}(4 \mathrm{CA})$ | 110.9 |
| $\mathrm{C}(5 \mathrm{~A})-\mathrm{C}(4 \mathrm{~A})-\mathrm{H}(4 \mathrm{CA})$ | 110.9 |
| $\mathrm{O}(2 \mathrm{~A})-\mathrm{C}(4 \mathrm{~A})-\mathrm{H}(4 \mathrm{CB})$ | 110.9 |
| $\mathrm{C}(5 \mathrm{~A})-\mathrm{C}(4 \mathrm{~A})-\mathrm{H}(4 \mathrm{CB})$ | 110.9 |
| $\mathrm{H}(4 \mathrm{CA})-\mathrm{C}(4 \mathrm{~A})-\mathrm{H}(4 \mathrm{CB})$ | 108.9 |
| $\mathrm{N}(1 \mathrm{~A})-\mathrm{C}(5 \mathrm{~A})-\mathrm{C}(11 \mathrm{~A})$ | 113.6(4) |
| $\mathrm{N}(1 \mathrm{~A})-\mathrm{C}(5 \mathrm{~A})-\mathrm{C}(4 \mathrm{~A})$ | 101.8(3) |
| $\mathrm{C}(11 \mathrm{~A})-\mathrm{C}(5 \mathrm{~A})-\mathrm{C}(4 \mathrm{~A})$ | 111.9(5) |
| $\mathrm{N}(1 \mathrm{~A})-\mathrm{C}(5 \mathrm{~A})-\mathrm{C}(10 \mathrm{~A})$ | 104.1(3) |
| $\mathrm{C}(11 \mathrm{~A})-\mathrm{C}(5 \mathrm{~A})-\mathrm{C}(10 \mathrm{~A})$ | 115.9(5) |
| $\mathrm{C}(4 \mathrm{~A})-\mathrm{C}(5 \mathrm{~A})-\mathrm{C}(10 \mathrm{~A})$ | 108.3(5) |


| $\mathrm{C}(5 \mathrm{~A})-\mathrm{C}(10 \mathrm{~A})-\mathrm{H}(10 \mathrm{D})$ | 109.5 |
| :---: | :---: |
| $\mathrm{C}(5 \mathrm{~A})-\mathrm{C}(10 \mathrm{~A})-\mathrm{H}(10 \mathrm{E})$ | 109.5 |
| $\mathrm{H}(10 \mathrm{D})-\mathrm{C}(10 \mathrm{~A})-\mathrm{H}(10 \mathrm{E})$ | 109.5 |
| $\mathrm{C}(5 \mathrm{~A})-\mathrm{C}(10 \mathrm{~A})-\mathrm{H}(10 \mathrm{~F})$ | 109.5 |
| $\mathrm{H}(10 \mathrm{D})-\mathrm{C}(10 \mathrm{~A})-\mathrm{H}(10 \mathrm{~F})$ | 109.5 |
| $\mathrm{H}(10 \mathrm{E})-\mathrm{C}(10 \mathrm{~A})-\mathrm{H}(10 \mathrm{~F})$ | 109.5 |
| $\mathrm{C}(5 \mathrm{~A})-\mathrm{C}(11 \mathrm{~A})-\mathrm{H}(11 \mathrm{D})$ | 109.5 |
| $\mathrm{C}(5 \mathrm{~A})-\mathrm{C}(11 \mathrm{~A})-\mathrm{H}(11 \mathrm{E})$ | 109.5 |
| $\mathrm{H}(11 \mathrm{D})-\mathrm{C}(11 \mathrm{~A})-\mathrm{H}(11 \mathrm{E})$ | 109.5 |
| $\mathrm{C}(5 \mathrm{~A})-\mathrm{C}(11 \mathrm{~A})-\mathrm{H}(11 \mathrm{~F})$ | 109.5 |
| $\mathrm{H}(11 \mathrm{D})-\mathrm{C}(11 \mathrm{~A})-\mathrm{H}(11 \mathrm{~F})$ | 109.5 |
| $\mathrm{H}(11 \mathrm{E})-\mathrm{C}(11 \mathrm{~A})-\mathrm{H}(11 \mathrm{~F})$ | 109.5 |
| $\mathrm{O}(3 \mathrm{~A})-\mathrm{C}(12 \mathrm{~A})-\mathrm{C}(13 \mathrm{~A})$ | 124.7(3) |
| $\mathrm{O}(3 \mathrm{~A})-\mathrm{C}(12 \mathrm{~A})-\mathrm{C}(17 \mathrm{~A})$ | 115.1(3) |
| $\mathrm{C}(13 \mathrm{~A})-\mathrm{C}(12 \mathrm{~A})-\mathrm{C}(17 \mathrm{~A})$ | 120.1(3) |
| $\mathrm{C}(12 \mathrm{~A})-\mathrm{C}(13 \mathrm{~A})-\mathrm{C}(14 \mathrm{~A})$ | 122.2(3) |
| $\mathrm{C}(12 \mathrm{~A})-\mathrm{C}(13 \mathrm{~A})-\mathrm{H}(13 \mathrm{~A})$ | 118.9 |
| $\mathrm{C}(14 \mathrm{~A})-\mathrm{C}(13 \mathrm{~A})-\mathrm{H}(13 \mathrm{~A})$ | 118.9 |
| $\mathrm{N}(2 \mathrm{~A})-\mathrm{C}(14 \mathrm{~A})-\mathrm{O}(4 \mathrm{~A})$ | 115.1(3) |
| $\mathrm{N}(2 \mathrm{~A})-\mathrm{C}(14 \mathrm{~A})-\mathrm{C}(13 \mathrm{~A})$ | 128.5(3) |
| $\mathrm{O}(4 \mathrm{~A})-\mathrm{C}(14 \mathrm{~A})-\mathrm{C}(13 \mathrm{~A})$ | 116.4(3) |
| $\mathrm{O}(4 \mathrm{~A})-\mathrm{C}(15 \mathrm{~A})-\mathrm{C}(16 \mathrm{~A})$ | 104.7(2) |
| $\mathrm{O}(4 \mathrm{~A})-\mathrm{C}(15 \mathrm{~A})-\mathrm{H}(15 \mathrm{~A})$ | 110.8 |
| $\mathrm{C}(16 \mathrm{~A})-\mathrm{C}(15 \mathrm{~A})-\mathrm{H}(15 \mathrm{~A})$ | 110.8 |
| $\mathrm{O}(4 \mathrm{~A})-\mathrm{C}(15 \mathrm{~A})-\mathrm{H}(15 \mathrm{~B})$ | 110.8 |
| $\mathrm{C}(16 \mathrm{~A})-\mathrm{C}(15 \mathrm{~A})-\mathrm{H}(15 \mathrm{~B})$ | 110.8 |
| $\mathrm{H}(15 \mathrm{~A})-\mathrm{C}(15 \mathrm{~A})-\mathrm{H}(15 \mathrm{~B})$ | 108.9 |
| $\mathrm{N}(2 \mathrm{~A})-\mathrm{C}(16 \mathrm{~A})-\mathrm{C}(21 \mathrm{~A})$ | 110.9(2) |
| $\mathrm{N}(2 \mathrm{~A})-\mathrm{C}(16 \mathrm{~A})-\mathrm{C}(15 \mathrm{~A})$ | 101.3(2) |
| $\mathrm{C}(21 \mathrm{~A})-\mathrm{C}(16 \mathrm{~A})-\mathrm{C}(15 \mathrm{~A})$ | 112.8(3) |
| $\mathrm{N}(2 \mathrm{~A})-\mathrm{C}(16 \mathrm{~A})-\mathrm{C}(22 \mathrm{~A})$ | 108.5(2) |
| $\mathrm{C}(21 \mathrm{~A})-\mathrm{C}(16 \mathrm{~A})-\mathrm{C}(22 \mathrm{~A})$ | 112.0(3) |
| $\mathrm{C}(15 \mathrm{~A})-\mathrm{C}(16 \mathrm{~A})-\mathrm{C}(22 \mathrm{~A})$ | 110.7(3) |
| $\mathrm{C}(20 \mathrm{~A})-\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(18 \mathrm{~A})$ | 111.6(4) |
| $\mathrm{C}(19 \mathrm{C})-\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(20 \mathrm{C})$ | 112.8(4) |
| $\mathrm{C}(19 \mathrm{C})-\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(12 \mathrm{~A})$ | 115.8(4) |


| $\mathrm{C}(20 \mathrm{~A})-\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(12 \mathrm{~A})$ | 113.3(4) |
| :---: | :---: |
| $\mathrm{C}(18 \mathrm{~A})-\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(12 \mathrm{~A})$ | 109.2(3) |
| $\mathrm{C}(20 \mathrm{C})-\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(12 \mathrm{~A})$ | 105.2(4) |
| C(19C)-C(17A)-C(18C) | 110.9(4) |
| C(20C)-C(17A)-C(18C) | 106.4(4) |
| $\mathrm{C}(12 \mathrm{~A})-\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(18 \mathrm{C})$ | 104.9(4) |
| $\mathrm{C}(20 \mathrm{~A})-\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(19 \mathrm{~A})$ | 107.4(4) |
| $\mathrm{C}(18 \mathrm{~A})-\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(19 \mathrm{~A})$ | 106.4(3) |
| $\mathrm{C}(12 \mathrm{~A})-\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(19 \mathrm{~A})$ | 108.6(3) |
| $\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(18 \mathrm{~A})-\mathrm{H}(18 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(18 \mathrm{~A})-\mathrm{H}(18 \mathrm{~B})$ | 109.5 |
| $\mathrm{H}(18 \mathrm{~A})-\mathrm{C}(18 \mathrm{~A})-\mathrm{H}(18 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(18 \mathrm{~A})-\mathrm{H}(18 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(18 \mathrm{~A})-\mathrm{C}(18 \mathrm{~A})-\mathrm{H}(18 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(18 \mathrm{~B})-\mathrm{C}(18 \mathrm{~A})-\mathrm{H}(18 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(19 \mathrm{~A})-\mathrm{H}(19 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(19 \mathrm{~A})-\mathrm{H}(19 \mathrm{~B})$ | 109.5 |
| $\mathrm{H}(19 \mathrm{~A})-\mathrm{C}(19 \mathrm{~A})-\mathrm{H}(19 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(19 \mathrm{~A})-\mathrm{H}(19 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(19 \mathrm{~A})-\mathrm{C}(19 \mathrm{~A})-\mathrm{H}(19 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(19 \mathrm{~B})-\mathrm{C}(19 \mathrm{~A})-\mathrm{H}(19 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(20 \mathrm{~A})-\mathrm{H}(20 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(20 \mathrm{~A})-\mathrm{H}(20 \mathrm{~B})$ | 109.5 |
| $\mathrm{H}(20 \mathrm{~A})-\mathrm{C}(20 \mathrm{~A})-\mathrm{H}(20 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(20 \mathrm{~A})-\mathrm{H}(20 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(20 \mathrm{~A})-\mathrm{C}(20 \mathrm{~A})-\mathrm{H}(20 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(20 \mathrm{~B})-\mathrm{C}(20 \mathrm{~A})-\mathrm{H}(20 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(18 \mathrm{C})-\mathrm{H}(18 \mathrm{G})$ | 109.5 |
| $\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(18 \mathrm{C})-\mathrm{H}(18 \mathrm{H})$ | 109.5 |
| H(18G)-C(18C)-H(18H) | 109.5 |
| $\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(18 \mathrm{C})-\mathrm{H}(18 \mathrm{I})$ | 109.5 |
| H(18G)-C(18C)-H(18I) | 109.5 |
| $\mathrm{H}(18 \mathrm{H})-\mathrm{C}(18 \mathrm{C})-\mathrm{H}(18 \mathrm{I})$ | 109.5 |
| $\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(19 \mathrm{C})-\mathrm{H}(19 \mathrm{G})$ | 109.5 |
| $\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(19 \mathrm{C})-\mathrm{H}(19 \mathrm{H})$ | 109.5 |
| H(19G)-C(19C)-H(19H) | 109.5 |


| $\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(19 \mathrm{C})-\mathrm{H}(19 \mathrm{I})$ | 109.5 |
| :---: | :---: |
| H(19G)-C(19C)-H(19I) | 109.5 |
| $\mathrm{H}(19 \mathrm{H})-\mathrm{C}(19 \mathrm{C})-\mathrm{H}(19 \mathrm{I})$ | 109.5 |
| $\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(20 \mathrm{C})-\mathrm{H}(20 \mathrm{G})$ | 109.5 |
| $\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(20 \mathrm{C})-\mathrm{H}(20 \mathrm{H})$ | 109.5 |
| $\mathrm{H}(20 \mathrm{G})-\mathrm{C}(20 \mathrm{C})-\mathrm{H}(20 \mathrm{H})$ | 109.5 |
| $\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(20 \mathrm{C})-\mathrm{H}(20 \mathrm{I})$ | 109.5 |
| H(20G)-C(20C)-H(20I) | 109.5 |
| $\mathrm{H}(20 \mathrm{H})-\mathrm{C}(20 \mathrm{C})-\mathrm{H}(20 \mathrm{I})$ | 109.5 |
| $\mathrm{C}(16 \mathrm{~A})-\mathrm{C}(21 \mathrm{~A})-\mathrm{H}(21 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(16 \mathrm{~A})-\mathrm{C}(21 \mathrm{~A})-\mathrm{H}(21 \mathrm{~B})$ | 109.5 |
| $\mathrm{H}(21 \mathrm{~A})-\mathrm{C}(21 \mathrm{~A})-\mathrm{H}(21 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(16 \mathrm{~A})-\mathrm{C}(21 \mathrm{~A})-\mathrm{H}(21 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(21 \mathrm{~A})-\mathrm{C}(21 \mathrm{~A})-\mathrm{H}(21 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(21 \mathrm{~B})-\mathrm{C}(21 \mathrm{~A})-\mathrm{H}(21 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(16 \mathrm{~A})-\mathrm{C}(22 \mathrm{~A})-\mathrm{H}(22 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(16 \mathrm{~A})-\mathrm{C}(22 \mathrm{~A})-\mathrm{H}(22 \mathrm{~B})$ | 109.5 |
| $\mathrm{H}(22 \mathrm{~A})-\mathrm{C}(22 \mathrm{~A})-\mathrm{H}(22 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(16 \mathrm{~A})-\mathrm{C}(22 \mathrm{~A})-\mathrm{H}(22 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(22 \mathrm{~A})-\mathrm{C}(22 \mathrm{~A})-\mathrm{H}(22 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(22 \mathrm{~B})-\mathrm{C}(22 \mathrm{~A})-\mathrm{H}(22 \mathrm{C})$ | 109.5 |
| $\mathrm{O}(1 \mathrm{~B})-\mathrm{Cu}(1 \mathrm{~B})-\mathrm{O}(3 \mathrm{~B})$ | 144.32(9) |
| $\mathrm{O}(1 \mathrm{~B})-\mathrm{Cu}(1 \mathrm{~B})-\mathrm{N}(2 \mathrm{~B})$ | 97.60(10) |
| $\mathrm{O}(3 \mathrm{~B})-\mathrm{Cu}(1 \mathrm{~B})-\mathrm{N}(2 \mathrm{~B})$ | 92.58(9) |
| $\mathrm{O}(1 \mathrm{~B})-\mathrm{Cu}(1 \mathrm{~B})-\mathrm{N}(1 \mathrm{~B})$ | 92.50(9) |
| $\mathrm{O}(3 \mathrm{~B})-\mathrm{Cu}(1 \mathrm{~B})-\mathrm{N}(1 \mathrm{~B})$ | 98.69(9) |
| $\mathrm{N}(2 \mathrm{~B})-\mathrm{Cu}(1 \mathrm{~B})-\mathrm{N}(1 \mathrm{~B})$ | 144.66(10) |
| $\mathrm{C}(1 \mathrm{~B})-\mathrm{O}(1 \mathrm{~B})-\mathrm{Cu}(1 \mathrm{~B})$ | 128.2(2) |
| $\mathrm{C}(3 \mathrm{~B})-\mathrm{O}(2 \mathrm{~B})-\mathrm{C}(4 \mathrm{~B})$ | 105.7(2) |
| $\mathrm{C}(12 \mathrm{~B})-\mathrm{O}(3 \mathrm{~B})-\mathrm{Cu}(1 \mathrm{~B})$ | 128.1(2) |
| $\mathrm{C}(14 \mathrm{~B})-\mathrm{O}(4 \mathrm{~B})-\mathrm{C}(15 \mathrm{~B})$ | 105.3(2) |
| $\mathrm{C}(3 \mathrm{~B})-\mathrm{N}(1 \mathrm{~B})-\mathrm{C}(5 \mathrm{~B})$ | 109.0(2) |
| $\mathrm{C}(3 \mathrm{~B})-\mathrm{N}(1 \mathrm{~B})-\mathrm{Cu}(1 \mathrm{~B})$ | 123.2(2) |
| $\mathrm{C}(5 \mathrm{~B})-\mathrm{N}(1 \mathrm{~B})-\mathrm{Cu}(1 \mathrm{~B})$ | 127.69(18) |
| $\mathrm{C}(14 \mathrm{~B})-\mathrm{N}(2 \mathrm{~B})-\mathrm{C}(16 \mathrm{~B})$ | 108.3(2) |
| $\mathrm{C}(14 \mathrm{~B})-\mathrm{N}(2 \mathrm{~B})-\mathrm{Cu}(1 \mathrm{~B})$ | 123.5(2) |


| $\mathrm{C}(16 \mathrm{~B})-\mathrm{N}(2 \mathrm{~B})-\mathrm{Cu}(1 \mathrm{~B})$ | 128.08(19) |
| :---: | :---: |
| $\mathrm{O}(1 \mathrm{~B})-\mathrm{C}(1 \mathrm{~B})-\mathrm{C}(2 \mathrm{~B})$ | 124.8(3) |
| $\mathrm{O}(1 \mathrm{~B})-\mathrm{C}(1 \mathrm{~B})-\mathrm{C}(6 \mathrm{~B})$ | 114.4(3) |
| $\mathrm{C}(2 \mathrm{~B})-\mathrm{C}(1 \mathrm{~B})-\mathrm{C}(6 \mathrm{~B})$ | 120.7(3) |
| $\mathrm{C}(1 \mathrm{~B})-\mathrm{C}(2 \mathrm{~B})-\mathrm{C}(3 \mathrm{~B})$ | 122.0(3) |
| $\mathrm{C}(1 \mathrm{~B})-\mathrm{C}(2 \mathrm{~B})-\mathrm{H}(2 \mathrm{BA})$ | 119.0 |
| $\mathrm{C}(3 \mathrm{~B})-\mathrm{C}(2 \mathrm{~B})-\mathrm{H}(2 \mathrm{BA})$ | 119.0 |
| $\mathrm{N}(1 \mathrm{~B})-\mathrm{C}(3 \mathrm{~B})-\mathrm{O}(2 \mathrm{~B})$ | 115.1(3) |
| $\mathrm{N}(1 \mathrm{~B})-\mathrm{C}(3 \mathrm{~B})-\mathrm{C}(2 \mathrm{~B})$ | 128.5(3) |
| $\mathrm{O}(2 \mathrm{~B})-\mathrm{C}(3 \mathrm{~B})-\mathrm{C}(2 \mathrm{~B})$ | 116.4(3) |
| $\mathrm{O}(2 \mathrm{~B})-\mathrm{C}(4 \mathrm{~B})-\mathrm{C}(5 \mathrm{~B})$ | 105.1(2) |
| $\mathrm{O}(2 \mathrm{~B})-\mathrm{C}(4 \mathrm{~B})-\mathrm{H}(4 \mathrm{BA})$ | 110.7 |
| $\mathrm{C}(5 \mathrm{~B})-\mathrm{C}(4 \mathrm{~B})-\mathrm{H}(4 \mathrm{BA})$ | 110.7 |
| $\mathrm{O}(2 \mathrm{~B})-\mathrm{C}(4 \mathrm{~B})-\mathrm{H}(4 \mathrm{BB})$ | 110.7 |
| $\mathrm{C}(5 \mathrm{~B})-\mathrm{C}(4 \mathrm{~B})-\mathrm{H}(4 \mathrm{BB})$ | 110.7 |
| $\mathrm{H}(4 \mathrm{BA})-\mathrm{C}(4 \mathrm{~B})-\mathrm{H}(4 \mathrm{BB})$ | 108.8 |
| $\mathrm{N}(1 \mathrm{~B})-\mathrm{C}(5 \mathrm{~B})-\mathrm{C}(11 \mathrm{~B})$ | 110.9(2) |
| $\mathrm{N}(1 \mathrm{~B})-\mathrm{C}(5 \mathrm{~B})-\mathrm{C}(10 \mathrm{~B})$ | 109.0(2) |
| $\mathrm{C}(11 \mathrm{~B})-\mathrm{C}(5 \mathrm{~B})-\mathrm{C}(10 \mathrm{~B})$ | 112.9(3) |
| $\mathrm{N}(1 \mathrm{~B})-\mathrm{C}(5 \mathrm{~B})-\mathrm{C}(4 \mathrm{~B})$ | 101.0(2) |
| $\mathrm{C}(11 \mathrm{~B})-\mathrm{C}(5 \mathrm{~B})-\mathrm{C}(4 \mathrm{~B})$ | 111.9(3) |
| $\mathrm{C}(10 \mathrm{~B})-\mathrm{C}(5 \mathrm{~B})-\mathrm{C}(4 \mathrm{~B})$ | 110.5(3) |
| $\mathrm{C}(7 \mathrm{~B})-\mathrm{C}(6 \mathrm{~B})-\mathrm{C}(8 \mathrm{~B})$ | 110.0(3) |
| $\mathrm{C}(7 \mathrm{~B})-\mathrm{C}(6 \mathrm{~B})-\mathrm{C}(9 \mathrm{~B})$ | 109.2(3) |
| $\mathrm{C}(8 \mathrm{~B})-\mathrm{C}(6 \mathrm{~B})-\mathrm{C}(9 \mathrm{~B})$ | 108.4(3) |
| $\mathrm{C}(7 \mathrm{~B})-\mathrm{C}(6 \mathrm{~B})-\mathrm{C}(1 \mathrm{~B})$ | 107.2(3) |
| $\mathrm{C}(8 \mathrm{~B})-\mathrm{C}(6 \mathrm{~B})-\mathrm{C}(1 \mathrm{~B})$ | 113.2(3) |
| $\mathrm{C}(9 \mathrm{~B})-\mathrm{C}(6 \mathrm{~B})-\mathrm{C}(1 \mathrm{~B})$ | 108.8(3) |
| $\mathrm{C}(6 \mathrm{~B})-\mathrm{C}(7 \mathrm{~B})-\mathrm{H}(7 \mathrm{BA})$ | 109.5 |
| $\mathrm{C}(6 \mathrm{~B})-\mathrm{C}(7 \mathrm{~B})-\mathrm{H}(7 \mathrm{BB})$ | 109.5 |
| $\mathrm{H}(7 \mathrm{BA})-\mathrm{C}(7 \mathrm{~B})-\mathrm{H}(7 \mathrm{BB})$ | 109.5 |
| $\mathrm{C}(6 \mathrm{~B})-\mathrm{C}(7 \mathrm{~B})-\mathrm{H}(7 \mathrm{BC})$ | 109.5 |
| H(7BA)-C(7B)-H(7BC) | 109.5 |
| $\mathrm{H}(7 \mathrm{BB})-\mathrm{C}(7 \mathrm{~B})-\mathrm{H}(7 \mathrm{BC})$ | 109.5 |
| $\mathrm{C}(6 \mathrm{~B})-\mathrm{C}(8 \mathrm{~B})-\mathrm{H}(8 \mathrm{BA})$ | 109.5 |
| $\mathrm{C}(6 \mathrm{~B})-\mathrm{C}(8 \mathrm{~B})-\mathrm{H}(8 \mathrm{BB})$ | 109.5 |


| $\mathrm{H}(8 \mathrm{BA})-\mathrm{C}(8 \mathrm{~B})-\mathrm{H}(8 \mathrm{BB})$ | 109.5 |
| :---: | :---: |
| $\mathrm{C}(6 \mathrm{~B})-\mathrm{C}(8 \mathrm{~B})-\mathrm{H}(8 \mathrm{BC})$ | 109.5 |
| $\mathrm{H}(8 \mathrm{BA})-\mathrm{C}(8 \mathrm{~B})-\mathrm{H}(8 \mathrm{BC})$ | 109.5 |
| $\mathrm{H}(8 \mathrm{BB})-\mathrm{C}(8 \mathrm{~B})-\mathrm{H}(8 \mathrm{BC})$ | 109.5 |
| $\mathrm{C}(6 \mathrm{~B})-\mathrm{C}(9 \mathrm{~B})-\mathrm{H}(9 \mathrm{BA})$ | 109.5 |
| $\mathrm{C}(6 \mathrm{~B})-\mathrm{C}(9 \mathrm{~B})-\mathrm{H}(9 \mathrm{BB})$ | 109.5 |
| $\mathrm{H}(9 \mathrm{BA})-\mathrm{C}(9 \mathrm{~B})-\mathrm{H}(9 \mathrm{BB})$ | 109.5 |
| $\mathrm{C}(6 \mathrm{~B})-\mathrm{C}(9 \mathrm{~B})-\mathrm{H}(9 \mathrm{CC})$ | 109.5 |
| H(9BA)-C(9B)-H(9BC) | 109.5 |
| $\mathrm{H}(9 \mathrm{BB})-\mathrm{C}(9 \mathrm{~B})-\mathrm{H}(9 \mathrm{BC})$ | 109.5 |
| $\mathrm{C}(5 \mathrm{~B})-\mathrm{C}(10 \mathrm{~B})-\mathrm{H}(10 \mathrm{G})$ | 109.5 |
| $\mathrm{C}(5 \mathrm{~B})-\mathrm{C}(10 \mathrm{~B})-\mathrm{H}(10 \mathrm{H})$ | 109.5 |
| $\mathrm{H}(10 \mathrm{G})-\mathrm{C}(10 \mathrm{~B})-\mathrm{H}(10 \mathrm{H})$ | 109.5 |
| $\mathrm{C}(5 \mathrm{~B})-\mathrm{C}(10 \mathrm{~B})-\mathrm{H}(10 \mathrm{I})$ | 109.5 |
| H(10G)-C(10B)-H(10I) | 109.5 |
| $\mathrm{H}(10 \mathrm{H})-\mathrm{C}(10 \mathrm{~B})-\mathrm{H}(10 \mathrm{I})$ | 109.5 |
| $\mathrm{C}(5 \mathrm{~B})-\mathrm{C}(11 \mathrm{~B})-\mathrm{H}(11 \mathrm{G})$ | 109.5 |
| $\mathrm{C}(5 \mathrm{~B})-\mathrm{C}(11 \mathrm{~B})-\mathrm{H}(11 \mathrm{H})$ | 109.5 |
| $\mathrm{H}(11 \mathrm{G})-\mathrm{C}(11 \mathrm{~B})-\mathrm{H}(11 \mathrm{H})$ | 109.5 |
| $\mathrm{C}(5 \mathrm{~B})-\mathrm{C}(11 \mathrm{~B})-\mathrm{H}(11 \mathrm{I})$ | 109.5 |
| $\mathrm{H}(11 \mathrm{G})-\mathrm{C}(11 \mathrm{~B})-\mathrm{H}(11 \mathrm{I})$ | 109.5 |
| $\mathrm{H}(11 \mathrm{H})-\mathrm{C}(11 \mathrm{~B})-\mathrm{H}(11 \mathrm{I})$ | 109.5 |
| $\mathrm{O}(3 \mathrm{~B})-\mathrm{C}(12 \mathrm{~B})-\mathrm{C}(13 \mathrm{~B})$ | 124.1(3) |
| $\mathrm{O}(3 \mathrm{~B})-\mathrm{C}(12 \mathrm{~B})-\mathrm{C}(17 \mathrm{~B})$ | 114.6(3) |
| $\mathrm{C}(13 \mathrm{~B})-\mathrm{C}(12 \mathrm{~B})-\mathrm{C}(17 \mathrm{~B})$ | 121.4(3) |
| $\mathrm{C}(12 \mathrm{~B})-\mathrm{C}(13 \mathrm{~B})-\mathrm{C}(14 \mathrm{~B})$ | 123.0(3) |
| $\mathrm{C}(12 \mathrm{~B})-\mathrm{C}(13 \mathrm{~B})-\mathrm{H}(13 \mathrm{~B})$ | 118.5 |
| $\mathrm{C}(14 \mathrm{~B})-\mathrm{C}(13 \mathrm{~B})-\mathrm{H}(13 \mathrm{~B})$ | 118.5 |
| $\mathrm{N}(2 \mathrm{~B})-\mathrm{C}(14 \mathrm{~B})-\mathrm{O}(4 \mathrm{~B})$ | 114.9(3) |
| $\mathrm{N}(2 \mathrm{~B})-\mathrm{C}(14 \mathrm{~B})-\mathrm{C}(13 \mathrm{~B})$ | 128.2(3) |
| $\mathrm{O}(4 \mathrm{~B})-\mathrm{C}(14 \mathrm{~B})-\mathrm{C}(13 \mathrm{~B})$ | 116.9(3) |
| $\mathrm{O}(4 \mathrm{~B})-\mathrm{C}(15 \mathrm{~B})-\mathrm{C}(16 \mathrm{~B})$ | 104.3(2) |
| $\mathrm{O}(4 \mathrm{~B})-\mathrm{C}(15 \mathrm{~B})-\mathrm{H}(15 \mathrm{C})$ | 110.9 |
| $\mathrm{C}(16 \mathrm{~B})-\mathrm{C}(15 \mathrm{~B})-\mathrm{H}(15 \mathrm{C})$ | 110.9 |
| $\mathrm{O}(4 \mathrm{~B})-\mathrm{C}(15 \mathrm{~B})-\mathrm{H}(15 \mathrm{D})$ | 110.9 |
| $\mathrm{C}(16 \mathrm{~B})-\mathrm{C}(15 \mathrm{~B})-\mathrm{H}(15 \mathrm{D})$ | 110.9 |


| $\mathrm{H}(15 \mathrm{C})-\mathrm{C}(15 \mathrm{~B})-\mathrm{H}(15 \mathrm{D})$ | 108.9 |
| :---: | :---: |
| $\mathrm{N}(2 \mathrm{~B})-\mathrm{C}(16 \mathrm{~B})-\mathrm{C}(21 \mathrm{~B})$ | 110.8(2) |
| $\mathrm{N}(2 \mathrm{~B})-\mathrm{C}(16 \mathrm{~B})-\mathrm{C}(15 \mathrm{~B})$ | 100.7(2) |
| $\mathrm{C}(21 \mathrm{~B})-\mathrm{C}(16 \mathrm{~B})-\mathrm{C}(15 \mathrm{~B})$ | 112.2(3) |
| $\mathrm{N}(2 \mathrm{~B})-\mathrm{C}(16 \mathrm{~B})-\mathrm{C}(22 \mathrm{~B})$ | 109.1(2) |
| $\mathrm{C}(21 \mathrm{~B})-\mathrm{C}(16 \mathrm{~B})-\mathrm{C}(22 \mathrm{~B})$ | 112.1(3) |
| $\mathrm{C}(15 \mathrm{~B})-\mathrm{C}(16 \mathrm{~B})-\mathrm{C}(22 \mathrm{~B})$ | 111.3(3) |
| $\mathrm{C}(19 \mathrm{~B})-\mathrm{C}(17 \mathrm{~B})-\mathrm{C}(18 \mathrm{~B})$ | 110.7(3) |
| C(19B)-C(17B)-C(20B) | 108.6(4) |
| $\mathrm{C}(18 \mathrm{~B})-\mathrm{C}(17 \mathrm{~B})-\mathrm{C}(20 \mathrm{~B})$ | 106.6(4) |
| $\mathrm{C}(19 \mathrm{~B})-\mathrm{C}(17 \mathrm{~B})-\mathrm{C}(12 \mathrm{~B})$ | 114.1(3) |
| $\mathrm{C}(18 \mathrm{~B})-\mathrm{C}(17 \mathrm{~B})-\mathrm{C}(12 \mathrm{~B})$ | 108.7(3) |
| $\mathrm{C}(20 \mathrm{~B})-\mathrm{C}(17 \mathrm{~B})-\mathrm{C}(12 \mathrm{~B})$ | 107.8(3) |
| C(17B)-C(18B)-H(18D) | 109.5 |
| $\mathrm{C}(17 \mathrm{~B})-\mathrm{C}(18 \mathrm{~B})-\mathrm{H}(18 \mathrm{E})$ | 109.5 |
| $\mathrm{H}(18 \mathrm{D})-\mathrm{C}(18 \mathrm{~B})-\mathrm{H}(18 \mathrm{E})$ | 109.5 |
| $\mathrm{C}(17 \mathrm{~B})-\mathrm{C}(18 \mathrm{~B})-\mathrm{H}(18 \mathrm{~F})$ | 109.5 |
| $\mathrm{H}(18 \mathrm{D})-\mathrm{C}(18 \mathrm{~B})-\mathrm{H}(18 \mathrm{~F})$ | 109.5 |
| $\mathrm{H}(18 \mathrm{E})-\mathrm{C}(18 \mathrm{~B})-\mathrm{H}(18 \mathrm{~F})$ | 109.5 |
| C(17B)-C(19B)-H(19D) | 109.5 |
| C(17B)-C(19B)-H(19E) | 109.5 |
| H(19D)-C(19B)-H(19E) | 109.5 |
| $\mathrm{C}(17 \mathrm{~B})-\mathrm{C}(19 \mathrm{~B})-\mathrm{H}(19 \mathrm{~F})$ | 109.5 |
| H(19D)-C(19B)-H(19F) | 109.5 |
| $\mathrm{H}(19 \mathrm{E})-\mathrm{C}(19 \mathrm{~B})-\mathrm{H}(19 \mathrm{~F})$ | 109.5 |
| $\mathrm{C}(17 \mathrm{~B})-\mathrm{C}(20 \mathrm{~B})-\mathrm{H}(20 \mathrm{D})$ | 109.5 |
| $\mathrm{C}(17 \mathrm{~B})-\mathrm{C}(20 \mathrm{~B})-\mathrm{H}(20 \mathrm{E})$ | 109.5 |
| $\mathrm{H}(20 \mathrm{D})-\mathrm{C}(20 \mathrm{~B})-\mathrm{H}(20 \mathrm{E})$ | 109.5 |
| $\mathrm{C}(17 \mathrm{~B})-\mathrm{C}(20 \mathrm{~B})-\mathrm{H}(20 \mathrm{~F})$ | 109.5 |
| $\mathrm{H}(20 \mathrm{D})-\mathrm{C}(20 \mathrm{~B})-\mathrm{H}(20 \mathrm{~F})$ | 109.5 |
| $\mathrm{H}(20 \mathrm{E})-\mathrm{C}(20 \mathrm{~B})-\mathrm{H}(20 \mathrm{~F})$ | 109.5 |
| $\mathrm{C}(16 \mathrm{~B})-\mathrm{C}(21 \mathrm{~B})-\mathrm{H}(21 \mathrm{D})$ | 109.5 |
| $\mathrm{C}(16 \mathrm{~B})-\mathrm{C}(21 \mathrm{~B})-\mathrm{H}(21 \mathrm{E})$ | 109.5 |
| $\mathrm{H}(21 \mathrm{D})-\mathrm{C}(21 \mathrm{~B})-\mathrm{H}(21 \mathrm{E})$ | 109.5 |
| $\mathrm{C}(16 \mathrm{~B})-\mathrm{C}(21 \mathrm{~B})-\mathrm{H}(21 \mathrm{~F})$ | 109.5 |
| $\mathrm{H}(21 \mathrm{D})-\mathrm{C}(21 \mathrm{~B})-\mathrm{H}(21 \mathrm{~F})$ | 109.5 |


| $\mathrm{H}(21 \mathrm{E})-\mathrm{C}(21 \mathrm{~B})-\mathrm{H}(21 \mathrm{~F})$ | 109.5 |
| :--- | :--- |
| $\mathrm{C}(16 \mathrm{~B})-\mathrm{C}(22 \mathrm{~B})-\mathrm{H}(22 \mathrm{D})$ | 109.5 |
| $\mathrm{C}(16 \mathrm{~B})-\mathrm{C}(22 \mathrm{~B})-\mathrm{H}(22 \mathrm{E})$ | 109.5 |
| $\mathrm{H}(22 \mathrm{D})-\mathrm{C}(22 \mathrm{~B})-\mathrm{H}(22 \mathrm{E})$ | 109.5 |
| $\mathrm{C}(16 \mathrm{~B})-\mathrm{C}(22 \mathrm{~B})-\mathrm{H}(22 \mathrm{~F})$ | 109.5 |
| $\mathrm{H}(22 \mathrm{D})-\mathrm{C}(22 \mathrm{~B})-\mathrm{H}(22 \mathrm{~F})$ | 109.5 |
| $\mathrm{H}(22 \mathrm{E})-\mathrm{C}(22 \mathrm{~B})-\mathrm{H}(22 \mathrm{~F})$ | 109.5 |

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for d1871_a. The anisotropic displacement factor exponent takes the form: $-2 p^{2}\left[h^{2} a^{* 2} U^{11}+\ldots+2 h k a^{*} b^{*} U^{12}\right]$

|  | $\mathrm{U}^{11}$ | $\mathrm{U}^{22}$ | $\mathrm{U}^{33}$ | $\mathrm{U}^{23}$ | $\mathrm{U}^{13}$ | $\mathrm{U}^{12}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{Cu}(1 \mathrm{~A})$ | 26(1) | 21(1) | 18(1) | 0(1) | 3(1) | 8(1) |
| $\mathrm{O}(1 \mathrm{~A})$ | 31(1) | 23(1) | 21(1) | 2(1) | 6(1) | 8(1) |
| $\mathrm{O}(2 \mathrm{~A})$ | 55(2) | 47(2) | 21(1) | 9(1) | 16(1) | 27(1) |
| $\mathrm{O}(3 \mathrm{~A})$ | 37(1) | 22(1) | 21(1) | 1(1) | -4(1) | 6 (1) |
| $\mathrm{O}(4 \mathrm{~A})$ | 33(1) | 34(1) | 21(1) | 5(1) | -5(1) | -3(1) |
| $\mathrm{N}(1 \mathrm{~A})$ | 28(2) | 29(2) | 23(1) | -2(1) | 4(1) | 15(1) |
| $\mathrm{N}(2 \mathrm{~A})$ | 18(1) | 21(1) | 18(1) | -2(1) | 2(1) | 3(1) |
| C(1A) | 17(2) | 24(2) | 28(2) | 3(1) | 4(1) | 6(1) |
| $\mathrm{C}(2 \mathrm{~A})$ | 30(2) | 31(2) | 23(2) | 8(1) | 5(1) | 14(1) |
| C(3A) | 26(2) | 39(2) | 20(2) | 2(1) | $6(1)$ | 14(2) |
| C(6A) | 32(2) | 21(2) | 35(2) | 2(1) | 12(2) | 9(1) |
| C(7A) | 38(2) | 26(2) | 83(3) | -14(2) | 14(2) | -1(2) |
| C(8A) | 99(3) | 37(2) | 53(3) | 19(2) | 29(2) | 42(2) |
| C(9A) | 39(2) | 32(2) | 41(2) | -4(2) | 17(2) | 13(2) |
| C(4C) | 66(10) | 61(7) | 23(5) | 3(5) | 4(5) | 53(6) |
| C(5C) | 29(2) | 27(2) | 26(2) | -4(1) | 10(1) | 10(1) |
| C(10C) | 40(5) | 29(5) | 43(5) | -9(4) | 16(4) | 4(4) |
| C(11C) | 56(6) | 39(6) | 42(6) | 11(5) | 20(5) | 42(5) |
| C(4A) | 47(7) | 63(6) | 15(4) | -1(4) | 2(4) | 40(4) |
| $\mathrm{C}(5 \mathrm{~A})$ | 29(2) | 27(2) | 26(2) | -4(1) | 10(1) | 10(1) |
| C(10A) | 37(4) | 37(4) | 36(4) | -17(3) | 11(3) | 2(3) |
| C(11A) | 72(6) | 41(6) | 35(4) | 13(5) | 14(4) | 45(5) |
| C(12A) | 21(2) | 20(2) | 30(2) | $0(1)$ | 5(1) | 9(1) |
| C(13A) | 25(2) | 24(2) | 24(2) | 3(1) | 4(1) | 3(1) |
| C(14A) | 24(2) | 27(2) | 19(2) | -1(1) | 2(1) | 8(1) |
| C(15A) | 32(2) | 29(2) | 33(2) | -1(2) | -4(2) | $0(2)$ |
| C(16A) | 23(2) | 24(2) | 19(2) | -5(1) | 1(1) | 3(1) |
| C(17A) | 28(2) | 21(2) | 37(2) | -2(1) | -1(2) | 6 (1) |
| C(18A) | 48(2) | 23(2) | 52(2) | 2(2) | -4(2) | $0(1)$ |
| C(19A) | 48(2) | 23(2) | 52(2) | 2(2) | -4(2) | $0(1)$ |
| C(20A) | 48(2) | 23(2) | 52(2) | 2(2) | -4(2) | $0(1)$ |
| 457 |  |  |  |  |  |  |


| C(18C) | 48(2) | 23(2) | 52(2) | 2(2) | -4(2) | 0 (1) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| C(19C) | 48(2) | 23(2) | 52(2) | 2(2) | -4(2) | 0 (1) |
| C(20C) | 48(2) | 23(2) | 52(2) | 2(2) | -4(2) | 0 (1) |
| C (21A) | 26(2) | 31(2) | 37(2) | -3(2) | 8(2) | 1(1) |
| $\mathrm{C}(22 \mathrm{~A})$ | 32(2) | 31(2) | 30(2) | -12(2) | 4(2) | 3(2) |
| $\mathrm{Cu}(1 \mathrm{~B})$ | 25(1) | 19(1) | 19(1) | -1(1) | 4(1) | 4(1) |
| $\mathrm{O}(1 \mathrm{~B})$ | 32(1) | 20(1) | 24(1) | 0 (1) | 3(1) | 6(1) |
| $\mathrm{O}(2 \mathrm{~B})$ | 32(1) | 22(1) | 27(1) | -4(1) | -1(1) | 1(1) |
| $\mathrm{O}(3 \mathrm{~B})$ | 30(1) | 16(1) | 27(1) | -2(1) | 8(1) | 4(1) |
| $\mathrm{O}(4 \mathrm{~B})$ | 36(1) | 34(1) | 31(1) | -11(1) | 12(1) | 8(1) |
| N(1B) | 22(1) | 17(1) | 18(1) | 2(1) | 4(1) | 4(1) |
| N(2B) | 19(1) | 24(1) | 21(1) | -1(1) | 5(1) | 4(1) |
| C(1B) | 23(2) | 22(2) | 31(2) | 7(1) | 12(1) | 5(1) |
| C(2B) | 28(2) | 15(2) | 28(2) | 0 (1) | 10(1) | 6 (1) |
| C(3B) | 18(2) | 22(2) | 24(2) | -4(1) | 8(1) | 0 (1) |
| $\mathrm{C}(4 \mathrm{~B})$ | 28(2) | 30(2) | 33(2) | 0 (2) | -4(2) | -1(1) |
| C(5B) | 23(2) | 26(2) | 22(2) | 3(1) | -2(1) | 4(1) |
| C(6B) | 31(2) | 25(2) | 39(2) | 11(2) | 6 (2) | 9(1) |
| C(7B) | 67(3) | 83(3) | 69(3) | 57(3) | 31(2) | 30(2) |
| C (8B) | 78(3) | 26(2) | 73(3) | 5(2) | -15(2) | 22(2) |
| C (9B) | 42(2) | 44(2) | 42(2) | 14(2) | 2(2) | 18(2) |
| C(10B) | 36(2) | 32(2) | 27(2) | 6(2) | 2(2) | -1(2) |
| C (11B) | 32(2) | 38(2) | 40(2) | 4(2) | 2(2) | 15(2) |
| C(12B) | 16(2) | 20(2) | 31(2) | -1(1) | 4(1) | 6 (1) |
| C(13B) | 25(2) | 18(2) | 34(2) | -7(1) | 4(1) | 3(1) |
| C (14B) | 22(2) | 27(2) | 26(2) | -7(1) | 2(1) | 9(1) |
| C(15B) | 35(2) | 45(2) | 29(2) | -5(2) | 12(2) | 12(2) |
| $\mathrm{C}(16 \mathrm{~B})$ | 24(2) | 34(2) | 20(2) | 1(1) | 6 (1) | 8(1) |
| C(17B) | 32(2) | 22(2) | 40(2) | 5(2) | 12(2) | 5(1) |
| C(18B) | 67(3) | 63(3) | 94(4) | 42(3) | 54(3) | 28(2) |
| C(19B) | 150(5) | 32(2) | 86(4) | -12(2) | 67(4) | -34(3) |
| C(20B) | 84(4) | 67(3) | 80(4) | 50(3) | -5(3) | -3(3) |
| C(21B) | 28(2) | 48(2) | 29(2) | 5(2) | 6 (2) | 0 (2) |
| C(22B) | 32(2) | 49(2) | 24(2) | 6(2) | 5(2) | 11(2) |

Table 5. Hydrogen coordinates $\left(\times 10^{4}\right)$ and isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for d1871_a.

|  | x | y | z | $\mathrm{U}(\mathrm{eq})$ |
| :---: | :---: | :---: | :---: | :---: |
| H(2AA) | 3841 | 9592 | 5680 | 32 |
| H(7AA) | 5508 | 11159 | 7379 | 76 |
| H(7AB) | 5186 | 10645 | 8220 | 76 |
| H(7AC) | 4784 | 11673 | 7969 | 76 |
| H(8AA) | 3908 | 11111 | 6068 | 85 |
| H(8AB) | 3124 | 11633 | 6602 | 85 |
| H(8AC) | 2521 | 10580 | 6043 | 85 |
| H(9AA) | 1957 | 9918 | 7411 | 53 |
| H(9AB) | 2639 | 10977 | 7935 | 53 |
| H(9AC) | 3004 | 9960 | 8259 | 53 |
| H(4AA) | 5174 | 6987 | 4634 | 54 |
| H(4AB) | 3711 | 6679 | 4468 | 54 |
| H(10A) | 2981 | 5484 | 5548 | 56 |
| H(10B) | 3996 | 5320 | 6353 | 56 |
| H(10C) | 4140 | 5085 | 5387 | 56 |
| H(11A) | 6366 | 7350 | 6201 | 59 |
| H(11B) | 6205 | 6194 | 5871 | 59 |
| H(11C) | 5928 | 6477 | 6790 | 59 |
| H(4CA) | 5876 | 7438 | 5164 | 46 |
| H(4CB) | 4693 | 6825 | 4475 | 46 |
| H(10D) | 2781 | 6269 | 5029 | 56 |
| H(10E) | 2975 | 5599 | 5834 | 56 |
| H(10F) | 3473 | 5366 | 4991 | 56 |
| H(11D) | 6257 | 6690 | 6495 | 65 |
| H(11E) | 5740 | 5681 | 5862 | 65 |
| H(11F) | 5241 | 5808 | 6723 | 65 |
| H(13A) | 3676 | 5210 | 9311 | 30 |
| H(15A) | 7111 | 7345 | 9843 | 41 |
| H(15B) | 6582 | 7951 | 10517 | 41 |
| H(18A) | 3640 | 3648 | 8220 | 66 |


| H(18B) | 2472 | 2938 | 7598 | 66 |
| :---: | :---: | :---: | :---: | :---: |
| H(18C) | 3380 | 3752 | 7199 | 66 |
| H(19A) | 2246 | 4093 | 9107 | 66 |
| H(19B) | 1122 | 4564 | 8677 | 66 |
| H(19C) | 1105 | 3406 | 8442 | 66 |
| H(20A) | 795 | 4879 | 7113 | 66 |
| H(20B) | 1621 | 4516 | 6516 | 66 |
| H(20C) | 712 | 3702 | 6915 | 66 |
| H(18G) | 3044 | 4239 | 6742 | 66 |
| H(18H) | 3648 | 3718 | 7559 | 66 |
| H(18I) | 2341 | 3180 | 6983 | 66 |
| H(19G) | 2755 | 3692 | 8891 | 66 |
| H(19H) | 1588 | 4161 | 8897 | 66 |
| H(19I) | 1456 | 3143 | 8312 | 66 |
| H(20G) | 1324 | 4988 | 6754 | 66 |
| H(20H) | 553 | 3949 | 6979 | 66 |
| H(20I) | 686 | 4967 | 7564 | 66 |
| H(21A) | 7091 | 8069 | 8460 | 48 |
| H(21B) | 7481 | 9063 | 9116 | 48 |
| H(21C) | 6422 | 8984 | 8269 | 48 |
| H(22A) | 4680 | 8614 | 9906 | 49 |
| H(22B) | 4855 | 9254 | 9096 | 49 |
| H(22C) | 5900 | 9453 | 9961 | 49 |
| H(2BA) | 173 | -697 | 1631 | 28 |
| H(4BA) | -2460 | 922 | 332 | 40 |
| H(4BB) | -1750 | 946 | -448 | 40 |
| H(7BA) | -57 | -815 | 3684 | 101 |
| H(7BB) | 909 | 94 | 4274 | 101 |
| H(7BC) | 1104 | -1035 | 4337 | 101 |
| H(8BA) | 612 | -1769 | 2552 | 93 |
| H(8BB) | 1869 | -1846 | 3175 | 93 |
| H(8BC) | 1876 | -1327 | 2285 | 93 |
| H(9BA) | 2911 | 664 | 4013 | 63 |
| H(9BB) | 3310 | 231 | 3188 | 63 |
| H(9BC) | 3220 | -430 | 3996 | 63 |
| H(10G) | 686 | 2961 | 330 | 51 |
|  |  |  |  |  |


| H(10H) | -412 | 2621 | -497 | 51 |
| :---: | :---: | :---: | :---: | :---: |
| H(10I) | 446 | 1864 | -159 | 51 |
| H(11G) | -898 | 3342 | 1148 | 55 |
| H(11H) | -1962 | 2437 | 1281 | 55 |
| H(11I) | -2019 | 2889 | 359 | 55 |
| H(13B) | 2001 | 5523 | 3235 | 32 |
| H(15C) | -784 | 3821 | 4362 | 42 |
| H(15D) | 248 | 3823 | 5220 | 42 |
| H(18D) | 4148 | 4892 | 1917 | 100 |
| H(18E) | 3842 | 5341 | 998 | 100 |
| H(18F) | 3199 | 4212 | 1124 | 100 |
| H(19D) | 3563 | 6343 | 2601 | 137 |
| H(19E) | 2238 | 6560 | 2262 | 137 |
| H(19F) | 3231 | 6774 | 1676 | 137 |
| H(20D) | 860 | 5561 | 987 | 124 |
| H(20E) | 1209 | 4596 | 579 | 124 |
| H(20F) | 1906 | 5704 | 443 | 124 |
| H(21D) | -1385 | 2242 | 3474 | 54 |
| H(21E) | -1188 | 1846 | 4420 | 54 |
| H(21F) | -606 | 1401 | 3695 | 54 |
| H(22D) | 1586 | 1932 | 4546 | 52 |
| H(22E) | 992 | 2196 | 5333 | 52 |
| H(22F) | 2013 | 3029 | 5052 | 52 |

Table 6. Torsion angles [ ${ }^{\circ}$ ] for d1871_a.

| $\mathrm{Cu}(1 \mathrm{~A})-\mathrm{O}(1 \mathrm{~A})-\mathrm{C}(1 \mathrm{~A})-\mathrm{C}(2 \mathrm{~A})$ | -7.6(4) |
| :---: | :---: |
| $\mathrm{Cu}(1 \mathrm{~A})-\mathrm{O}(1 \mathrm{~A})-\mathrm{C}(1 \mathrm{~A})-\mathrm{C}(6 \mathrm{~A})$ | 174.64(18) |
| $\mathrm{O}(1 \mathrm{~A})-\mathrm{C}(1 \mathrm{~A})-\mathrm{C}(2 \mathrm{~A})-\mathrm{C}(3 \mathrm{~A})$ | -1.5(5) |
| $\mathrm{C}(6 \mathrm{~A})-\mathrm{C}(1 \mathrm{~A})-\mathrm{C}(2 \mathrm{~A})-\mathrm{C}(3 \mathrm{~A})$ | 176.2(3) |
| $\mathrm{C}(5 \mathrm{~A})-\mathrm{N}(1 \mathrm{~A})-\mathrm{C}(3 \mathrm{~A})-\mathrm{O}(2 \mathrm{~A})$ | 1.3(4) |
| $\mathrm{C}(5 \mathrm{C})-\mathrm{N}(1 \mathrm{~A})-\mathrm{C}(3 \mathrm{~A})-\mathrm{O}(2 \mathrm{~A})$ | 1.3(4) |
| $\mathrm{Cu}(1 \mathrm{~A})-\mathrm{N}(1 \mathrm{~A})-\mathrm{C}(3 \mathrm{~A})-\mathrm{O}(2 \mathrm{~A})$ | 173.53(19) |
| $\mathrm{C}(5 \mathrm{~A})-\mathrm{N}(1 \mathrm{~A})-\mathrm{C}(3 \mathrm{~A})-\mathrm{C}(2 \mathrm{~A})$ | -177.4(3) |
| $\mathrm{C}(5 \mathrm{C})-\mathrm{N}(1 \mathrm{~A})-\mathrm{C}(3 \mathrm{~A})-\mathrm{C}(2 \mathrm{~A})$ | -177.4(3) |
| $\mathrm{Cu}(1 \mathrm{~A})-\mathrm{N}(1 \mathrm{~A})-\mathrm{C}(3 \mathrm{~A})-\mathrm{C}(2 \mathrm{~A})$ | -5.2(5) |
| $\mathrm{C}(4 \mathrm{~A})-\mathrm{O}(2 \mathrm{~A})-\mathrm{C}(3 \mathrm{~A})-\mathrm{N}(1 \mathrm{~A})$ | -15.3(5) |
| $\mathrm{C}(4 \mathrm{C})-\mathrm{O}(2 \mathrm{~A})-\mathrm{C}(3 \mathrm{~A})-\mathrm{N}(1 \mathrm{~A})$ | 9.1(6) |
| $\mathrm{C}(4 \mathrm{~A})-\mathrm{O}(2 \mathrm{~A})-\mathrm{C}(3 \mathrm{~A})-\mathrm{C}(2 \mathrm{~A})$ | 163.5(5) |
| $\mathrm{C}(4 \mathrm{C})-\mathrm{O}(2 \mathrm{~A})-\mathrm{C}(3 \mathrm{~A})-\mathrm{C}(2 \mathrm{~A})$ | -172.0(6) |
| $\mathrm{C}(1 \mathrm{~A})-\mathrm{C}(2 \mathrm{~A})-\mathrm{C}(3 \mathrm{~A})-\mathrm{N}(1 \mathrm{~A})$ | 8.5(5) |
| $\mathrm{C}(1 \mathrm{~A})-\mathrm{C}(2 \mathrm{~A})-\mathrm{C}(3 \mathrm{~A})-\mathrm{O}(2 \mathrm{~A})$ | -170.2(3) |
| $\mathrm{O}(1 \mathrm{~A})-\mathrm{C}(1 \mathrm{~A})-\mathrm{C}(6 \mathrm{~A})-\mathrm{C}(9 \mathrm{~A})$ | -45.5(3) |
| $\mathrm{C}(2 \mathrm{~A})-\mathrm{C}(1 \mathrm{~A})-\mathrm{C}(6 \mathrm{~A})-\mathrm{C}(9 \mathrm{~A})$ | 136.6(3) |
| $\mathrm{O}(1 \mathrm{~A})-\mathrm{C}(1 \mathrm{~A})-\mathrm{C}(6 \mathrm{~A})-\mathrm{C}(8 \mathrm{~A})$ | -166.3(3) |
| $\mathrm{C}(2 \mathrm{~A})-\mathrm{C}(1 \mathrm{~A})-\mathrm{C}(6 \mathrm{~A})-\mathrm{C}(8 \mathrm{~A})$ | 15.8(4) |
| $\mathrm{O}(1 \mathrm{~A})-\mathrm{C}(1 \mathrm{~A})-\mathrm{C}(6 \mathrm{~A})-\mathrm{C}(7 \mathrm{~A})$ | 72.0(3) |
| $\mathrm{C}(2 \mathrm{~A})-\mathrm{C}(1 \mathrm{~A})-\mathrm{C}(6 \mathrm{~A})-\mathrm{C}(7 \mathrm{~A})$ | -105.9(3) |
| $\mathrm{C}(3 \mathrm{~A})-\mathrm{O}(2 \mathrm{~A})-\mathrm{C}(4 \mathrm{C})-\mathrm{C}(5 \mathrm{C})$ | -14.9(9) |
| $\mathrm{C}(3 \mathrm{~A})-\mathrm{N}(1 \mathrm{~A})-\mathrm{C}(5 \mathrm{C})-\mathrm{C}(4 \mathrm{C})$ | -10.5(6) |
| $\mathrm{Cu}(1 \mathrm{~A})-\mathrm{N}(1 \mathrm{~A})-\mathrm{C}(5 \mathrm{C})-\mathrm{C}(4 \mathrm{C})$ | 177.7(5) |
| $\mathrm{C}(3 \mathrm{~A})-\mathrm{N}(1 \mathrm{~A})-\mathrm{C}(5 \mathrm{C})-\mathrm{C}(11 \mathrm{C})$ | 105.2(5) |
| $\mathrm{Cu}(1 \mathrm{~A})-\mathrm{N}(1 \mathrm{~A})-\mathrm{C}(5 \mathrm{C})-\mathrm{C}(11 \mathrm{C})$ | -66.5(5) |
| $\mathrm{C}(3 \mathrm{~A})-\mathrm{N}(1 \mathrm{~A})-\mathrm{C}(5 \mathrm{C})-\mathrm{C}(10 \mathrm{C})$ | -138.2(5) |
| $\mathrm{Cu}(1 \mathrm{~A})-\mathrm{N}(1 \mathrm{~A})-\mathrm{C}(5 \mathrm{C})-\mathrm{C}(10 \mathrm{C})$ | 50.1(5) |
| $\mathrm{O}(2 \mathrm{~A})-\mathrm{C}(4 \mathrm{C})-\mathrm{C}(5 \mathrm{C})-\mathrm{N}(1 \mathrm{~A})$ | 15.1(8) |
| $\mathrm{O}(2 \mathrm{~A})-\mathrm{C}(4 \mathrm{C})-\mathrm{C}(5 \mathrm{C})-\mathrm{C}(11 \mathrm{C})$ | -94.9(8) |
| $\mathrm{O}(2 \mathrm{~A})-\mathrm{C}(4 \mathrm{C})-\mathrm{C}(5 \mathrm{C})-\mathrm{C}(10 \mathrm{C})$ | 143.5(7) |
| $\mathrm{C}(3 \mathrm{~A})-\mathrm{O}(2 \mathrm{~A})-\mathrm{C}(4 \mathrm{~A})-\mathrm{C}(5 \mathrm{~A})$ | 21.9(7) |
| $\mathrm{C}(3 \mathrm{~A})-\mathrm{N}(1 \mathrm{~A})-\mathrm{C}(5 \mathrm{~A})-\mathrm{C}(11 \mathrm{~A})$ | 133.0(5) |
|  |  |


| $\mathrm{Cu}(1 \mathrm{~A})-\mathrm{N}(1 \mathrm{~A})-\mathrm{C}(5 \mathrm{~A})-\mathrm{C}(11 \mathrm{~A})$ | -38.7(5) |
| :---: | :---: |
| $\mathrm{C}(3 \mathrm{~A})-\mathrm{N}(1 \mathrm{~A})-\mathrm{C}(5 \mathrm{~A})-\mathrm{C}(4 \mathrm{~A})$ | 12.5(5) |
| $\mathrm{Cu}(1 \mathrm{~A})-\mathrm{N}(1 \mathrm{~A})-\mathrm{C}(5 \mathrm{~A})-\mathrm{C}(4 \mathrm{~A})$ | -159.2(4) |
| $\mathrm{C}(3 \mathrm{~A})-\mathrm{N}(1 \mathrm{~A})-\mathrm{C}(5 \mathrm{~A})-\mathrm{C}(10 \mathrm{~A})$ | -100.0(4) |
| $\mathrm{Cu}(1 \mathrm{~A})-\mathrm{N}(1 \mathrm{~A})-\mathrm{C}(5 \mathrm{~A})-\mathrm{C}(10 \mathrm{~A})$ | 88.3(4) |
| $\mathrm{O}(2 \mathrm{~A})-\mathrm{C}(4 \mathrm{~A})-\mathrm{C}(5 \mathrm{~A})-\mathrm{N}(1 \mathrm{~A})$ | -20.6(6) |
| $\mathrm{O}(2 \mathrm{~A})-\mathrm{C}(4 \mathrm{~A})-\mathrm{C}(5 \mathrm{~A})-\mathrm{C}(11 \mathrm{~A})$ | -142.3(6) |
| $\mathrm{O}(2 \mathrm{~A})-\mathrm{C}(4 \mathrm{~A})-\mathrm{C}(5 \mathrm{~A})-\mathrm{C}(10 \mathrm{~A})$ | 88.7(7) |
| $\mathrm{Cu}(1 \mathrm{~A})-\mathrm{O}(3 \mathrm{~A})-\mathrm{C}(12 \mathrm{~A})-\mathrm{C}(13 \mathrm{~A})$ | -5.1(4) |
| $\mathrm{Cu}(1 \mathrm{~A})-\mathrm{O}(3 \mathrm{~A})-\mathrm{C}(12 \mathrm{~A})-\mathrm{C}(17 \mathrm{~A})$ | 177.86(18) |
| $\mathrm{O}(3 \mathrm{~A})-\mathrm{C}(12 \mathrm{~A})-\mathrm{C}(13 \mathrm{~A})-\mathrm{C}(14 \mathrm{~A})$ | -2.6(5) |
| $\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(12 \mathrm{~A})-\mathrm{C}(13 \mathrm{~A})-\mathrm{C}(14 \mathrm{~A})$ | 174.3(3) |
| $\mathrm{C}(16 \mathrm{~A})-\mathrm{N}(2 \mathrm{~A})-\mathrm{C}(14 \mathrm{~A})-\mathrm{O}(4 \mathrm{~A})$ | -2.8(3) |
| $\mathrm{Cu}(1 \mathrm{~A})-\mathrm{N}(2 \mathrm{~A})-\mathrm{C}(14 \mathrm{~A})-\mathrm{O}(4 \mathrm{~A})$ | 175.24(18) |
| $\mathrm{C}(16 \mathrm{~A})-\mathrm{N}(2 \mathrm{~A})-\mathrm{C}(14 \mathrm{~A})-\mathrm{C}(13 \mathrm{~A})$ | 177.5(3) |
| $\mathrm{Cu}(1 \mathrm{~A})-\mathrm{N}(2 \mathrm{~A})-\mathrm{C}(14 \mathrm{~A})-\mathrm{C}(13 \mathrm{~A})$ | -4.5(4) |
| $\mathrm{C}(15 \mathrm{~A})-\mathrm{O}(4 \mathrm{~A})-\mathrm{C}(14 \mathrm{~A})-\mathrm{N}(2 \mathrm{~A})$ | -12.1(3) |
| $\mathrm{C}(15 \mathrm{~A})-\mathrm{O}(4 \mathrm{~A})-\mathrm{C}(14 \mathrm{~A})-\mathrm{C}(13 \mathrm{~A})$ | 167.7(3) |
| $\mathrm{C}(12 \mathrm{~A})-\mathrm{C}(13 \mathrm{~A})-\mathrm{C}(14 \mathrm{~A})-\mathrm{N}(2 \mathrm{~A})$ | $7.9(5)$ |
| $\mathrm{C}(12 \mathrm{~A})-\mathrm{C}(13 \mathrm{~A})-\mathrm{C}(14 \mathrm{~A})-\mathrm{O}(4 \mathrm{~A})$ | -171.8(3) |
| $\mathrm{C}(14 \mathrm{~A})-\mathrm{O}(4 \mathrm{~A})-\mathrm{C}(15 \mathrm{~A})-\mathrm{C}(16 \mathrm{~A})$ | 21.0(3) |
| $\mathrm{C}(14 \mathrm{~A})-\mathrm{N}(2 \mathrm{~A})-\mathrm{C}(16 \mathrm{~A})-\mathrm{C}(21 \mathrm{~A})$ | 135.5(3) |
| $\mathrm{Cu}(1 \mathrm{~A})-\mathrm{N}(2 \mathrm{~A})-\mathrm{C}(16 \mathrm{~A})-\mathrm{C}(21 \mathrm{~A})$ | -42.5(3) |
| $\mathrm{C}(14 \mathrm{~A})-\mathrm{N}(2 \mathrm{~A})-\mathrm{C}(16 \mathrm{~A})-\mathrm{C}(15 \mathrm{~A})$ | 15.5(3) |
| $\mathrm{Cu}(1 \mathrm{~A})-\mathrm{N}(2 \mathrm{~A})-\mathrm{C}(16 \mathrm{~A})-\mathrm{C}(15 \mathrm{~A})$ | -162.4(2) |
| $\mathrm{C}(14 \mathrm{~A})-\mathrm{N}(2 \mathrm{~A})-\mathrm{C}(16 \mathrm{~A})-\mathrm{C}(22 \mathrm{~A})$ | -101.1(3) |
| $\mathrm{Cu}(1 \mathrm{~A})-\mathrm{N}(2 \mathrm{~A})-\mathrm{C}(16 \mathrm{~A})-\mathrm{C}(22 \mathrm{~A})$ | 81.0(3) |
| $\mathrm{O}(4 \mathrm{~A})-\mathrm{C}(15 \mathrm{~A})-\mathrm{C}(16 \mathrm{~A})-\mathrm{N}(2 \mathrm{~A})$ | -21.8(3) |
| $\mathrm{O}(4 \mathrm{~A})-\mathrm{C}(15 \mathrm{~A})-\mathrm{C}(16 \mathrm{~A})-\mathrm{C}(21 \mathrm{~A})$ | -140.5(3) |
| $\mathrm{O}(4 \mathrm{~A})-\mathrm{C}(15 \mathrm{~A})-\mathrm{C}(16 \mathrm{~A})-\mathrm{C}(22 \mathrm{~A})$ | 93.1(3) |
| $\mathrm{O}(3 \mathrm{~A})-\mathrm{C}(12 \mathrm{~A})-\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(19 \mathrm{C})$ | -168.0(4) |
| $\mathrm{C}(13 \mathrm{~A})-\mathrm{C}(12 \mathrm{~A})-\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(19 \mathrm{C})$ | 14.9(5) |
| $\mathrm{O}(3 \mathrm{~A})-\mathrm{C}(12 \mathrm{~A})-\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(20 \mathrm{~A})$ | -23.7(5) |
| $\mathrm{C}(13 \mathrm{~A})-\mathrm{C}(12 \mathrm{~A})-\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(20 \mathrm{~A})$ | 159.1(4) |
| $\mathrm{O}(3 \mathrm{~A})-\mathrm{C}(12 \mathrm{~A})-\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(18 \mathrm{~A})$ | 101.3(4) |
| $\mathrm{C}(13 \mathrm{~A})-\mathrm{C}(12 \mathrm{~A})-\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(18 \mathrm{~A})$ | -75.8(4) |


| $\mathrm{O}(3 \mathrm{~A})-\mathrm{C}(12 \mathrm{~A})-\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(20 \mathrm{C})$ | -42.7(5) |
| :---: | :---: |
| $\mathrm{C}(13 \mathrm{~A})-\mathrm{C}(12 \mathrm{~A})-\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(20 \mathrm{C})$ | 140.2(4) |
| $\mathrm{O}(3 \mathrm{~A})-\mathrm{C}(12 \mathrm{~A})-\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(18 \mathrm{C})$ | 69.4(4) |
| $\mathrm{C}(13 \mathrm{~A})-\mathrm{C}(12 \mathrm{~A})-\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(18 \mathrm{C})$ | -107.8(4) |
| $\mathrm{O}(3 \mathrm{~A})-\mathrm{C}(12 \mathrm{~A})-\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(19 \mathrm{~A})$ | -143.0(4) |
| $\mathrm{C}(13 \mathrm{~A})-\mathrm{C}(12 \mathrm{~A})-\mathrm{C}(17 \mathrm{~A})-\mathrm{C}(19 \mathrm{~A})$ | 39.8(4) |
| $\mathrm{Cu}(1 \mathrm{~B})-\mathrm{O}(1 \mathrm{~B})-\mathrm{C}(1 \mathrm{~B})-\mathrm{C}(2 \mathrm{~B})$ | -7.3(4) |
| $\mathrm{Cu}(1 \mathrm{~B})-\mathrm{O}(1 \mathrm{~B})-\mathrm{C}(1 \mathrm{~B})-\mathrm{C}(6 \mathrm{~B})$ | 175.30(19) |
| $\mathrm{O}(1 \mathrm{~B})-\mathrm{C}(1 \mathrm{~B})-\mathrm{C}(2 \mathrm{~B})-\mathrm{C}(3 \mathrm{~B})$ | -0.9(5) |
| $\mathrm{C}(6 \mathrm{~B})-\mathrm{C}(1 \mathrm{~B})-\mathrm{C}(2 \mathrm{~B})-\mathrm{C}(3 \mathrm{~B})$ | 176.4(3) |
| $\mathrm{C}(5 \mathrm{~B})-\mathrm{N}(1 \mathrm{~B})-\mathrm{C}(3 \mathrm{~B})-\mathrm{O}(2 \mathrm{~B})$ | -3.7(3) |
| $\mathrm{Cu}(1 \mathrm{~B})-\mathrm{N}(1 \mathrm{~B})-\mathrm{C}(3 \mathrm{~B})-\mathrm{O}(2 \mathrm{~B})$ | 172.17(18) |
| $\mathrm{C}(5 \mathrm{~B})-\mathrm{N}(1 \mathrm{~B})-\mathrm{C}(3 \mathrm{~B})-\mathrm{C}(2 \mathrm{~B})$ | 176.3(3) |
| $\mathrm{Cu}(1 \mathrm{~B})-\mathrm{N}(1 \mathrm{~B})-\mathrm{C}(3 \mathrm{~B})-\mathrm{C}(2 \mathrm{~B})$ | -7.8(4) |
| $\mathrm{C}(4 \mathrm{~B})-\mathrm{O}(2 \mathrm{~B})-\mathrm{C}(3 \mathrm{~B})-\mathrm{N}(1 \mathrm{~B})$ | -9.9(3) |
| $\mathrm{C}(4 \mathrm{~B})-\mathrm{O}(2 \mathrm{~B})-\mathrm{C}(3 \mathrm{~B})-\mathrm{C}(2 \mathrm{~B})$ | 170.0(3) |
| $\mathrm{C}(1 \mathrm{~B})-\mathrm{C}(2 \mathrm{~B})-\mathrm{C}(3 \mathrm{~B})-\mathrm{N}(1 \mathrm{~B})$ | 9.1(5) |
| $\mathrm{C}(1 \mathrm{~B})-\mathrm{C}(2 \mathrm{~B})-\mathrm{C}(3 \mathrm{~B})-\mathrm{O}(2 \mathrm{~B})$ | -170.8(3) |
| $\mathrm{C}(3 \mathrm{~B})-\mathrm{O}(2 \mathrm{~B})-\mathrm{C}(4 \mathrm{~B})-\mathrm{C}(5 \mathrm{~B})$ | 18.5(3) |
| $\mathrm{C}(3 \mathrm{~B})-\mathrm{N}(1 \mathrm{~B})-\mathrm{C}(5 \mathrm{~B})-\mathrm{C}(11 \mathrm{~B})$ | 133.4(3) |
| $\mathrm{Cu}(1 \mathrm{~B})-\mathrm{N}(1 \mathrm{~B})-\mathrm{C}(5 \mathrm{~B})-\mathrm{C}(11 \mathrm{~B})$ | -42.2(3) |
| $\mathrm{C}(3 \mathrm{~B})-\mathrm{N}(1 \mathrm{~B})-\mathrm{C}(5 \mathrm{~B})-\mathrm{C}(10 \mathrm{~B})$ | -101.7(3) |
| $\mathrm{Cu}(1 \mathrm{~B})-\mathrm{N}(1 \mathrm{~B})-\mathrm{C}(5 \mathrm{~B})-\mathrm{C}(10 \mathrm{~B})$ | 82.7(3) |
| $\mathrm{C}(3 \mathrm{~B})-\mathrm{N}(1 \mathrm{~B})-\mathrm{C}(5 \mathrm{~B})-\mathrm{C}(4 \mathrm{~B})$ | 14.6(3) |
| $\mathrm{Cu}(1 \mathrm{~B})-\mathrm{N}(1 \mathrm{~B})-\mathrm{C}(5 \mathrm{~B})-\mathrm{C}(4 \mathrm{~B})$ | -161.0(2) |
| $\mathrm{O}(2 \mathrm{~B})-\mathrm{C}(4 \mathrm{~B})-\mathrm{C}(5 \mathrm{~B})-\mathrm{N}(1 \mathrm{~B})$ | -19.8(3) |
| $\mathrm{O}(2 \mathrm{~B})-\mathrm{C}(4 \mathrm{~B})-\mathrm{C}(5 \mathrm{~B})-\mathrm{C}(11 \mathrm{~B})$ | -137.8(3) |
| $\mathrm{O}(2 \mathrm{~B})-\mathrm{C}(4 \mathrm{~B})-\mathrm{C}(5 \mathrm{~B})-\mathrm{C}(10 \mathrm{~B})$ | 95.5(3) |
| $\mathrm{O}(1 \mathrm{~B})-\mathrm{C}(1 \mathrm{~B})-\mathrm{C}(6 \mathrm{~B})-\mathrm{C}(7 \mathrm{~B})$ | 71.2(4) |
| $\mathrm{C}(2 \mathrm{~B})-\mathrm{C}(1 \mathrm{~B})-\mathrm{C}(6 \mathrm{~B})-\mathrm{C}(7 \mathrm{~B})$ | -106.3(4) |
| $\mathrm{O}(1 \mathrm{~B})-\mathrm{C}(1 \mathrm{~B})-\mathrm{C}(6 \mathrm{~B})-\mathrm{C}(8 \mathrm{~B})$ | -167.4(3) |
| $\mathrm{C}(2 \mathrm{~B})-\mathrm{C}(1 \mathrm{~B})-\mathrm{C}(6 \mathrm{~B})-\mathrm{C}(8 \mathrm{~B})$ | 15.1(4) |
| $\mathrm{O}(1 \mathrm{~B})-\mathrm{C}(1 \mathrm{~B})-\mathrm{C}(6 \mathrm{~B})-\mathrm{C}(9 \mathrm{~B})$ | -46.7(4) |
| $\mathrm{C}(2 \mathrm{~B})-\mathrm{C}(1 \mathrm{~B})-\mathrm{C}(6 \mathrm{~B})-\mathrm{C}(9 \mathrm{~B})$ | 135.8(3) |
| $\mathrm{Cu}(1 \mathrm{~B})-\mathrm{O}(3 \mathrm{~B})-\mathrm{C}(12 \mathrm{~B})-\mathrm{C}(13 \mathrm{~B})$ | -5.7(4) |
| $\mathrm{Cu}(1 \mathrm{~B})-\mathrm{O}(3 \mathrm{~B})-\mathrm{C}(12 \mathrm{~B})-\mathrm{C}(17 \mathrm{~B})$ | 175.68(19) |


| $\mathrm{O}(3 \mathrm{~B})-\mathrm{C}(12 \mathrm{~B})-\mathrm{C}(13 \mathrm{~B})-\mathrm{C}(14 \mathrm{~B})$ | -0.7(5) |
| :---: | :---: |
| $\mathrm{C}(17 \mathrm{~B})-\mathrm{C}(12 \mathrm{~B})-\mathrm{C}(13 \mathrm{~B})-\mathrm{C}(14 \mathrm{~B})$ | 177.8(3) |
| $\mathrm{C}(16 \mathrm{~B})-\mathrm{N}(2 \mathrm{~B})-\mathrm{C}(14 \mathrm{~B})-\mathrm{O}(4 \mathrm{~B})$ | -4.1(3) |
| $\mathrm{Cu}(1 \mathrm{~B})-\mathrm{N}(2 \mathrm{~B})-\mathrm{C}(14 \mathrm{~B})-\mathrm{O}(4 \mathrm{~B})$ | 172.05(18) |
| $\mathrm{C}(16 \mathrm{~B})-\mathrm{N}(2 \mathrm{~B})-\mathrm{C}(14 \mathrm{~B})-\mathrm{C}(13 \mathrm{~B})$ | 176.3(3) |
| $\mathrm{Cu}(1 \mathrm{~B})-\mathrm{N}(2 \mathrm{~B})-\mathrm{C}(14 \mathrm{~B})-\mathrm{C}(13 \mathrm{~B})$ | -7.6(4) |
| $\mathrm{C}(15 \mathrm{~B})-\mathrm{O}(4 \mathrm{~B})-\mathrm{C}(14 \mathrm{~B})-\mathrm{N}(2 \mathrm{~B})$ | -12.6(3) |
| $\mathrm{C}(15 \mathrm{~B})-\mathrm{O}(4 \mathrm{~B})-\mathrm{C}(14 \mathrm{~B})-\mathrm{C}(13 \mathrm{~B})$ | 167.0(3) |
| $\mathrm{C}(12 \mathrm{~B})-\mathrm{C}(13 \mathrm{~B})-\mathrm{C}(14 \mathrm{~B})-\mathrm{N}(2 \mathrm{~B})$ | 8.0(5) |
| $\mathrm{C}(12 \mathrm{~B})-\mathrm{C}(13 \mathrm{~B})-\mathrm{C}(14 \mathrm{~B})-\mathrm{O}(4 \mathrm{~B})$ | -171.6(3) |
| $\mathrm{C}(14 \mathrm{~B})-\mathrm{O}(4 \mathrm{~B})-\mathrm{C}(15 \mathrm{~B})-\mathrm{C}(16 \mathrm{~B})$ | 23.1(3) |
| $\mathrm{C}(14 \mathrm{~B})-\mathrm{N}(2 \mathrm{~B})-\mathrm{C}(16 \mathrm{~B})-\mathrm{C}(21 \mathrm{~B})$ | 136.8(3) |
| $\mathrm{Cu}(1 \mathrm{~B})-\mathrm{N}(2 \mathrm{~B})-\mathrm{C}(16 \mathrm{~B})-\mathrm{C}(21 \mathrm{~B})$ | -39.1(3) |
| $\mathrm{C}(14 \mathrm{~B})-\mathrm{N}(2 \mathrm{~B})-\mathrm{C}(16 \mathrm{~B})-\mathrm{C}(15 \mathrm{~B})$ | 18.0(3) |
| $\mathrm{Cu}(1 \mathrm{~B})-\mathrm{N}(2 \mathrm{~B})-\mathrm{C}(16 \mathrm{~B})-\mathrm{C}(15 \mathrm{~B})$ | -158.0(2) |
| $\mathrm{C}(14 \mathrm{~B})-\mathrm{N}(2 \mathrm{~B})-\mathrm{C}(16 \mathrm{~B})-\mathrm{C}(22 \mathrm{~B})$ | -99.2(3) |
| $\mathrm{Cu}(1 \mathrm{~B})-\mathrm{N}(2 \mathrm{~B})-\mathrm{C}(16 \mathrm{~B})-\mathrm{C}(22 \mathrm{~B})$ | 84.8(3) |
| $\mathrm{O}(4 \mathrm{~B})-\mathrm{C}(15 \mathrm{~B})-\mathrm{C}(16 \mathrm{~B})-\mathrm{N}(2 \mathrm{~B})$ | -24.4(3) |
| $\mathrm{O}(4 \mathrm{~B})-\mathrm{C}(15 \mathrm{~B})-\mathrm{C}(16 \mathrm{~B})-\mathrm{C}(21 \mathrm{~B})$ | -142.3(3) |
| $\mathrm{O}(4 \mathrm{~B})-\mathrm{C}(15 \mathrm{~B})-\mathrm{C}(16 \mathrm{~B})-\mathrm{C}(22 \mathrm{~B})$ | 91.1(3) |
| $\mathrm{O}(3 \mathrm{~B})-\mathrm{C}(12 \mathrm{~B})-\mathrm{C}(17 \mathrm{~B})-\mathrm{C}(19 \mathrm{~B})$ | -176.8(3) |
| $\mathrm{C}(13 \mathrm{~B})-\mathrm{C}(12 \mathrm{~B})-\mathrm{C}(17 \mathrm{~B})-\mathrm{C}(19 \mathrm{~B})$ | 4.5(5) |
| $\mathrm{O}(3 \mathrm{~B})-\mathrm{C}(12 \mathrm{~B})-\mathrm{C}(17 \mathrm{~B})-\mathrm{C}(18 \mathrm{~B})$ | -52.8(4) |
| $\mathrm{C}(13 \mathrm{~B})-\mathrm{C}(12 \mathrm{~B})-\mathrm{C}(17 \mathrm{~B})-\mathrm{C}(18 \mathrm{~B})$ | 128.6(3) |
| $\mathrm{O}(3 \mathrm{~B})-\mathrm{C}(12 \mathrm{~B})-\mathrm{C}(17 \mathrm{~B})-\mathrm{C}(20 \mathrm{~B})$ | 62.4(4) |
| $\mathrm{C}(13 \mathrm{~B})-\mathrm{C}(12 \mathrm{~B})-\mathrm{C}(17 \mathrm{~B})-\mathrm{C}(20 \mathrm{~B})$ | -116.3(4) |

Symmetry transformations used to generate equivalent atoms:


F9: Crystal data and structure refinement for d1804_a (15).

Identification code
Empirical formula
Formula weight
Temperature
Wavelength
Crystal system
Space group
Unit cell dimensions

Volume

Z
Density (calculated)
Absorption coefficient
F(000)
Crystal size
Theta range for data collection
Index ranges
Reflections collected
Independent reflections
Completeness to theta $=25.242^{\circ}$
Absorption correction
Max. and min. transmission
Refinement method
d1804_a (15)
C21 H26 Ir N O2
516.63

150(2) K
$0.71073 \AA$
Monoclinic
P2 $1 / n$
$a=8.4355(6) \AA \quad a=90^{\circ}$.
$b=12.5712(9) \AA \quad b=102.943(2)^{\circ}$.
$\mathrm{c}=17.6529(12) \AA$
$g=90^{\circ}$.
1824.4(2) $\AA^{3}$

4
$1.881 \mathrm{Mg} / \mathrm{m}^{3}$
$7.332 \mathrm{~mm}^{-1}$
1008
$0.180 \times 0.120 \times 0.050 \mathrm{~mm}^{3}$
2.006 to $27.539^{\circ}$.
$-10<=\mathrm{h}<=10,-16<=\mathrm{k}<=16,-22<=1<=19$
23640
$4189[\mathrm{R}(\mathrm{int})=0.0637]$
100.0 \%

Semi-empirical from equivalents
0.7456 and 0.5347

Full-matrix least-squares on $\mathrm{F}^{2}$

Data / restraints / parameters
Goodness-of-fit on $\mathrm{F}^{2}$
Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ]
R indices (all data)
Extinction coefficient
Largest diff. peak and hole

4189 / 48 / 228
0.991
$\mathrm{R} 1=0.0232, \mathrm{wR} 2=0.0361$
$\mathrm{R} 1=0.0492, \mathrm{wR} 2=0.0410$
n/a
2.276 and -1.027 e. $\AA^{-3}$

Table 2. Atomic coordinates ( $\times 10^{4}$ ) and equivalent isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for d1804_a. $\mathrm{U}(\mathrm{eq})$ is defined as one third of the trace of the orthogonalized $\mathrm{U}^{\mathrm{ij}}$ tensor.

|  | x | y | z | U(eq) |
| :---: | :---: | :---: | :---: | :---: |
| $\operatorname{Ir}(1)$ | 4308(1) | 7066(1) | 4099(1) | 12(1) |
| $\mathrm{O}(1)$ | 5373(3) | 6368(2) | 3296(1) | 16(1) |
| $\mathrm{O}(2)$ | 8397(3) | 5479(2) | 5460(1) | 20(1) |
| N(1) | 6155(4) | 6472(2) | 4988(2) | 12(1) |
| C(1) | 2209(4) | 7040(3) | 3180(2) | 16(1) |
| C(2) | 3056(4) | 8014(3) | 3171(2) | 16(1) |
| C(3) | 2427(5) | 9070(3) | 3414(2) | 22(1) |
| C(4) | 3110(5) | 9298(3) | 4274(2) | 20(1) |
| C(5) | 3566(5) | 8293(3) | 4750(2) | 18(1) |
| C(6) | 2504(5) | 7419(3) | 4731(2) | 18(1) |
| C(7) | $770(5)$ | 7412(3) | 4255(2) | 22(1) |
| C(8) | 649(4) | 6927(3) | 3450(2) | 20(1) |
| C(9) | 6603(4) | 5715(3) | 3410(2) | 13(1) |
| $\mathrm{C}(10)$ | 7509(4) | 5436(3) | 4119(2) | 14(1) |
| $\mathrm{C}(11)$ | 7259(5) | 5822(3) | 4832(2) | 15(1) |
| $\mathrm{C}(12)$ | 7794(5) | 5796(3) | 6129(2) | 20(1) |
| C(13) | 6695(5) | 6741(3) | 5844(2) | 15(1) |
| C(14) | 7682(5) | 7767(3) | 5917(2) | 20(1) |
| $\mathrm{C}(15)$ | 5347(4) | 6782(3) | 6284(2) | 18(1) |
| $\mathrm{C}(16)$ | 6964(4) | 5280(3) | 2676(2) | 15(1) |
| $\mathrm{C}(17)$ | 7623(4) | 4272(3) | 2647(2) | 19(1) |
| C(18) | 7922(4) | 3879(3) | 1959(2) | 23(1) |
| $\mathrm{C}(19)$ | 7590(5) | 4497(3) | 1297(2) | 27(1) |
| $\mathrm{C}(20)$ | 6930(5) | 5501(3) | 1314(2) | 27(1) |
| C(21) | 6610(5) | 5891(3) | 2003(2) | 21(1) |

Table 3. Bond lengths $[\AA]$ and angles [ $\left.{ }^{\circ}\right]$ for d1804_a.

| $\mathrm{Ir}(1)-\mathrm{O}(1)$ | 2.039(2) |
| :---: | :---: |
| $\operatorname{Ir}(1)-\mathrm{N}(1)$ | 2.087(3) |
| $\operatorname{Ir}(1)-\mathrm{C}(5)$ | 2.101(4) |
| $\operatorname{Ir}(1)-\mathrm{C}(2)$ | 2.108(3) |
| $\mathrm{Ir}(1)-\mathrm{C}(1)$ | 2.117(3) |
| $\operatorname{Ir}(1)-\mathrm{C}(6)$ | $2.126(4)$ |
| $\mathrm{O}(1)-\mathrm{C}(9)$ | 1.303(4) |
| $\mathrm{O}(2)-\mathrm{C}(11)$ | 1.363(4) |
| $\mathrm{O}(2)-\mathrm{C}(12)$ | 1.443(4) |
| $\mathrm{N}(1)-\mathrm{C}(11)$ | 1.314(4) |
| $\mathrm{N}(1)-\mathrm{C}(13)$ | 1.516(4) |
| $\mathrm{C}(1)-\mathrm{C}(2)$ | $1.419(5)$ |
| $\mathrm{C}(1)-\mathrm{C}(8)$ | 1.504(5) |
| $\mathrm{C}(1)-\mathrm{H}(1 \mathrm{~A})$ | 1.0000 |
| $\mathrm{C}(2)-\mathrm{C}(3)$ | 1.527(5) |
| $\mathrm{C}(2)-\mathrm{H}(2 \mathrm{~A})$ | 1.0000 |
| $\mathrm{C}(3)-\mathrm{C}(4)$ | $1.525(5)$ |
| $\mathrm{C}(3)-\mathrm{H}(3 \mathrm{~A})$ | 0.9900 |
| $\mathrm{C}(3)-\mathrm{H}(3 \mathrm{~B})$ | 0.9900 |
| $\mathrm{C}(4)-\mathrm{C}(5)$ | 1.518(5) |
| $\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~A})$ | 0.9900 |
| $\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~B})$ | 0.9900 |
| $\mathrm{C}(5)-\mathrm{C}(6)$ | 1.413(5) |
| $\mathrm{C}(5)-\mathrm{H}(5 \mathrm{~A})$ | 1.0000 |
| $\mathrm{C}(6)$-C(7) | $1.515(5)$ |
| $\mathrm{C}(6)-\mathrm{H}(6 \mathrm{~A})$ | 1.0000 |
| $\mathrm{C}(7)-\mathrm{C}(8)$ | $1.529(5)$ |
| $\mathrm{C}(7)-\mathrm{H}(7 \mathrm{~A})$ | 0.9900 |
| $\mathrm{C}(7)-\mathrm{H}(7 \mathrm{~B})$ | 0.9900 |
| $\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~A})$ | 0.9900 |
| $\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~B})$ | 0.9900 |
| $\mathrm{C}(9)-\mathrm{C}(10)$ | 1.358(5) |
| C(9)-C(16) | $1.499(5)$ |
| $\mathrm{C}(10)-\mathrm{C}(11)$ | 1.408(5) |
| $\mathrm{C}(10)-\mathrm{H}(10 \mathrm{~A})$ | 0.9500 |


| $\mathrm{C}(12)-\mathrm{C}(13)$ | 1.521(5) |
| :---: | :---: |
| $\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~A})$ | 0.9900 |
| $\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~B})$ | 0.9900 |
| $\mathrm{C}(13)-\mathrm{C}(15)$ | 1.514(5) |
| $\mathrm{C}(13)-\mathrm{C}(14)$ | $1.525(5)$ |
| $\mathrm{C}(14)-\mathrm{H}(14 \mathrm{~A})$ | 0.9800 |
| $\mathrm{C}(14)-\mathrm{H}(14 \mathrm{~B})$ | 0.9800 |
| $\mathrm{C}(14)-\mathrm{H}(14 \mathrm{C})$ | 0.9800 |
| $\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~A})$ | 0.9800 |
| $\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~B})$ | 0.9800 |
| $\mathrm{C}(15)-\mathrm{H}(15 \mathrm{C})$ | 0.9800 |
| $\mathrm{C}(16)-\mathrm{C}(17)$ | 1.390 (5) |
| $\mathrm{C}(16)-\mathrm{C}(21)$ | 1.390 (5) |
| $\mathrm{C}(17)-\mathrm{C}(18)$ | $1.386(5)$ |
| $\mathrm{C}(17)-\mathrm{H}(17 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(18)-\mathrm{C}(19)$ | $1.379(5)$ |
| $\mathrm{C}(18)-\mathrm{H}(18 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(19)-\mathrm{C}(20)$ | 1.382(6) |
| $\mathrm{C}(19)-\mathrm{H}(19 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(20)-\mathrm{C}(21)$ | 1.393 (5) |
| $\mathrm{C}(20)-\mathrm{H}(20 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(21)-\mathrm{H}(21 \mathrm{~A})$ | 0.9500 |
| $\mathrm{O}(1)-\mathrm{Ir}(1)-\mathrm{N}(1)$ | 89.87(10) |
| $\mathrm{O}(1)-\operatorname{Ir}(1)-\mathrm{C}(5)$ | 158.12(13) |
| $\mathrm{N}(1)-\operatorname{Ir}(1)-\mathrm{C}(5)$ | 96.61(13) |
| $\mathrm{O}(1)-\operatorname{Ir}(1)-\mathrm{C}(2)$ | 85.69(12) |
| $\mathrm{N}(1)-\operatorname{Ir}(1)-\mathrm{C}(2)$ | 161.21(13) |
| $\mathrm{C}(5)-\operatorname{Ir}(1)-\mathrm{C}(2)$ | 81.46(14) |
| $\mathrm{O}(1)-\operatorname{Ir}(1)-\mathrm{C}(1)$ | 83.31(12) |
| $\mathrm{N}(1)-\operatorname{Ir}(1)-\mathrm{C}(1)$ | 157.88(14) |
| $\mathrm{C}(5)-\operatorname{Ir}(1)-\mathrm{C}(1)$ | 97.48(15) |
| $\mathrm{C}(2)-\operatorname{Ir}(1)-\mathrm{C}(1)$ | 39.24(13) |
| $\mathrm{O}(1)-\operatorname{Ir}(1)-\mathrm{C}(6)$ | 159.01(12) |
| $\mathrm{N}(1)-\operatorname{Ir}(1)-\mathrm{C}(6)$ | 100.44(13) |
| $\mathrm{C}(5)-\operatorname{Ir}(1)-\mathrm{C}(6)$ | 39.06(13) |


| $\mathrm{C}(2)-\operatorname{Ir}(1)-\mathrm{C}(6)$ | 89.85(14) |
| :---: | :---: |
| $\mathrm{C}(1)-\operatorname{Ir}(1)-\mathrm{C}(6)$ | 80.32(14) |
| $\mathrm{C}(9)-\mathrm{O}(1)-\operatorname{Ir}(1)$ | 128.5(2) |
| $\mathrm{C}(11)-\mathrm{O}(2)-\mathrm{C}(12)$ | 105.4(3) |
| $\mathrm{C}(11)-\mathrm{N}(1)-\mathrm{C}(13)$ | 106.2(3) |
| $\mathrm{C}(11)-\mathrm{N}(1)-\operatorname{Ir}(1)$ | 120.6(2) |
| $\mathrm{C}(13)-\mathrm{N}(1)-\operatorname{Ir}(1)$ | 132.6(2) |
| $\mathrm{C}(2)-\mathrm{C}(1)-\mathrm{C}(8)$ | 124.3(3) |
| $\mathrm{C}(2)-\mathrm{C}(1)-\operatorname{Ir}(1)$ | 70.05(19) |
| $\mathrm{C}(8)-\mathrm{C}(1)-\operatorname{Ir}(1)$ | 113.5(2) |
| $\mathrm{C}(2)-\mathrm{C}(1)-\mathrm{H}(1 \mathrm{~A})$ | 113.8 |
| $\mathrm{C}(8)-\mathrm{C}(1)-\mathrm{H}(1 \mathrm{~A})$ | 113.8 |
| $\operatorname{Ir}(1)-\mathrm{C}(1)-\mathrm{H}(1 \mathrm{~A})$ | 113.8 |
| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)$ | 122.7(3) |
| $\mathrm{C}(1)-\mathrm{C}(2)-\operatorname{Ir}(1)$ | 70.71(19) |
| $\mathrm{C}(3)-\mathrm{C}(2)-\operatorname{Ir}(1)$ | 114.7(2) |
| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{H}(2 \mathrm{~A})$ | 113.9 |
| $\mathrm{C}(3)-\mathrm{C}(2)-\mathrm{H}(2 \mathrm{~A})$ | 113.9 |
| $\operatorname{Ir}(1)-\mathrm{C}(2)-\mathrm{H}(2 \mathrm{~A})$ | 113.9 |
| $\mathrm{C}(4)-\mathrm{C}(3)-\mathrm{C}(2)$ | 111.4(3) |
| $\mathrm{C}(4)-\mathrm{C}(3)-\mathrm{H}(3 \mathrm{~A})$ | 109.3 |
| $\mathrm{C}(2)-\mathrm{C}(3)-\mathrm{H}(3 \mathrm{~A})$ | 109.3 |
| $\mathrm{C}(4)-\mathrm{C}(3)-\mathrm{H}(3 \mathrm{~B})$ | 109.3 |
| $\mathrm{C}(2)-\mathrm{C}(3)-\mathrm{H}(3 \mathrm{~B})$ | 109.3 |
| $\mathrm{H}(3 \mathrm{~A})-\mathrm{C}(3)-\mathrm{H}(3 \mathrm{~B})$ | 108.0 |
| $\mathrm{C}(5)-\mathrm{C}(4)-\mathrm{C}(3)$ | 112.8(3) |
| $\mathrm{C}(5)-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~A})$ | 109.0 |
| $\mathrm{C}(3)-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~A})$ | 109.0 |
| $\mathrm{C}(5)-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~B})$ | 109.0 |
| $\mathrm{C}(3)-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~B})$ | 109.0 |
| $\mathrm{H}(4 \mathrm{~A})-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~B})$ | 107.8 |
| $\mathrm{C}(6)-\mathrm{C}(5)-\mathrm{C}(4)$ | 123.6(3) |
| $\mathrm{C}(6)-\mathrm{C}(5)-\operatorname{Ir}(1)$ | 71.4(2) |
| $\mathrm{C}(4)-\mathrm{C}(5)-\operatorname{Ir}(1)$ | 112.2(2) |
| $\mathrm{C}(6)-\mathrm{C}(5)-\mathrm{H}(5 \mathrm{~A})$ | 114.1 |
| $\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{H}(5 \mathrm{~A})$ | 114.1 |


| $\operatorname{Ir}(1)-\mathrm{C}(5)-\mathrm{H}(5 \mathrm{~A})$ | 114.1 |
| :---: | :---: |
| $\mathrm{C}(5)-\mathrm{C}(6)-\mathrm{C}(7)$ | 123.1(4) |
| $\mathrm{C}(5)-\mathrm{C}(6)-\operatorname{Ir}(1)$ | 69.5(2) |
| $\mathrm{C}(7)-\mathrm{C}(6)-\operatorname{Ir}(1)$ | 115.0(3) |
| $\mathrm{C}(5)-\mathrm{C}(6)-\mathrm{H}(6 \mathrm{~A})$ | 113.9 |
| $\mathrm{C}(7)-\mathrm{C}(6)-\mathrm{H}(6 \mathrm{~A})$ | 113.9 |
| $\operatorname{Ir}(1)-\mathrm{C}(6)-\mathrm{H}(6 \mathrm{~A})$ | 113.9 |
| $\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{C}(8)$ | 111.9(3) |
| $\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{H}(7 \mathrm{~A})$ | 109.2 |
| $\mathrm{C}(8)-\mathrm{C}(7)-\mathrm{H}(7 \mathrm{~A})$ | 109.2 |
| $\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{H}(7 \mathrm{~B})$ | 109.2 |
| $\mathrm{C}(8)-\mathrm{C}(7)-\mathrm{H}(7 \mathrm{~B})$ | 109.2 |
| $\mathrm{H}(7 \mathrm{~A})-\mathrm{C}(7)-\mathrm{H}(7 \mathrm{~B})$ | 107.9 |
| $\mathrm{C}(1)-\mathrm{C}(8)-\mathrm{C}(7)$ | 112.1(3) |
| $\mathrm{C}(1)-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~A})$ | 109.2 |
| $\mathrm{C}(7)-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~A})$ | 109.2 |
| $\mathrm{C}(1)-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~B})$ | 109.2 |
| $\mathrm{C}(7)-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~B})$ | 109.2 |
| $\mathrm{H}(8 \mathrm{~A})-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~B})$ | 107.9 |
| $\mathrm{O}(1)-\mathrm{C}(9)-\mathrm{C}(10)$ | 124.8(3) |
| $\mathrm{O}(1)-\mathrm{C}(9)-\mathrm{C}(16)$ | 113.9(3) |
| $\mathrm{C}(10)-\mathrm{C}(9)-\mathrm{C}(16)$ | 121.4(3) |
| $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(11)$ | 124.6(3) |
| $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{H}(10 \mathrm{~A})$ | 117.7 |
| $\mathrm{C}(11)-\mathrm{C}(10)-\mathrm{H}(10 \mathrm{~A})$ | 117.7 |
| $\mathrm{N}(1)-\mathrm{C}(11)-\mathrm{O}(2)$ | 115.4(3) |
| $\mathrm{N}(1)-\mathrm{C}(11)-\mathrm{C}(10)$ | 131.1(3) |
| $\mathrm{O}(2)-\mathrm{C}(11)-\mathrm{C}(10)$ | 113.5(3) |
| $\mathrm{O}(2)-\mathrm{C}(12)-\mathrm{C}(13)$ | 104.2(3) |
| $\mathrm{O}(2)-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~A})$ | 110.9 |
| $\mathrm{C}(13)-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~A})$ | 110.9 |
| $\mathrm{O}(2)-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~B})$ | 110.9 |
| $\mathrm{C}(13)-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~B})$ | 110.9 |
| $\mathrm{H}(12 \mathrm{~A})-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~B})$ | 108.9 |
| $\mathrm{C}(15)-\mathrm{C}(13)-\mathrm{N}(1)$ | 115.2(3) |
| $\mathrm{C}(15)-\mathrm{C}(13)-\mathrm{C}(12)$ | 109.3(3) |


| $\mathrm{N}(1)-\mathrm{C}(13)-\mathrm{C}(12)$ | 100.4(3) |
| :---: | :---: |
| $\mathrm{C}(15)-\mathrm{C}(13)-\mathrm{C}(14)$ | 112.7(3) |
| $\mathrm{N}(1)-\mathrm{C}(13)-\mathrm{C}(14)$ | 108.0(3) |
| $\mathrm{C}(12)-\mathrm{C}(13)-\mathrm{C}(14)$ | 110.6(3) |
| $\mathrm{C}(13)-\mathrm{C}(14)-\mathrm{H}(14 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(13)-\mathrm{C}(14)-\mathrm{H}(14 \mathrm{~B})$ | 109.5 |
| $\mathrm{H}(14 \mathrm{~A})-\mathrm{C}(14)-\mathrm{H}(14 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(13)-\mathrm{C}(14)-\mathrm{H}(14 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(14 \mathrm{~A})-\mathrm{C}(14)-\mathrm{H}(14 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(14 \mathrm{~B})-\mathrm{C}(14)-\mathrm{H}(14 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(13)-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(13)-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~B})$ | 109.5 |
| $\mathrm{H}(15 \mathrm{~A})-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(13)-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(15 \mathrm{~A})-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(15 \mathrm{~B})-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(17)-\mathrm{C}(16)-\mathrm{C}(21)$ | 118.9(3) |
| $\mathrm{C}(17)-\mathrm{C}(16)-\mathrm{C}(9)$ | 121.7(3) |
| $\mathrm{C}(21)-\mathrm{C}(16)-\mathrm{C}(9)$ | 119.5(3) |
| $\mathrm{C}(18)-\mathrm{C}(17)-\mathrm{C}(16)$ | 120.7(4) |
| $\mathrm{C}(18)-\mathrm{C}(17)-\mathrm{H}(17 \mathrm{~A})$ | 119.7 |
| $\mathrm{C}(16)-\mathrm{C}(17)-\mathrm{H}(17 \mathrm{~A})$ | 119.7 |
| $\mathrm{C}(19)-\mathrm{C}(18)-\mathrm{C}(17)$ | 120.0(4) |
| $\mathrm{C}(19)-\mathrm{C}(18)-\mathrm{H}(18 \mathrm{~A})$ | 120.0 |
| $\mathrm{C}(17)-\mathrm{C}(18)-\mathrm{H}(18 \mathrm{~A})$ | 120.0 |
| $\mathrm{C}(18)-\mathrm{C}(19)-\mathrm{C}(20)$ | 120.2(4) |
| $\mathrm{C}(18)-\mathrm{C}(19)-\mathrm{H}(19 \mathrm{~A})$ | 119.9 |
| $\mathrm{C}(20)-\mathrm{C}(19)-\mathrm{H}(19 \mathrm{~A})$ | 119.9 |
| $\mathrm{C}(19)-\mathrm{C}(20)-\mathrm{C}(21)$ | 119.9(4) |
| $\mathrm{C}(19)-\mathrm{C}(20)-\mathrm{H}(20 \mathrm{~A})$ | 120.1 |
| $\mathrm{C}(21)-\mathrm{C}(20)-\mathrm{H}(20 \mathrm{~A})$ | 120.1 |
| $\mathrm{C}(16)-\mathrm{C}(21)-\mathrm{C}(20)$ | 120.4(4) |
| $\mathrm{C}(16)-\mathrm{C}(21)-\mathrm{H}(21 \mathrm{~A})$ | 119.8 |
| $\mathrm{C}(20)-\mathrm{C}(21)-\mathrm{H}(21 \mathrm{~A})$ | 119.8 |

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for d1804_a. The anisotropic displacement factor exponent takes the form: $-2 p^{2}\left[h^{2} a^{* 2} U^{11}+\ldots+2 h k a^{*} b^{*} U^{12}\right]$

|  | $\mathrm{U}^{11}$ | $\mathrm{U}^{22}$ | $\mathrm{U}^{33}$ | $\mathrm{U}^{23}$ | $\mathrm{U}^{13}$ | $\mathrm{U}^{12}$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
|  |  |  |  |  |  |  |
| $\mathrm{Ir}(1)$ | $12(1)$ | $12(1)$ | $11(1)$ | $0(1)$ | $2(1)$ | $1(1)$ |
| $\mathrm{O}(1)$ | $17(2)$ | $21(2)$ | $12(1)$ | $-1(1)$ | $4(1)$ | $3(1)$ |
| $\mathrm{O}(2)$ | $19(2)$ | $25(2)$ | $14(1)$ | $0(1)$ | $-2(1)$ | $5(1)$ |
| $\mathrm{N}(1)$ | $13(2)$ | $14(2)$ | $9(2)$ | $-1(1)$ | $1(1)$ | $-2(1)$ |
| $\mathrm{C}(1)$ | $14(2)$ | $21(2)$ | $11(2)$ | $0(2)$ | $-3(1)$ | $3(2)$ |
| $\mathrm{C}(2)$ | $16(2)$ | $21(2)$ | $7(2)$ | $3(2)$ | $-6(1)$ | $3(2)$ |
| $\mathrm{C}(3)$ | $25(2)$ | $19(2)$ | $20(2)$ | $1(2)$ | $0(2)$ | $4(2)$ |
| $\mathrm{C}(4)$ | $23(2)$ | $16(2)$ | $20(2)$ | $-2(2)$ | $4(2)$ | $2(2)$ |
| $\mathrm{C}(5)$ | $19(2)$ | $21(2)$ | $15(2)$ | $-3(1)$ | $5(2)$ | $2(2)$ |
| $\mathrm{C}(6)$ | $20(2)$ | $21(2)$ | $15(2)$ | $-2(2)$ | $5(2)$ | $2(2)$ |
| $\mathrm{C}(7)$ | $15(2)$ | $28(2)$ | $22(2)$ | $-1(2)$ | $5(2)$ | $3(2)$ |
| $\mathrm{C}(8)$ | $13(2)$ | $23(2)$ | $23(2)$ | $2(2)$ | $0(2)$ | $1(2)$ |
| $\mathrm{C}(9)$ | $10(2)$ | $12(2)$ | $19(2)$ | $-2(2)$ | $6(2)$ | $-6(2)$ |
| $\mathrm{C}(10)$ | $11(2)$ | $11(2)$ | $18(2)$ | $-2(2)$ | $0(2)$ | $0(2)$ |
| $\mathrm{C}(11)$ | $17(2)$ | $14(2)$ | $13(2)$ | $2(2)$ | $-2(2)$ | $-5(2)$ |
| $\mathrm{C}(12)$ | $22(2)$ | $23(2)$ | $15(2)$ | $2(2)$ | $1(2)$ | $3(2)$ |
| $\mathrm{C}(13)$ | $16(2)$ | $18(2)$ | $9(2)$ | $0(2)$ | $0(2)$ | $-2(2)$ |
| $\mathrm{C}(14)$ | $22(2)$ | $22(2)$ | $16(2)$ | $-1(2)$ | $1(2)$ | $-5(2)$ |
| $\mathrm{C}(15)$ | $19(2)$ | $24(2)$ | $9(2)$ | $0(2)$ | $1(2)$ | $-1(2)$ |
| $\mathrm{C}(16)$ | $10(2)$ | $20(2)$ | $15(2)$ | $-5(2)$ | $3(2)$ | $-4(2)$ |
| $\mathrm{C}(17)$ | $17(2)$ | $19(2)$ | $21(2)$ | $-4(2)$ | $4(2)$ | $0(2)$ |
| $\mathrm{C}(18)$ | $18(2)$ | $21(2)$ | $31(2)$ | $-10(2)$ | $6(2)$ | $1(2)$ |
| $\mathrm{C}(19)$ | $26(2)$ | $35(3)$ | $25(2)$ | $-11(2)$ | $16(2)$ | $-2(2)$ |
|  | $34(3)$ | $31(3)$ | $17(2)$ | $1(2)$ | $8(2)$ | $-4(2)$ |
|  | $23(2)$ | $20(2)$ | $1(2)$ | $5(2)$ | $3(2)$ |  |

Table 5. Hydrogen coordinates ( $\times 10^{4}$ ) and isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for d1804_a.

|  | x | y | z | U(eq) |
| :---: | :---: | :---: | :---: | :---: |
| H(1A) | 2297 | 6546 | 2747 | 20 |
| H(2A) | 3620 | 8076 | 2731 | 19 |
| H(3A) | 2742 | 9652 | 3099 | 26 |
| H(3B) | 1225 | 9049 | 3311 | 26 |
| H(4A) | 4086 | 9754 | 4328 | 23 |
| H(4B) | 2290 | 9696 | 4483 | 23 |
| H(5A) | 4315 | 8416 | 5268 | 22 |
| H(6A) | 2654 | 7032 | 5237 | 22 |
| H(7A) | 351 | 8150 | 4197 | 26 |
| H(7B) | 80 | 6998 | 4534 | 26 |
| H(8A) | 373 | 6163 | 3465 | 24 |
| H(8B) | -239 | 7281 | 3073 | 24 |
| H(10A) | 8373 | 4946 | 4135 | 17 |
| H(12A) | 8699 | 6004 | 6564 | 24 |
| H(12B) | 7174 | 5211 | 6303 | 24 |
| H(14A) | 8630 | 7663 | 5689 | 30 |
| H(14B) | 8048 | 7956 | 6467 | 30 |
| H(14C) | 7003 | 8340 | 5640 | 30 |
| H(15A) | 5819 | 6745 | 6844 | 26 |
| H(15B) | 4609 | 6180 | 6129 | 26 |
| H(15C) | 4742 | 7450 | 6164 | 26 |
| H(17A) | 7871 | 3847 | 3104 | 23 |
| H(18A) | 8356 | 3184 | 1943 | 28 |
| H(19A) | 7815 | 4232 | 828 | 32 |
| H(20A) | 6696 | 5924 | 856 | 32 |
| H(21A) | 6147 | 6578 | 2012 | 25 |

Table 6. Torsion angles [ ${ }^{\circ}$ ] for d1804_a.

| $\mathrm{C}(8)-\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)$ | -2.1(5) |
| :---: | :---: |
| $\operatorname{Ir}(1)-\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)$ | -107.5(3) |
| $\mathrm{C}(8)-\mathrm{C}(1)-\mathrm{C}(2)-\operatorname{Ir}(1)$ | 105.5(3) |
| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)-\mathrm{C}(4)$ | 92.4(4) |
| $\operatorname{Ir}(1)-\mathrm{C}(2)-\mathrm{C}(3)-\mathrm{C}(4)$ | 10.2(4) |
| $\mathrm{C}(2)-\mathrm{C}(3)-\mathrm{C}(4)-\mathrm{C}(5)$ | -26.2(5) |
| $\mathrm{C}(3)-\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{C}(6)$ | -51.4(5) |
| $\mathrm{C}(3)-\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{Ir}(1)$ | 30.5(4) |
| $\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{C}(6)-\mathrm{C}(7)$ | -2.4(6) |
| $\operatorname{Ir}(1)-\mathrm{C}(5)-\mathrm{C}(6)-\mathrm{C}(7)$ | -107.2(3) |
| $\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{C}(6)-\operatorname{Ir}(1)$ | 104.8(3) |
| $\mathrm{C}(5)-\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{C}(8)$ | 92.8(4) |
| $\operatorname{Ir}(1)-\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{C}(8)$ | 11.8(4) |
| $\mathrm{C}(2)-\mathrm{C}(1)-\mathrm{C}(8)-\mathrm{C}(7)$ | -51.7(5) |
| $\operatorname{Ir}(1)-\mathrm{C}(1)-\mathrm{C}(8)-\mathrm{C}(7)$ | 29.5(4) |
| $\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{C}(8)-\mathrm{C}(1)$ | -26.4(5) |
| $\operatorname{Ir}(1)-\mathrm{O}(1)-\mathrm{C}(9)-\mathrm{C}(10)$ | -5.5(5) |
| $\operatorname{Ir}(1)-\mathrm{O}(1)-\mathrm{C}(9)-\mathrm{C}(16)$ | 174.7(2) |
| $\mathrm{O}(1)-\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(11)$ | -0.8(6) |
| $\mathrm{C}(16)-\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(11)$ | 179.1(3) |
| $\mathrm{C}(13)-\mathrm{N}(1)-\mathrm{C}(11)-\mathrm{O}(2)$ | 7.8(4) |
| $\operatorname{Ir}(1)-\mathrm{N}(1)-\mathrm{C}(11)-\mathrm{O}(2)$ | -179.5(2) |
| $\mathrm{C}(13)-\mathrm{N}(1)-\mathrm{C}(11)-\mathrm{C}(10)$ | -170.0(4) |
| $\operatorname{Ir}(1)-\mathrm{N}(1)-\mathrm{C}(11)-\mathrm{C}(10)$ | 2.7(5) |
| $\mathrm{C}(12)-\mathrm{O}(2)-\mathrm{C}(11)-\mathrm{N}(1)$ | 11.4(4) |
| $\mathrm{C}(12)-\mathrm{O}(2)-\mathrm{C}(11)-\mathrm{C}(10)$ | -170.4(3) |
| $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(11)-\mathrm{N}(1)$ | 2.1(6) |
| $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(11)-\mathrm{O}(2)$ | -175.7(3) |
| $\mathrm{C}(11)-\mathrm{O}(2)-\mathrm{C}(12)-\mathrm{C}(13)$ | -25.1(4) |
| $\mathrm{C}(11)-\mathrm{N}(1)-\mathrm{C}(13)-\mathrm{C}(15)$ | -139.4(3) |
| $\operatorname{Ir}(1)-\mathrm{N}(1)-\mathrm{C}(13)-\mathrm{C}(15)$ | 49.1(4) |
| $\mathrm{C}(11)-\mathrm{N}(1)-\mathrm{C}(13)-\mathrm{C}(12)$ | -22.2(4) |
| $\operatorname{Ir}(1)-\mathrm{N}(1)-\mathrm{C}(13)-\mathrm{C}(12)$ | 166.3(2) |
| $\mathrm{C}(11)-\mathrm{N}(1)-\mathrm{C}(13)-\mathrm{C}(14)$ | 93.6(3) |
|  |  |


| $\mathrm{Ir}(1)-\mathrm{N}(1)-\mathrm{C}(13)-\mathrm{C}(14)$ | $-77.8(4)$ |
| :--- | :---: |
| $\mathrm{O}(2)-\mathrm{C}(12)-\mathrm{C}(13)-\mathrm{C}(15)$ | $149.8(3)$ |
| $\mathrm{O}(2)-\mathrm{C}(12)-\mathrm{C}(13)-\mathrm{N}(1)$ | $28.3(3)$ |
| $\mathrm{O}(2)-\mathrm{C}(12)-\mathrm{C}(13)-\mathrm{C}(14)$ | $-85.5(3)$ |
| $\mathrm{O}(1)-\mathrm{C}(9)-\mathrm{C}(16)-\mathrm{C}(17)$ | $-149.1(3)$ |
| $\mathrm{C}(10)-\mathrm{C}(9)-\mathrm{C}(16)-\mathrm{C}(17)$ | $31.1(5)$ |
| $\mathrm{O}(1)-\mathrm{C}(9)-\mathrm{C}(16)-\mathrm{C}(21)$ | $29.9(5)$ |
| $\mathrm{C}(10)-\mathrm{C}(9)-\mathrm{C}(16)-\mathrm{C}(21)$ | $-149.9(4)$ |
| $\mathrm{C}(21)-\mathrm{C}(16)-\mathrm{C}(17)-\mathrm{C}(18)$ | $-0.1(6)$ |
| $\mathrm{C}(9)-\mathrm{C}(16)-\mathrm{C}(17)-\mathrm{C}(18)$ | $178.9(3)$ |
| $\mathrm{C}(16)-\mathrm{C}(17)-\mathrm{C}(18)-\mathrm{C}(19)$ | $1.0(6)$ |
| $\mathrm{C}(17)-\mathrm{C}(18)-\mathrm{C}(19)-\mathrm{C}(20)$ | $-1.2(6)$ |
| $\mathrm{C}(18)-\mathrm{C}(19)-\mathrm{C}(20)-\mathrm{C}(21)$ | $0.4(6)$ |
| $\mathrm{C}(17)-\mathrm{C}(16)-\mathrm{C}(21)-\mathrm{C}(20)$ | $-0.7(6)$ |
| $\mathrm{C}(9)-\mathrm{C}(16)-\mathrm{C}(21)-\mathrm{C}(20)$ | $-179.8(4)$ |
| $\mathrm{C}(19)-\mathrm{C}(20)-\mathrm{C}(21)-\mathrm{C}(16)$ | $0.6(6)$ |

Symmetry transformations used to generate equivalent atoms:


F10: Crystal data and structure refinement for d1872_a (16).

Identification code
Empirical formula
Formula weight
Temperature
Wavelength
Crystal system
Space group
Unit cell dimensions

Volume

Z

Density (calculated)
Absorption coefficient
F(000)
Crystal size
Theta range for data collection
Index ranges
Reflections collected
Independent reflections
Completeness to theta $=25.242 \infty$
d1872_a (16)
C22 H29 I Ir N O2
658.56

150(2) K
$0.71073 \approx$
Monoclinic
P21/n
$a=14.6277(6) \approx \quad \alpha=90 \infty$.
$b=9.7486(4) \approx \quad \beta=101.6540(10) \infty$.
$\mathrm{c}=14.6525(6) \approx \quad \gamma=90 \infty$.
2046.37(15) $\approx^{3}$

4
$2.138 \mathrm{Mg} / \mathrm{m}^{3}$
$8.050 \mathrm{~mm}^{-1}$
1256
$0.180 \times 0.170 \times 0.040 \mathrm{~mm}^{3}$
1.794 to $27.541 \infty$.
$-19<=\mathrm{h}<=19,-12<=\mathrm{k}<=12,-19<=1<=19$
30365
$4701[\mathrm{R}(\mathrm{int})=0.0325]$
100.0 \%

Absorption correction
Max. and min. transmission
Refinement method
Data / restraints / parameters
Goodness-of-fit on $\mathrm{F}^{2}$
Final R indices [I>2sigma(I)]
R indices (all data)
Extinction coefficient
Largest diff. peak and hole

Semi-empirical from equivalents
0.7456 and 0.5749

Full-matrix least-squares on $\mathrm{F}^{2}$
4701 / 0 / 247
1.069
$\mathrm{R} 1=0.0178, \mathrm{wR} 2=0.0343$
$R 1=0.0273, w R 2=0.0367$
n/a
0.741 and -0.905 e. $\approx^{-3}$

Table 2. Atomic coordinates $\left(\times 10^{4}\right)$ and equivalent isotropic displacement parameters $\left(\approx^{2} \times 10^{3}\right)$ for d1872_a. $\mathrm{U}(\mathrm{eq})$ is defined as one third of the trace of the orthogonalized $\mathrm{U}^{\mathrm{ij}}$ tensor.

|  | x | y | Z | U(eq) |
| :---: | :---: | :---: | :---: | :---: |
| $\operatorname{Ir}(1)$ | 2177(1) | 3248(1) | 4367(1) | 12(1) |
| I(1) | 3162(1) | 3484(1) | 6255(1) | 18(1) |
| $\mathrm{O}(1)$ | 3401(1) | 2494(2) | 4104(2) | 16(1) |
| $\mathrm{O}(2)$ | 3748(1) | 6843(2) | 4180(2) | 17(1) |
| N(1) | 2646(2) | 5285(2) | 4314(2) | 12(1) |
| C(1) | 4109(2) | 3199(3) | 3951(2) | 13(1) |
| C(2) | 4185(2) | 4595(3) | 3990(2) | 15(1) |
| C(3) | 3489(2) | 5506(3) | 4173(2) | 14(1) |
| C(4) | 3037(2) | 7619(3) | 4499(2) | 17(1) |
| C(5) | 2187(2) | 6656(3) | 4378(2) | 16(1) |
| C(6) | 4858(2) | 2318(3) | 3693(2) | 13(1) |
| C(7) | 4866(2) | 916(3) | 3902(2) | 19(1) |
| C(8) | 5518(2) | 56(3) | 3634(2) | 23(1) |
| C(9) | 6165(2) | 570(4) | 3150(2) | 24(1) |
| C(10) | 6173(2) | 1953(4) | 2960(2) | 23(1) |
| C(11) | 5525(2) | 2835(3) | 3227(2) | 17(1) |
| C(12) | 1727(2) | 6762(3) | 5220(2) | 19(1) |
| C(13) | 1508(2) | 7005(3) | 3474(2) | 19(1) |
| C(14) | 676(2) | 3674(3) | 4101(2) | 16(1) |
| C(15) | 137(2) | 2639(3) | 3429(2) | 20(1) |
| C(16) | 594(2) | 1211(3) | 3488(2) | 21(1) |
| C(17) | 1637(2) | 1232(3) | 3872(2) | 19(1) |
| C(18) | 2036(2) | 1117(3) | 4821(2) | 18(1) |
| C(19) | 1476(2) | 982(3) | 5572(2) | 20(1) |
| C(20) | 727(2) | 2095(3) | 5505(2) | 18(1) |
| C(21) | 970(2) | 3425(3) | 5057(2) | 15(1) |
| C(22) | 1882(2) | 3577(3) | 2861(2) | 15(1) |

Table 3. Bond lengths [ $\approx]$ and angles [ $\infty$ ] for d1872_a.

| $\mathrm{Ir}(1)-\mathrm{O}(1)$ | 2.0426(19) |
| :---: | :---: |
| $\operatorname{Ir}(1)-\mathrm{N}(1)$ | 2.108(2) |
| $\operatorname{Ir}(1)-\mathrm{C}(22)$ | 2.184(3) |
| $\operatorname{Ir}(1)-\mathrm{C}(17)$ | 2.187(3) |
| $\operatorname{Ir}(1)-\mathrm{C}(14)$ | 2.191(3) |
| $\operatorname{Ir}(1)-\mathrm{C}(18)$ | 2.204(3) |
| $\operatorname{Ir}(1)-\mathrm{C}(21)$ | 2.211(3) |
| $\operatorname{Ir}(1)-\mathrm{I}(1)$ | 2.8598(2) |
| $\mathrm{O}(1)-\mathrm{C}(1)$ | 1.299(3) |
| $\mathrm{O}(2)-\mathrm{C}(3)$ | 1.357(3) |
| $\mathrm{O}(2)-\mathrm{C}(4)$ | 1.439(3) |
| $\mathrm{N}(1)$-C(3) | $1.309(4)$ |
| $\mathrm{N}(1)-\mathrm{C}(5)$ | 1.507(3) |
| $\mathrm{C}(1)-\mathrm{C}(2)$ | 1.366(4) |
| $\mathrm{C}(1)-\mathrm{C}(6)$ | 1.500(4) |
| $\mathrm{C}(2)-\mathrm{C}(3)$ | 1.417(4) |
| $\mathrm{C}(2)-\mathrm{H}(2 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(4)-\mathrm{C}(5)$ | 1.539(4) |
| $\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~A})$ | 0.9900 |
| $\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~B})$ | 0.9900 |
| $\mathrm{C}(5)-\mathrm{C}(12)$ | 1.524(4) |
| $\mathrm{C}(5)-\mathrm{C}(13)$ | 1.525(4) |
| $\mathrm{C}(6)-\mathrm{C}(11)$ | 1.394(4) |
| $\mathrm{C}(6)-\mathrm{C}(7)$ | 1.400(4) |
| $\mathrm{C}(7)-\mathrm{C}(8)$ | 1.385(4) |
| $\mathrm{C}(7)-\mathrm{H}(7 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(8)$-C(9) | $1.385(5)$ |
| $\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(9)-\mathrm{C}(10)$ | 1.378(5) |
| $\mathrm{C}(9)-\mathrm{H}(9 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(10)-\mathrm{C}(11)$ | 1.392(4) |
| $\mathrm{C}(10)-\mathrm{H}(10 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(11)-\mathrm{H}(11 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~A})$ | 0.9800 |


| $\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~B})$ | 0.9800 |
| :---: | :---: |
| $\mathrm{C}(12)-\mathrm{H}(12 \mathrm{C})$ | 0.9800 |
| $\mathrm{C}(13)-\mathrm{H}(13 \mathrm{~A})$ | 0.9800 |
| $\mathrm{C}(13)-\mathrm{H}(13 \mathrm{~B})$ | 0.9800 |
| $\mathrm{C}(13)-\mathrm{H}(13 \mathrm{C})$ | 0.9800 |
| $\mathrm{C}(14)-\mathrm{C}(21)$ | 1.401(4) |
| $\mathrm{C}(14)-\mathrm{C}(15)$ | 1.516(4) |
| $\mathrm{C}(14)-\mathrm{H}(14 \mathrm{~A})$ | 1.0000 |
| $\mathrm{C}(15)-\mathrm{C}(16)$ | 1.539(4) |
| $\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~A})$ | 0.9900 |
| $\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~B})$ | 0.9900 |
| $\mathrm{C}(16)-\mathrm{C}(17)$ | 1.516(4) |
| $\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~A})$ | 0.9900 |
| $\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~B})$ | 0.9900 |
| $\mathrm{C}(17)-\mathrm{C}(18)$ | 1.401(5) |
| $\mathrm{C}(17)-\mathrm{H}(17 \mathrm{~A})$ | 1.0000 |
| $\mathrm{C}(18)$-C(19) | 1.503(4) |
| $\mathrm{C}(18)-\mathrm{H}(18 \mathrm{~A})$ | 1.0000 |
| $\mathrm{C}(19)-\mathrm{C}(20)$ | 1.530(4) |
| $\mathrm{C}(19)-\mathrm{H}(19 \mathrm{~A})$ | 0.9900 |
| $\mathrm{C}(19)-\mathrm{H}(19 \mathrm{~B})$ | 0.9900 |
| $\mathrm{C}(20)-\mathrm{C}(21)$ | 1.527(4) |
| $\mathrm{C}(20)-\mathrm{H}(20 \mathrm{~A})$ | 0.9900 |
| $\mathrm{C}(20)-\mathrm{H}(20 \mathrm{~B})$ | 0.9900 |
| $\mathrm{C}(21)-\mathrm{H}(21 \mathrm{~A})$ | 1.0000 |
| $\mathrm{C}(22)-\mathrm{H}(22 \mathrm{~A})$ | 0.9800 |
| $\mathrm{C}(22)-\mathrm{H}(22 \mathrm{~B})$ | 0.9800 |
| $\mathrm{C}(22)-\mathrm{H}(22 \mathrm{C})$ | 0.9800 |
| $\mathrm{O}(1)-\operatorname{Ir}(1)-\mathrm{N}(1)$ | 91.57(8) |
| $\mathrm{O}(1)-\mathrm{Ir}(1)-\mathrm{C}(22)$ | 82.21(10) |
| $\mathrm{N}(1)-\operatorname{Ir}(1)-\mathrm{C}(22)$ | 79.87(10) |
| $\mathrm{O}(1)-\operatorname{Ir}(1)-\mathrm{C}(17)$ | 83.47(10) |
| $\mathrm{N}(1)-\operatorname{Ir}(1)-\mathrm{C}(17)$ | 158.96(11) |
| $\mathrm{C}(22)-\operatorname{Ir}(1)-\mathrm{C}(17)$ | 79.20(12) |
| $\mathrm{O}(1)-\operatorname{Ir}(1)-\mathrm{C}(14)$ | 156.93(10) |


| $\mathrm{N}(1)-\operatorname{Ir}(1)-\mathrm{C}(14)$ | 97.87(10) |
| :---: | :---: |
| $\mathrm{C}(22)-\operatorname{Ir}(1)-\mathrm{C}(14)$ | 78.83(11) |
| $\mathrm{C}(17)-\operatorname{Ir}(1)-\mathrm{C}(14)$ | 80.19(11) |
| $\mathrm{O}(1)-\operatorname{Ir}(1)-\mathrm{C}(18)$ | 81.78(10) |
| $\mathrm{N}(1)-\operatorname{Ir}(1)-\mathrm{C}(18)$ | 161.82(11) |
| $\mathrm{C}(22)-\operatorname{Ir}(1)-\mathrm{C}(18)$ | 115.62(11) |
| $\mathrm{C}(17)-\mathrm{Ir}(1)-\mathrm{C}(18)$ | 37.21(12) |
| $\mathrm{C}(14)-\operatorname{Ir}(1)-\mathrm{C}(18)$ | 94.65(12) |
| $\mathrm{O}(1)-\operatorname{Ir}(1)-\mathrm{C}(21)$ | 157.73(9) |
| $\mathrm{N}(1)-\operatorname{Ir}(1)-\mathrm{C}(21)$ | 103.83(10) |
| $\mathrm{C}(22)-\operatorname{Ir}(1)-\mathrm{C}(21)$ | 115.93(11) |
| $\mathrm{C}(17)-\operatorname{Ir}(1)-\mathrm{C}(21)$ | 87.35(11) |
| $\mathrm{C}(14)-\operatorname{Ir}(1)-\mathrm{C}(21)$ | 37.10(11) |
| $\mathrm{C}(18)-\operatorname{Ir}(1)-\mathrm{C}(21)$ | 78.67(11) |
| $\mathrm{O}(1)-\operatorname{Ir}(1)-\mathrm{I}(1)$ | 85.50(6) |
| $\mathrm{N}(1)-\operatorname{Ir}(1)-\mathrm{I}(1)$ | 81.65(6) |
| $\mathrm{C}(22)-\operatorname{Ir}(1)-\mathrm{I}(1)$ | 157.45(8) |
| $\mathrm{C}(17)-\operatorname{Ir}(1)-\mathrm{I}(1)$ | 118.12(9) |
| $\mathrm{C}(14)-\operatorname{Ir}(1)-\mathrm{I}(1)$ | 116.60(8) |
| $\mathrm{C}(18)-\operatorname{Ir}(1)-\mathrm{I}(1)$ | 80.98(8) |
| $\mathrm{C}(21)-\operatorname{Ir}(1)-\mathrm{I}(1)$ | 81.03(8) |
| $\mathrm{C}(1)-\mathrm{O}(1)-\operatorname{Ir}(1)$ | 126.99(18) |
| $\mathrm{C}(3)-\mathrm{O}(2)-\mathrm{C}(4)$ | 106.7(2) |
| $\mathrm{C}(3)-\mathrm{N}(1)-\mathrm{C}(5)$ | 108.0(2) |
| $\mathrm{C}(3)-\mathrm{N}(1)-\operatorname{Ir}(1)$ | 119.03(19) |
| $\mathrm{C}(5)-\mathrm{N}(1)-\operatorname{Ir}(1)$ | 132.90(18) |
| $\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(2)$ | 125.6(3) |
| $\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(6)$ | 112.9(2) |
| $\mathrm{C}(2)-\mathrm{C}(1)-\mathrm{C}(6)$ | 121.5(3) |
| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)$ | 125.2(3) |
| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{H}(2 \mathrm{~A})$ | 117.4 |
| $\mathrm{C}(3)-\mathrm{C}(2)-\mathrm{H}(2 \mathrm{~A})$ | 117.4 |
| $\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{O}(2)$ | 115.3(2) |
| $\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{C}(2)$ | 131.5(3) |
| $\mathrm{O}(2)-\mathrm{C}(3)-\mathrm{C}(2)$ | 113.1(3) |
| $\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{C}(5)$ | 105.2(2) |


| $\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~A})$ | 110.7 |
| :---: | :---: |
| $\mathrm{C}(5)-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~A})$ | 110.7 |
| $\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~B})$ | 110.7 |
| $\mathrm{C}(5)-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~B})$ | 110.7 |
| $\mathrm{H}(4 \mathrm{~A})-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~B})$ | 108.8 |
| $\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(12)$ | 112.7(2) |
| $\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(13)$ | 111.3(2) |
| $\mathrm{C}(12)-\mathrm{C}(5)-\mathrm{C}(13)$ | 111.8(3) |
| $\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(4)$ | 100.9(2) |
| $\mathrm{C}(12)-\mathrm{C}(5)-\mathrm{C}(4)$ | 110.1(3) |
| $\mathrm{C}(13)-\mathrm{C}(5)-\mathrm{C}(4)$ | 109.4(2) |
| $\mathrm{C}(11)-\mathrm{C}(6)-\mathrm{C}(7)$ | 119.0(3) |
| $\mathrm{C}(11)-\mathrm{C}(6)-\mathrm{C}(1)$ | 122.4(3) |
| $\mathrm{C}(7)-\mathrm{C}(6)-\mathrm{C}(1)$ | 118.6(3) |
| $\mathrm{C}(8)-\mathrm{C}(7)-\mathrm{C}(6)$ | 120.3(3) |
| $\mathrm{C}(8)-\mathrm{C}(7)-\mathrm{H}(7 \mathrm{~A})$ | 119.8 |
| $\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{H}(7 \mathrm{~A})$ | 119.8 |
| $\mathrm{C}(9)-\mathrm{C}(8)-\mathrm{C}(7)$ | 120.4(3) |
| $\mathrm{C}(9)-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~A})$ | 119.8 |
| $\mathrm{C}(7)-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~A})$ | 119.8 |
| $\mathrm{C}(10)-\mathrm{C}(9)-\mathrm{C}(8)$ | 119.5(3) |
| $\mathrm{C}(10)-\mathrm{C}(9)-\mathrm{H}(9 \mathrm{~A})$ | 120.2 |
| $\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{H}(9 \mathrm{~A})$ | 120.2 |
| $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(11)$ | 120.8(3) |
| $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{H}(10 \mathrm{~A})$ | 119.6 |
| $\mathrm{C}(11)-\mathrm{C}(10)-\mathrm{H}(10 \mathrm{~A})$ | 119.6 |
| $\mathrm{C}(10)-\mathrm{C}(11)-\mathrm{C}(6)$ | 119.9(3) |
| $\mathrm{C}(10)-\mathrm{C}(11)-\mathrm{H}(11 \mathrm{~A})$ | 120.1 |
| $\mathrm{C}(6)-\mathrm{C}(11)-\mathrm{H}(11 \mathrm{~A})$ | 120.1 |
| $\mathrm{C}(5)-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(5)-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~B})$ | 109.5 |
| $\mathrm{H}(12 \mathrm{~A})-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(5)-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(12 \mathrm{~A})-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(12 \mathrm{~B})-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(5)-\mathrm{C}(13)-\mathrm{H}(13 \mathrm{~A})$ | 109.5 |


| $\mathrm{C}(5)-\mathrm{C}(13)-\mathrm{H}(13 \mathrm{~B})$ | 109.5 |
| :---: | :---: |
| $\mathrm{H}(13 \mathrm{~A})-\mathrm{C}(13)-\mathrm{H}(13 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(5)-\mathrm{C}(13)-\mathrm{H}(13 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(13 \mathrm{~A})-\mathrm{C}(13)-\mathrm{H}(13 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(13 \mathrm{~B})-\mathrm{C}(13)-\mathrm{H}(13 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(21)-\mathrm{C}(14)-\mathrm{C}(15)$ | 123.3(3) |
| $\mathrm{C}(21)-\mathrm{C}(14)-\mathrm{Ir}(1)$ | 72.25(17) |
| $\mathrm{C}(15)-\mathrm{C}(14)-\operatorname{Ir}(1)$ | 111.1(2) |
| $\mathrm{C}(21)-\mathrm{C}(14)-\mathrm{H}(14 \mathrm{~A})$ | 114.3 |
| $\mathrm{C}(15)-\mathrm{C}(14)-\mathrm{H}(14 \mathrm{~A})$ | 114.3 |
| $\operatorname{Ir}(1)-\mathrm{C}(14)-\mathrm{H}(14 \mathrm{~A})$ | 114.3 |
| $\mathrm{C}(14)-\mathrm{C}(15)-\mathrm{C}(16)$ | 113.7(3) |
| $\mathrm{C}(14)-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~A})$ | 108.8 |
| $\mathrm{C}(16)-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~A})$ | 108.8 |
| $\mathrm{C}(14)-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~B})$ | 108.8 |
| $\mathrm{C}(16)-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~B})$ | 108.8 |
| $\mathrm{H}(15 \mathrm{~A})-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~B})$ | 107.7 |
| $\mathrm{C}(17)-\mathrm{C}(16)-\mathrm{C}(15)$ | 113.7(2) |
| $\mathrm{C}(17)-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~A})$ | 108.8 |
| $\mathrm{C}(15)-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~A})$ | 108.8 |
| $\mathrm{C}(17)-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~B})$ | 108.8 |
| $\mathrm{C}(15)-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~B})$ | 108.8 |
| $\mathrm{H}(16 \mathrm{~A})-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~B})$ | 107.7 |
| $\mathrm{C}(18)-\mathrm{C}(17)-\mathrm{C}(16)$ | 123.7(3) |
| $\mathrm{C}(18)-\mathrm{C}(17)-\operatorname{Ir}(1)$ | 72.06(17) |
| $\mathrm{C}(16)-\mathrm{C}(17)-\operatorname{Ir}(1)$ | 113.8(2) |
| $\mathrm{C}(18)-\mathrm{C}(17)-\mathrm{H}(17 \mathrm{~A})$ | 113.5 |
| $\mathrm{C}(16)-\mathrm{C}(17)-\mathrm{H}(17 \mathrm{~A})$ | 113.5 |
| $\operatorname{Ir}(1)-\mathrm{C}(17)-\mathrm{H}(17 \mathrm{~A})$ | 113.5 |
| $\mathrm{C}(17)-\mathrm{C}(18)-\mathrm{C}(19)$ | 123.6(3) |
| $\mathrm{C}(17)-\mathrm{C}(18)-\operatorname{Ir}(1)$ | 70.73(17) |
| $\mathrm{C}(19)-\mathrm{C}(18)-\operatorname{Ir}(1)$ | 113.7(2) |
| $\mathrm{C}(17)-\mathrm{C}(18)-\mathrm{H}(18 \mathrm{~A})$ | 113.8 |
| $\mathrm{C}(19)-\mathrm{C}(18)-\mathrm{H}(18 \mathrm{~A})$ | 113.8 |
| $\operatorname{Ir}(1)-\mathrm{C}(18)-\mathrm{H}(18 \mathrm{~A})$ | 113.8 |
| $\mathrm{C}(18)-\mathrm{C}(19)-\mathrm{C}(20)$ | 112.3(3) |


| $\mathrm{C}(18)-\mathrm{C}(19)-\mathrm{H}(19 \mathrm{~A})$ | 109.1 |
| :--- | :--- |
| $\mathrm{C}(20)-\mathrm{C}(19)-\mathrm{H}(19 \mathrm{~A})$ | 109.1 |
| $\mathrm{C}(18)-\mathrm{C}(19)-\mathrm{H}(19 \mathrm{~B})$ | 109.1 |
| $\mathrm{C}(20)-\mathrm{C}(19)-\mathrm{H}(19 \mathrm{~B})$ | 109.1 |
| $\mathrm{H}(19 \mathrm{~A})-\mathrm{C}(19)-\mathrm{H}(19 \mathrm{~B})$ | 107.9 |
| $\mathrm{C}(21)-\mathrm{C}(20)-\mathrm{C}(19)$ | $113.8(3)$ |
| $\mathrm{C}(21)-\mathrm{C}(20)-\mathrm{H}(20 \mathrm{~A})$ | 108.8 |
| $\mathrm{C}(19)-\mathrm{C}(20)-\mathrm{H}(20 \mathrm{~A})$ | 108.8 |
| $\mathrm{C}(21)-\mathrm{C}(20)-\mathrm{H}(20 \mathrm{~B})$ | 108.8 |
| $\mathrm{C}(19)-\mathrm{C}(20)-\mathrm{H}(20 \mathrm{~B})$ | 108.8 |
| $\mathrm{H}(20 \mathrm{~A})-\mathrm{C}(20)-\mathrm{H}(20 \mathrm{~B})$ | 107.7 |
| $\mathrm{C}(14)-\mathrm{C}(21)-\mathrm{C}(20)$ | $121.7(3)$ |
| $\mathrm{C}(14)-\mathrm{C}(21)-\mathrm{Hr}(1)$ | $70.65(17)$ |
| $\mathrm{C}(20)-\mathrm{C}(21)-\mathrm{Ir}(1)$ | $113.97(19)$ |
| $\mathrm{C}(14)-\mathrm{C}(21)-\mathrm{H}(21 \mathrm{~A})$ | 114.4 |
| $\mathrm{C}(20)-\mathrm{C}(21)-\mathrm{H}(21 \mathrm{~A})$ | 114.4 |
| $\mathrm{Ir}(1)-\mathrm{C}(21)-\mathrm{H}(21 \mathrm{~A})$ | 114.4 |
| $\mathrm{Ir}(1)-\mathrm{C}(22)-\mathrm{H}(22 \mathrm{~A})$ | 109.5 |
| $\mathrm{Ir}(1)-\mathrm{C}(22)-\mathrm{H}(22 \mathrm{~B})$ | 109.5 |
| $\mathrm{H}(22 \mathrm{~A})-\mathrm{C}(22)-\mathrm{H}(22 \mathrm{~B})$ | 109.5 |
| $\mathrm{Ir}(1)-\mathrm{C}(22)-\mathrm{H}(22 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(22 \mathrm{~A})-\mathrm{C}(22)-\mathrm{H}(22 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(22 \mathrm{~B})-\mathrm{C}(22)-\mathrm{H}(22 \mathrm{C})$ | 109.5 |
|  |  |

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters $\left(\approx^{2} \times 10^{3}\right)$ for d1872_a. The anisotropic displacement factor exponent takes the form: $-2 \pi^{2}\left[h^{2} a^{* 2} U^{11}+\ldots+2 h k a^{*} b^{*} U^{12}\right]$

|  | $\mathrm{U}^{11}$ | $\mathrm{U}^{22}$ | $\mathrm{U}^{33}$ | $\mathrm{U}^{23}$ | $\mathrm{U}^{13}$ | $\mathrm{U}^{12}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\operatorname{Ir}(1)$ | 9(1) | 12(1) | 13(1) | -2(1) | 3(1) | 1(1) |
| I(1) | 16(1) | 18(1) | 17(1) | 2(1) | 0(1) | $0(1)$ |
| $\mathrm{O}(1)$ | 10(1) | 14(1) | 24(1) | -2(1) | 7(1) | 2(1) |
| $\mathrm{O}(2)$ | 15(1) | 14(1) | 23(1) | 0(1) | 6(1) | 1(1) |
| N(1) | 10(1) | 13(1) | 13(1) | -1(1) | 3(1) | 4(1) |
| C(1) | 9(1) | 20(1) | 10(2) | -1(1) | 1(1) | 2(1) |
| C(2) | 12(2) | 20(2) | 16(2) | 1(1) | 6(1) | 1(1) |
| C(3) | 16(2) | 14(1) | 11(2) | 0(1) | 1(1) | 2(1) |
| C(4) | 19(2) | 14(1) | 18(2) | -1(1) | 3(1) | 3(1) |
| C(5) | 16(2) | 11(1) | 19(2) | $0(1)$ | 3(1) | 2(1) |
| C(6) | 10(2) | 19(1) | 10(2) | -3(1) | -1(1) | 1(1) |
| C(7) | 16(2) | 20(2) | 20(2) | -2(1) | 2(1) | 4(1) |
| C(8) | 24(2) | 22(2) | 21(2) | -5(1) | -2(2) | 6(1) |
| C(9) | 17(2) | 37(2) | 17(2) | -10(2) | -1(1) | 13(2) |
| C(10) | 16(2) | 39(2) | 14(2) | -1(1) | 4(1) | 5(1) |
| C(11) | 13(2) | 25(2) | 13(2) | 1(1) | 2(1) | 3(1) |
| C(12) | 21(2) | 16(2) | 22(2) | -2(1) | 8(1) | 6(1) |
| C(13) | 16(2) | 20(2) | 20(2) | 6(1) | O(1) | 2(1) |
| C(14) | 7(1) | 18(2) | 22(2) | -1(1) | 4(1) | 4(1) |
| C(15) | 12(2) | 28(2) | 19(2) | -2(1) | $0(1)$ | -3(1) |
| C(16) | 19(2) | 24(2) | 21(2) | -10(1) | 3(1) | -10(1) |
| C(17) | 17(2) | 12(1) | 28(2) | -8(1) | 8(1) | -2(1) |
| C(18) | 18(2) | 10(1) | 28(2) | -3(1) | 6(1) | -1(1) |
| C(19) | 17(2) | 16(2) | 27(2) | 4(1) | 5(1) | -3(1) |
| C(20) | 16(2) | 20(2) | 20(2) | 2(1) | 5(1) | 1(1) |
| C(21) | 11(2) | 18(2) | 18(2) | -2(1) | 6(1) | 4(1) |
| C(22) | 4(1) | 17(2) | 24(2) | -4(1) | 4(1) | -2(1) |

Table 5. Hydrogen coordinates $\left(\times 10^{4}\right)$ and isotropic displacement parameters $\left(\approx^{2} \times 10^{3}\right)$ for d1872_a.

|  | x | y | z | $\mathrm{U}(\mathrm{eq})$ |
| :---: | :---: | :---: | :---: | :---: |
| H(2A) | 4750 | 4987 | 3885 | 18 |
| H(4A) | 2883 | 8461 | 4123 | 20 |
| H(4B) | 3247 | 7881 | 5161 | 20 |
| H(7A) | 4423 | 553 | 4230 | 23 |
| H(8A) | 5522 | -893 | 3783 | 28 |
| H(9A) | 6599 | -27 | 2951 | 29 |
| H(10A) | 6627 | 2311 | 2642 | 27 |
| H(11A) | 5538 | 3787 | 3092 | 21 |
| H(12A) | 1127 | 6279 | 5089 | 29 |
| H(12B) | 1623 | 7729 | 5350 | 29 |
| H(12C) | 2134 | 6345 | 5763 | 29 |
| H(13A) | 983 | 6362 | 3380 | 29 |
| H(13B) | 1830 | 6935 | 2950 | 29 |
| H(13C) | 1276 | 7942 | 3510 | 29 |
| H(14A) | 509 | 4652 | 3941 | 19 |
| H(15A) | 75 | 2992 | 2785 | 24 |
| H(15B) | -500 | 2548 | 3557 | 24 |
| H(16A) | 293 | 616 | 3889 | 25 |
| H(16B) | 477 | 800 | 2857 | 25 |
| H(17A) | 2009 | 773 | 3457 | 22 |
| H(18A) | 2637 | 596 | 4952 | 22 |
| H(19A) | 1902 | 1040 | 6188 | 24 |
| H(19B) | 1173 | 70 | 5523 | 24 |
| H(20A) | 133 | 1734 | 5138 | 22 |
| H(20B) | 629 | 2301 | 6139 | 22 |
| H(21A) | 981 | 4257 | 5458 | 18 |
| H(22A) | 1430 | 4325 | 2704 | 23 |
| H(22B) | 1623 | 2736 | 2545 | 23 |
| H(22C) | 2461 | 3818 | 2660 | 23 |

Table 6. Torsion angles [ $\infty$ ] for d1872_a.

| $\operatorname{Ir}(1)-\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(2)$ | 3.9(4) |
| :---: | :---: |
| $\operatorname{Ir}(1)-\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(6)$ | -174.50(18) |
| $\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)$ | -2.2(5) |
| $\mathrm{C}(6)-\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)$ | 176.1(3) |
| $\mathrm{C}(5)-\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{O}(2)$ | 3.9(3) |
| $\operatorname{Ir}(1)-\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{O}(2)$ | -177.90(18) |
| $\mathrm{C}(5)-\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{C}(2)$ | -174.3(3) |
| $\operatorname{Ir}(1)-\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{C}(2)$ | 3.8(4) |
| $\mathrm{C}(4)-\mathrm{O}(2)-\mathrm{C}(3)-\mathrm{N}(1)$ | $9.2(3)$ |
| $\mathrm{C}(4)-\mathrm{O}(2)-\mathrm{C}(3)-\mathrm{C}(2)$ | -172.2(2) |
| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)-\mathrm{N}(1)$ | -2.3(5) |
| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)-\mathrm{O}(2)$ | 179.4(3) |
| $\mathrm{C}(3)-\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{C}(5)$ | -17.7(3) |
| $\mathrm{C}(3)-\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(12)$ | -131.6(3) |
| $\operatorname{Ir}(1)-\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(12)$ | 50.6(4) |
| $\mathrm{C}(3)-\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(13)$ | 101.8(3) |
| $\operatorname{Ir}(1)-\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(13)$ | -76.0(3) |
| $\mathrm{C}(3)-\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(4)$ | -14.2(3) |
| $\operatorname{Ir}(1)-\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(4)$ | 168.0(2) |
| $\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{N}(1)$ | 19.0(3) |
| $\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{C}(12)$ | 138.2(2) |
| $\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{C}(13)$ | -98.5(3) |
| $\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(6)-\mathrm{C}(11)$ | 159.6(3) |
| $\mathrm{C}(2)-\mathrm{C}(1)-\mathrm{C}(6)-\mathrm{C}(11)$ | -18.9(4) |
| $\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(6)-\mathrm{C}(7)$ | -18.3(4) |
| $\mathrm{C}(2)-\mathrm{C}(1)-\mathrm{C}(6)-\mathrm{C}(7)$ | 163.2(3) |
| $\mathrm{C}(11)-\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{C}(8)$ | -1.2(5) |
| $\mathrm{C}(1)-\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{C}(8)$ | 176.8(3) |
| $\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{C}(8)-\mathrm{C}(9)$ | -0.5(5) |
| $\mathrm{C}(7)-\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{C}(10)$ | 1.9(5) |
| $\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(11)$ | -1.7(5) |
| $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(11)-\mathrm{C}(6)$ | 0.0(5) |
| $\mathrm{C}(7)-\mathrm{C}(6)-\mathrm{C}(11)-\mathrm{C}(10)$ | 1.4(4) |
| $\mathrm{C}(1)-\mathrm{C}(6)-\mathrm{C}(11)-\mathrm{C}(10)$ | -176.5(3) |


| $\mathrm{C}(21)-\mathrm{C}(14)-\mathrm{C}(15)-\mathrm{C}(16)$ | $-51.5(4)$ |
| :--- | :---: |
| $\mathrm{Ir}(1)-\mathrm{C}(14)-\mathrm{C}(15)-\mathrm{C}(16)$ | $30.6(3)$ |
| $\mathrm{C}(14)-\mathrm{C}(15)-\mathrm{C}(16)-\mathrm{C}(17)$ | $-24.2(4)$ |
| $\mathrm{C}(15)-\mathrm{C}(16)-\mathrm{C}(17)-\mathrm{C}(18)$ | $89.6(4)$ |
| $\mathrm{C}(15)-\mathrm{C}(16)-\mathrm{C}(17)-\operatorname{Ir}(1)$ | $5.9(4)$ |
| $\mathrm{C}(16)-\mathrm{C}(17)-\mathrm{C}(18)-\mathrm{C}(19)$ | $-1.0(5)$ |
| $\mathrm{Ir}(1)-\mathrm{C}(17)-\mathrm{C}(18)-\mathrm{C}(19)$ | $106.1(3)$ |
| $\mathrm{C}(16)-\mathrm{C}(17)-\mathrm{C}(18)-\operatorname{Ir}(1)$ | $-107.2(3)$ |
| $\mathrm{C}(17)-\mathrm{C}(18)-\mathrm{C}(19)-\mathrm{C}(20)$ | $-51.4(4)$ |
| $\mathrm{Ir}(1)-\mathrm{C}(18)-\mathrm{C}(19)-\mathrm{C}(20)$ | $30.5(3)$ |
| $\mathrm{C}(18)-\mathrm{C}(19)-\mathrm{C}(20)-\mathrm{C}(21)$ | $-27.6(4)$ |
| $\mathrm{C}(15)-\mathrm{C}(14)-\mathrm{C}(21)-\mathrm{C}(20)$ | $-2.8(4)$ |
| $\mathrm{Ir}(1)-\mathrm{C}(14)-\mathrm{C}(21)-\mathrm{C}(20)$ | $-106.8(3)$ |
| $\mathrm{C}(15)-\mathrm{C}(14)-\mathrm{C}(21)-\operatorname{Ir}(1)$ | $104.0(3)$ |
| $\mathrm{C}(19)-\mathrm{C}(20)-\mathrm{C}(21)-\mathrm{C}(14)$ | $93.4(3)$ |
| $\mathrm{C}(19)-\mathrm{C}(20)-\mathrm{C}(21)-\operatorname{Ir}(1)$ | $12.1(3)$ |

Symmetry transformations used to generate equivalent atoms:


F11: Crystal data and structure refinement for 18.

| Identification code | d18124_a (18) |
| :---: | :---: |
| Empirical formula | C39 H42 Ir N O2 Sn |
| Formula weight | 867.62 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 A |
| Crystal system | Monoclinic |
| Space group | $\mathrm{P} 21 / \mathrm{n}$ |
| Unit cell dimensions | $\mathrm{a}=13.2953(8) \AA \quad \alpha=90^{\circ}$. |
|  | $\mathrm{b}=17.8294(12) \AA$ A $\quad \beta=92.525(2)^{\circ}$. |
|  | $\mathrm{c}=14.0144(9) \AA \AA^{\text {A }}$, $\quad \gamma=90^{\circ}$. |
| Volume | 3318.8(4) $\AA^{3}$ |
| Z | 4 |
| Density (calculated) | $1.736 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $4.793 \mathrm{~mm}^{-1}$ |
| F(000) | 1704 |
| Crystal size | $0.130 \times 0.120 \times 0.090 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 1.849 to $27.533{ }^{\circ}$. |
| Index ranges | $-17<=\mathrm{h}<=16,-23<=\mathrm{k}<=23,-18<=1<=16$ |
| Reflections collected | 70635 |
| Independent reflections | $7637[\mathrm{R}(\mathrm{int})=0.0404]$ |
| Completeness to theta $=25.242^{\circ}$ | 100.0\% |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.7456 and 0.6796 |

Refinement method
Data / restraints / parameters
Goodness-of-fit on $\mathrm{F}^{2}$
Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ]
R indices (all data)
Extinction coefficient
Largest diff. peak and hole

Full-matrix least-squares on $\mathrm{F}^{2}$
7637 / 0 / 403
1.048
$\mathrm{R} 1=0.0199, \mathrm{wR} 2=0.0359$
$R 1=0.0320, w R 2=0.0399$
n/a
1.669 and $-0.604 \mathrm{e} . \AA^{-3}$

Table 2. Atomic coordinates ( $\times 10^{4}$ ) and equivalent isotropic displacement parameters ( $\AA^{2} \times 10^{3}$ ) for $\mathrm{d} 18124 \_$a. $\mathrm{U}(\mathrm{eq})$ is defined as one third of the trace of the orthogonalized $\mathrm{U}^{\mathrm{ij}}$ tensor.

|  | x | y | z | $\mathrm{U}(\mathrm{eq})$ |
| :---: | :---: | :---: | :---: | :---: |
| $\operatorname{Ir}(1)$ | 5417(1) | 1734(1) | 6988(1) | 15(1) |
| $\mathrm{Sn}(1)$ | 5982(1) | 3097(1) | 7440(1) | 16(1) |
| $\mathrm{O}(1)$ | 5848(1) | 1998(1) | 5558(1) | 21(1) |
| $\mathrm{O}(2)$ | 8341(2) | 803(1) | 6850(1) | 32(1) |
| N(1) | 6861(2) | 1286(1) | 7244(2) | 17(1) |
| C(1) | 6591(2) | 1702(2) | 5136(2) | 20(1) |
| C(2) | 7346(2) | 1276(2) | 5567(2) | 26(1) |
| C(3) | 7457(2) | 1138(2) | 6557(2) | 22(1) |
| C(4) | 8241(2) | 604(2) | 7840(2) | 30(1) |
| C(5) | 7410(2) | 1119(1) | 8182(2) | 20(1) |
| C(6) | 6595(2) | 1874(2) | 4085(2) | 22(1) |
| C(7) | 6018(2) | 2472(2) | 3731(2) | 26(1) |
| C(8) | 5994(2) | 2652(2) | 2766(2) | 31(1) |
| C(9) | 6537(2) | 2229(2) | 2142(2) | 30(1) |
| C(10) | 7101(2) | 1628(2) | 2480(2) | 30(1) |
| C(11) | 7133(2) | 1452(2) | 3441(2) | 28(1) |
| C(12) | 6775(2) | 721(2) | 8897(2) | 34(1) |
| C(13) | 7852(2) | 1838(2) | 8609(2) | 33(1) |
| C(14) | 4817(2) | 538(2) | 7169(2) | 28(1) |
| C(15) | 4842(2) | 668(2) | 6202(2) | 30(1) |
| C(16) | 3912(3) | 848(2) | 5573(3) | 39(1) |
| C(17) | 3672(2) | 1680(2) | 5495(2) | 29(1) |
| C(18) | 4007(2) | 2143(2) | 6352(2) | 21(1) |
| C(19) | 3856(2) | 1966(2) | 7304(2) | 22(1) |
| C(20) | 3269(2) | 1270(2) | 7598(3) | 36(1) |
| C(21) | 3898(2) | 567(2) | 7752(3) | 38(1) |
| C(22) | 7436(2) | 3423(1) | 6936(2) | 20(1) |
| C(23) | 7598(2) | 3431(2) | 5957(2) | 27(1) |
| C(24) | 8537(2) | 3596(2) | 5612(2) | 35(1) |
| C(25) | 9340(2) | 3748(2) | 6238(3) | 36(1) |
| C(26) | 9204(2) | 3743(2) | 7206(3) | 32(1) |
|  |  | 493 |  |  |


| $\mathrm{C}(27)$ | $8264(2)$ | $3586(2)$ | $7555(2)$ | $25(1)$ |
| :--- | ---: | ---: | ---: | ---: |
| $\mathrm{C}(28)$ | $5920(2)$ | $3407(1)$ | $8926(2)$ | $19(1)$ |
| $\mathrm{C}(29)$ | $6307(2)$ | $4088(2)$ | $9271(2)$ | $21(1)$ |
| $\mathrm{C}(30)$ | $6066(2)$ | $4356(2)$ | $10165(2)$ | $25(1)$ |
| $\mathrm{C}(31)$ | $5430(2)$ | $3957(2)$ | $10723(2)$ | $28(1)$ |
| $\mathrm{C}(32)$ | $5051(2)$ | $3272(2)$ | $10405(2)$ | $28(1)$ |
| $\mathrm{C}(33)$ | $5300(2)$ | $3004(2)$ | $9519(2)$ | $25(1)$ |
| $\mathrm{C}(34)$ | $4962(2)$ | $3957(1)$ | $6854(2)$ | $17(1)$ |
| $\mathrm{C}(35)$ | $4757(2)$ | $4043(2)$ | $5878(2)$ | $24(1)$ |
| $\mathrm{C}(36)$ | $4102(2)$ | $4591(2)$ | $5521(2)$ | $28(1)$ |
| $\mathrm{C}(37)$ | $3633(2)$ | $5068(2)$ | $6135(2)$ | $31(1)$ |
| $\mathrm{C}(38)$ | $3822(2)$ | $4998(2)$ | $7105(2)$ | $32(1)$ |
| $\mathrm{C}(39)$ | $4478(2)$ | $4444(2)$ | $7458(2)$ | $23(1)$ |

Table 3. Bond lengths [ $\AA$ ] and angles [ ${ }^{\circ}$ ] for d18124_a.

| $\operatorname{Ir}(1)-\mathrm{N}(1)$ | 2.095(2) |
| :---: | :---: |
| $\mathrm{Ir}(1)-\mathrm{O}(1)$ | 2.1592(19) |
| $\operatorname{Ir}(1)-\mathrm{C}(18)$ | 2.166(2) |
| $\operatorname{Ir}(1)-\mathrm{C}(19)$ | 2.180(3) |
| $\operatorname{Ir}(1)-\mathrm{C}(14)$ | 2.294(3) |
| $\operatorname{Ir}(1)-\mathrm{C}(15)$ | 2.310(3) |
| $\operatorname{Ir}(1)-\operatorname{Sn}(1)$ | 2.6137(2) |
| $\operatorname{Ir}(1)-\mathrm{H}(1 \mathrm{IR})$ | 1.37(3) |
| $\mathrm{Sn}(1)-\mathrm{C}(28)$ | 2.160(3) |
| $\mathrm{Sn}(1)-\mathrm{C}(22)$ | 2.166(3) |
| $\mathrm{Sn}(1)-\mathrm{C}(34)$ | 2.182(2) |
| $\mathrm{O}(1)-\mathrm{C}(1)$ | 1.286(3) |
| $\mathrm{O}(2)-\mathrm{C}(3)$ | $1.365(3)$ |
| $\mathrm{O}(2)-\mathrm{C}(4)$ | 1.445 (3) |
| $\mathrm{N}(1)$-C(3) | 1.302(3) |
| $\mathrm{N}(1)-\mathrm{C}(5)$ | $1.505(3)$ |
| $\mathrm{C}(1)-\mathrm{C}(2)$ | 1.377(4) |
| $\mathrm{C}(1)-\mathrm{C}(6)$ | 1.505(4) |
| $\mathrm{C}(2)-\mathrm{C}(3)$ | 1.411(4) |
| $\mathrm{C}(2)-\mathrm{H}(2 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(4)-\mathrm{C}(5)$ | 1.529(4) |
| $\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~A})$ | 0.9900 |
| $\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~B})$ | 0.9900 |
| $\mathrm{C}(5)-\mathrm{C}(12)$ | 1.514(4) |
| $\mathrm{C}(5)-\mathrm{C}(13)$ | 1.521(4) |
| $\mathrm{C}(6)-\mathrm{C}(7)$ | 1.392(4) |
| $\mathrm{C}(6)-\mathrm{C}(11)$ | 1.397(4) |
| $\mathrm{C}(7)-\mathrm{C}(8)$ | 1.388(4) |
| $\mathrm{C}(7)-\mathrm{H}(7 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(8)-\mathrm{C}(9)$ | 1.383(4) |
| $\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(9)-\mathrm{C}(10)$ | 1.380(4) |
| $\mathrm{C}(9)-\mathrm{H}(9 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(10)-\mathrm{C}(11)$ | 1.382(4) |


| $\mathrm{C}(10)-\mathrm{H}(10 \mathrm{~A})$ | 0.9500 |
| :---: | :---: |
| $\mathrm{C}(11)-\mathrm{H}(11 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~A})$ | 0.9800 |
| $\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~B})$ | 0.9800 |
| $\mathrm{C}(12)-\mathrm{H}(12 \mathrm{C})$ | 0.9800 |
| $\mathrm{C}(13)-\mathrm{H}(13 \mathrm{~A})$ | 0.9800 |
| $\mathrm{C}(13)-\mathrm{H}(13 \mathrm{~B})$ | 0.9800 |
| $\mathrm{C}(13)-\mathrm{H}(13 \mathrm{C})$ | 0.9800 |
| $\mathrm{C}(14)-\mathrm{C}(15)$ | 1.377(4) |
| $\mathrm{C}(14)-\mathrm{C}(21)$ | 1.501(4) |
| $\mathrm{C}(14)-\mathrm{H}(14 \mathrm{~A})$ | 1.0000 |
| $\mathrm{C}(15)-\mathrm{C}(16)$ | 1.521(4) |
| $\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~A})$ | 1.0000 |
| $\mathrm{C}(16)-\mathrm{C}(17)$ | 1.521(4) |
| $\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~A})$ | 0.9900 |
| $\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~B})$ | 0.9900 |
| $\mathrm{C}(17)-\mathrm{C}(18)$ | 1.508(4) |
| $\mathrm{C}(17)-\mathrm{H}(17 \mathrm{~A})$ | 0.9900 |
| $\mathrm{C}(17)-\mathrm{H}(17 \mathrm{~B})$ | 0.9900 |
| $\mathrm{C}(18)-\mathrm{C}(19)$ | 1.393(4) |
| $\mathrm{C}(18)-\mathrm{H}(18 \mathrm{~A})$ | 1.0000 |
| $\mathrm{C}(19)$-C(20) | 1.531(4) |
| $\mathrm{C}(19)-\mathrm{H}(19 \mathrm{~A})$ | 1.0000 |
| $\mathrm{C}(20)-\mathrm{C}(21)$ | 1.517(4) |
| $\mathrm{C}(20)-\mathrm{H}(20 \mathrm{~A})$ | 0.9900 |
| $\mathrm{C}(20)-\mathrm{H}(20 \mathrm{~B})$ | 0.9900 |
| $\mathrm{C}(21)-\mathrm{H}(21 \mathrm{~A})$ | 0.9900 |
| $\mathrm{C}(21)-\mathrm{H}(21 \mathrm{~B})$ | 0.9900 |
| $\mathrm{C}(22)$-C(23) | 1.398(4) |
| $\mathrm{C}(22)-\mathrm{C}(27)$ | 1.402(4) |
| $\mathrm{C}(23)-\mathrm{C}(24)$ | 1.390(4) |
| $\mathrm{C}(23)-\mathrm{H}(23 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(24)$-C(25) | 1.378(5) |
| $\mathrm{C}(24)-\mathrm{H}(24 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(25)-\mathrm{C}(26)$ | 1.377(5) |
| $\mathrm{C}(25)-\mathrm{H}(25 \mathrm{~A})$ | 0.9500 |


| C(26)-C(27) | 1.391(4) |
| :---: | :---: |
| $\mathrm{C}(26)-\mathrm{H}(26 \mathrm{~A})$ | 0.9500 |
| C(27)-H(27A) | 0.9500 |
| C(28)-C(33) | 1.396(4) |
| C(28)-C(29) | 1.397(4) |
| $\mathrm{C}(29)$ - $\mathrm{C}(30)$ | 1.392(4) |
| $\mathrm{C}(29)-\mathrm{H}(29 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(30)-\mathrm{C}(31)$ | 1.376(4) |
| $\mathrm{C}(30)-\mathrm{H}(30 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(31)-\mathrm{C}(32)$ | 1.387(4) |
| $\mathrm{C}(31)-\mathrm{H}(31 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(32)-\mathrm{C}(33)$ | 1.385(4) |
| $\mathrm{C}(32)-\mathrm{H}(32 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(33)-\mathrm{H}(33 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(34)-\mathrm{C}(39)$ | 1.391(4) |
| $\mathrm{C}(34)-\mathrm{C}(35)$ | 1.391(4) |
| $\mathrm{C}(35)-\mathrm{C}(36)$ | 1.389(4) |
| $\mathrm{C}(35)-\mathrm{H}(35 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(36)-\mathrm{C}(37)$ | 1.379(4) |
| $\mathrm{C}(36)-\mathrm{H}(36 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(37)-\mathrm{C}(38)$ | 1.376(4) |
| $\mathrm{C}(37)-\mathrm{H}(37 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(38)-\mathrm{C}(39)$ | 1.394(4) |
| $\mathrm{C}(38)-\mathrm{H}(38 \mathrm{~A})$ | 0.9500 |
| $\mathrm{C}(39)-\mathrm{H}(39 \mathrm{~A})$ | 0.9500 |
| $\mathrm{N}(1)-\operatorname{Ir}(1)-\mathrm{O}(1)$ | 87.95(8) |
| $\mathrm{N}(1)-\operatorname{Ir}(1)-\mathrm{C}(18)$ | 165.61(10) |
| $\mathrm{O}(1)-\operatorname{Ir}(1)-\mathrm{C}(18)$ | 78.79(9) |
| $\mathrm{N}(1)-\operatorname{Ir}(1)-\mathrm{C}(19)$ | 155.50(10) |
| $\mathrm{O}(1)-\operatorname{Ir}(1)-\mathrm{C}(19)$ | 116.16(9) |
| $\mathrm{C}(18)-\mathrm{Ir}(1)-\mathrm{C}(19)$ | 37.39(10) |
| $\mathrm{N}(1)-\operatorname{Ir}(1)-\mathrm{C}(14)$ | 86.95(9) |
| $\mathrm{O}(1)-\operatorname{Ir}(1)-\mathrm{C}(14)$ | 114.38(9) |
| $\mathrm{C}(18)-\mathrm{Ir}(1)-\mathrm{C}(14)$ | 93.41(10) |
| $\mathrm{C}(19)-\operatorname{Ir}(1)-\mathrm{C}(14)$ | 79.33(10) |


| $\mathrm{N}(1)-\operatorname{Ir}(1)-\mathrm{C}(15)$ | 92.83(9) |
| :---: | :---: |
| $\mathrm{O}(1)-\operatorname{Ir}(1)-\mathrm{C}(15)$ | 80.36(10) |
| $\mathrm{C}(18)-\operatorname{Ir}(1)-\mathrm{C}(15)$ | 79.56(10) |
| $\mathrm{C}(19)-\operatorname{Ir}(1)-\mathrm{C}(15)$ | 87.41(11) |
| $\mathrm{C}(14)-\operatorname{Ir}(1)-\mathrm{C}(15)$ | 34.79(11) |
| $\mathrm{N}(1)-\operatorname{Ir}(1)-\operatorname{Sn}(1)$ | 93.55(6) |
| $\mathrm{O}(1)-\operatorname{Ir}(1)-\mathrm{Sn}(1)$ | 86.42(5) |
| $\mathrm{C}(18)-\operatorname{Ir}(1)-\operatorname{Sn}(1)$ | 91.19(7) |
| $\mathrm{C}(19)-\operatorname{Ir}(1)-\operatorname{Sn}(1)$ | 92.31(7) |
| $\mathrm{C}(14)-\operatorname{Ir}(1)-\operatorname{Sn}(1)$ | 159.20(8) |
| $\mathrm{C}(15)-\operatorname{Ir}(1)-\operatorname{Sn}(1)$ | 165.09(8) |
| $\mathrm{N}(1)-\operatorname{Ir}(1)-\mathrm{H}(1 \mathrm{IR})$ | 84.6(13) |
| $\mathrm{O}(1)-\operatorname{Ir}(1)-\mathrm{H}(1 \mathrm{IR})$ | 165.3(13) |
| $\mathrm{C}(18)-\mathrm{Ir}(1)-\mathrm{H}(1 \mathrm{IR})$ | 109.6(13) |
| $\mathrm{C}(19)-\mathrm{Ir}(1)-\mathrm{H}(1 \mathrm{IR})$ | 72.8(13) |
| $\mathrm{C}(14)-\mathrm{Ir}(1)-\mathrm{H}(1 \mathrm{IR})$ | 78.0(13) |
| $\mathrm{C}(15)-\mathrm{Ir}(1)-\mathrm{H}(1 \mathrm{IR})$ | 112.6(13) |
| $\mathrm{Sn}(1)-\operatorname{Ir}(1)-\mathrm{H}(1 \mathrm{IR})$ | 81.4(13) |
| $\mathrm{C}(28)-\mathrm{Sn}(1)-\mathrm{C}(22)$ | 108.56(10) |
| $\mathrm{C}(28)-\mathrm{Sn}(1)-\mathrm{C}(34)$ | 97.70(10) |
| $\mathrm{C}(22)-\mathrm{Sn}(1)-\mathrm{C}(34)$ | 103.76(10) |
| $\mathrm{C}(28)-\mathrm{Sn}(1)-\operatorname{Ir}(1)$ | 116.66(7) |
| $\mathrm{C}(22)-\operatorname{Sn}(1)-\operatorname{Ir}(1)$ | 114.89(7) |
| $\mathrm{C}(34)-\mathrm{Sn}(1)-\operatorname{Ir}(1)$ | 113.26(6) |
| $\mathrm{C}(1)-\mathrm{O}(1)-\operatorname{Ir}(1)$ | 125.28(17) |
| $\mathrm{C}(3)-\mathrm{O}(2)-\mathrm{C}(4)$ | 106.4(2) |
| $\mathrm{C}(3)-\mathrm{N}(1)-\mathrm{C}(5)$ | 108.5(2) |
| $\mathrm{C}(3)-\mathrm{N}(1)-\operatorname{Ir}(1)$ | 122.24(18) |
| $\mathrm{C}(5)-\mathrm{N}(1)-\operatorname{Ir}(1)$ | 129.15(17) |
| $\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(2)$ | 125.8(3) |
| $\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(6)$ | 113.7(2) |
| $\mathrm{C}(2)-\mathrm{C}(1)-\mathrm{C}(6)$ | 120.5(2) |
| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)$ | 124.7(3) |
| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{H}(2 \mathrm{~A})$ | 117.6 |
| $\mathrm{C}(3)-\mathrm{C}(2)-\mathrm{H}(2 \mathrm{~A})$ | 117.6 |
| $\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{O}(2)$ | 114.2(2) |


| $\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{C}(2)$ | 130.7(2) |
| :---: | :---: |
| $\mathrm{O}(2)-\mathrm{C}(3)-\mathrm{C}(2)$ | 115.1(2) |
| $\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{C}(5)$ | 104.6(2) |
| $\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~A})$ | 110.8 |
| $\mathrm{C}(5)-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~A})$ | 110.8 |
| $\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~B})$ | 110.8 |
| $\mathrm{C}(5)-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~B})$ | 110.8 |
| $\mathrm{H}(4 \mathrm{~A})-\mathrm{C}(4)-\mathrm{H}(4 \mathrm{~B})$ | 108.9 |
| $\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(12)$ | 114.0(2) |
| $\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(13)$ | 109.9(2) |
| $\mathrm{C}(12)-\mathrm{C}(5)-\mathrm{C}(13)$ | 110.6(3) |
| $\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(4)$ | 100.1(2) |
| $\mathrm{C}(12)-\mathrm{C}(5)-\mathrm{C}(4)$ | 111.0(2) |
| $\mathrm{C}(13)-\mathrm{C}(5)-\mathrm{C}(4)$ | 110.9(2) |
| $\mathrm{C}(7)-\mathrm{C}(6)-\mathrm{C}(11)$ | 118.2(3) |
| $\mathrm{C}(7)-\mathrm{C}(6)-\mathrm{C}(1)$ | 118.7(3) |
| $\mathrm{C}(11)-\mathrm{C}(6)-\mathrm{C}(1)$ | 123.1(3) |
| $\mathrm{C}(8)-\mathrm{C}(7)-\mathrm{C}(6)$ | 120.9(3) |
| $\mathrm{C}(8)-\mathrm{C}(7)-\mathrm{H}(7 \mathrm{~A})$ | 119.6 |
| $\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{H}(7 \mathrm{~A})$ | 119.6 |
| $\mathrm{C}(9)-\mathrm{C}(8)-\mathrm{C}(7)$ | 120.0(3) |
| $\mathrm{C}(9)-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~A})$ | 120.0 |
| $\mathrm{C}(7)-\mathrm{C}(8)-\mathrm{H}(8 \mathrm{~A})$ | 120.0 |
| $\mathrm{C}(10)-\mathrm{C}(9)-\mathrm{C}(8)$ | 119.8(3) |
| $\mathrm{C}(10)-\mathrm{C}(9)-\mathrm{H}(9 \mathrm{~A})$ | 120.1 |
| $\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{H}(9 \mathrm{~A})$ | 120.1 |
| $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(11)$ | 120.3(3) |
| $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{H}(10 \mathrm{~A})$ | 119.9 |
| $\mathrm{C}(11)-\mathrm{C}(10)-\mathrm{H}(10 \mathrm{~A})$ | 119.9 |
| $\mathrm{C}(10)-\mathrm{C}(11)-\mathrm{C}(6)$ | 120.9(3) |
| $\mathrm{C}(10)-\mathrm{C}(11)-\mathrm{H}(11 \mathrm{~A})$ | 119.6 |
| $\mathrm{C}(6)-\mathrm{C}(11)-\mathrm{H}(11 \mathrm{~A})$ | 119.6 |
| $\mathrm{C}(5)-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(5)-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~B})$ | 109.5 |
| $\mathrm{H}(12 \mathrm{~A})-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(5)-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{C})$ | 109.5 |


| $\mathrm{H}(12 \mathrm{~A})-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{C})$ | 109.5 |
| :---: | :---: |
| $\mathrm{H}(12 \mathrm{~B})-\mathrm{C}(12)-\mathrm{H}(12 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(5)-\mathrm{C}(13)-\mathrm{H}(13 \mathrm{~A})$ | 109.5 |
| $\mathrm{C}(5)-\mathrm{C}(13)-\mathrm{H}(13 \mathrm{~B})$ | 109.5 |
| $\mathrm{H}(13 \mathrm{~A})-\mathrm{C}(13)-\mathrm{H}(13 \mathrm{~B})$ | 109.5 |
| $\mathrm{C}(5)-\mathrm{C}(13)-\mathrm{H}(13 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(13 \mathrm{~A})-\mathrm{C}(13)-\mathrm{H}(13 \mathrm{C})$ | 109.5 |
| $\mathrm{H}(13 \mathrm{~B})-\mathrm{C}(13)-\mathrm{H}(13 \mathrm{C})$ | 109.5 |
| $\mathrm{C}(15)-\mathrm{C}(14)-\mathrm{C}(21)$ | 125.8(3) |
| $\mathrm{C}(15)-\mathrm{C}(14)-\operatorname{Ir}(1)$ | 73.23(16) |
| $\mathrm{C}(21)-\mathrm{C}(14)-\operatorname{Ir}(1)$ | 108.88(19) |
| $\mathrm{C}(15)-\mathrm{C}(14)-\mathrm{H}(14 \mathrm{~A})$ | 113.8 |
| $\mathrm{C}(21)-\mathrm{C}(14)-\mathrm{H}(14 \mathrm{~A})$ | 113.8 |
| $\operatorname{Ir}(1)-\mathrm{C}(14)-\mathrm{H}(14 \mathrm{~A})$ | 113.8 |
| $\mathrm{C}(14)-\mathrm{C}(15)-\mathrm{C}(16)$ | 123.5(3) |
| $\mathrm{C}(14)-\mathrm{C}(15)-\operatorname{Ir}(1)$ | 71.98(16) |
| $\mathrm{C}(16)-\mathrm{C}(15)-\operatorname{Ir}(1)$ | 110.25(18) |
| $\mathrm{C}(14)-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~A})$ | 114.5 |
| $\mathrm{C}(16)-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~A})$ | 114.5 |
| $\operatorname{Ir}(1)-\mathrm{C}(15)-\mathrm{H}(15 \mathrm{~A})$ | 114.5 |
| $\mathrm{C}(17)-\mathrm{C}(16)-\mathrm{C}(15)$ | 114.2(2) |
| $\mathrm{C}(17)-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~A})$ | 108.7 |
| $\mathrm{C}(15)-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~A})$ | 108.7 |
| $\mathrm{C}(17)-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~B})$ | 108.7 |
| $\mathrm{C}(15)-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~B})$ | 108.7 |
| $\mathrm{H}(16 \mathrm{~A})-\mathrm{C}(16)-\mathrm{H}(16 \mathrm{~B})$ | 107.6 |
| $\mathrm{C}(18)-\mathrm{C}(17)-\mathrm{C}(16)$ | 115.0(2) |
| $\mathrm{C}(18)-\mathrm{C}(17)-\mathrm{H}(17 \mathrm{~A})$ | 108.5 |
| $\mathrm{C}(16)-\mathrm{C}(17)-\mathrm{H}(17 \mathrm{~A})$ | 108.5 |
| $\mathrm{C}(18)-\mathrm{C}(17)-\mathrm{H}(17 \mathrm{~B})$ | 108.5 |
| $\mathrm{C}(16)-\mathrm{C}(17)-\mathrm{H}(17 \mathrm{~B})$ | 108.5 |
| $\mathrm{H}(17 \mathrm{~A})-\mathrm{C}(17)-\mathrm{H}(17 \mathrm{~B})$ | 107.5 |
| $\mathrm{C}(19)-\mathrm{C}(18)-\mathrm{C}(17)$ | 126.0(3) |
| $\mathrm{C}(19)-\mathrm{C}(18)-\operatorname{Ir}(1)$ | 71.86(15) |
| $\mathrm{C}(17)-\mathrm{C}(18)-\operatorname{Ir}(1)$ | 111.31(18) |
| $\mathrm{C}(19)-\mathrm{C}(18)-\mathrm{H}(18 \mathrm{~A})$ | 113.4 |


| $\mathrm{C}(17)-\mathrm{C}(18)-\mathrm{H}(18 \mathrm{~A})$ | 113.4 |
| :---: | :---: |
| $\operatorname{Ir}(1)-\mathrm{C}(18)-\mathrm{H}(18 \mathrm{~A})$ | 113.4 |
| $\mathrm{C}(18)-\mathrm{C}(19)-\mathrm{C}(20)$ | 122.5(3) |
| $\mathrm{C}(18)-\mathrm{C}(19)-\mathrm{Ir}(1)$ | 70.75(15) |
| $\mathrm{C}(20)-\mathrm{C}(19)-\operatorname{Ir}(1)$ | 113.75(18) |
| $\mathrm{C}(18)-\mathrm{C}(19)-\mathrm{H}(19 \mathrm{~A})$ | 114.2 |
| $\mathrm{C}(20)-\mathrm{C}(19)-\mathrm{H}(19 \mathrm{~A})$ | 114.2 |
| $\operatorname{Ir}(1)-\mathrm{C}(19)-\mathrm{H}(19 \mathrm{~A})$ | 114.2 |
| $\mathrm{C}(21)-\mathrm{C}(20)-\mathrm{C}(19)$ | 115.0(2) |
| $\mathrm{C}(21)-\mathrm{C}(20)-\mathrm{H}(20 \mathrm{~A})$ | 108.5 |
| $\mathrm{C}(19)-\mathrm{C}(20)-\mathrm{H}(20 \mathrm{~A})$ | 108.5 |
| $\mathrm{C}(21)-\mathrm{C}(20)-\mathrm{H}(20 \mathrm{~B})$ | 108.5 |
| $\mathrm{C}(19)-\mathrm{C}(20)-\mathrm{H}(20 \mathrm{~B})$ | 108.5 |
| $\mathrm{H}(20 \mathrm{~A})-\mathrm{C}(20)-\mathrm{H}(20 \mathrm{~B})$ | 107.5 |
| $\mathrm{C}(14)-\mathrm{C}(21)-\mathrm{C}(20)$ | 114.1(3) |
| $\mathrm{C}(14)-\mathrm{C}(21)-\mathrm{H}(21 \mathrm{~A})$ | 108.7 |
| $\mathrm{C}(20)-\mathrm{C}(21)-\mathrm{H}(21 \mathrm{~A})$ | 108.7 |
| $\mathrm{C}(14)-\mathrm{C}(21)-\mathrm{H}(21 \mathrm{~B})$ | 108.7 |
| $\mathrm{C}(20)-\mathrm{C}(21)-\mathrm{H}(21 \mathrm{~B})$ | 108.7 |
| $\mathrm{H}(21 \mathrm{~A})-\mathrm{C}(21)-\mathrm{H}(21 \mathrm{~B})$ | 107.6 |
| $\mathrm{C}(23)-\mathrm{C}(22)-\mathrm{C}(27)$ | 117.0(3) |
| $\mathrm{C}(23)-\mathrm{C}(22)-\mathrm{Sn}(1)$ | 120.1(2) |
| $\mathrm{C}(27)-\mathrm{C}(22)-\mathrm{Sn}(1)$ | 122.8(2) |
| $\mathrm{C}(24)-\mathrm{C}(23)-\mathrm{C}(22)$ | 121.5(3) |
| $\mathrm{C}(24)-\mathrm{C}(23)-\mathrm{H}(23 \mathrm{~A})$ | 119.2 |
| $\mathrm{C}(22)-\mathrm{C}(23)-\mathrm{H}(23 \mathrm{~A})$ | 119.2 |
| $\mathrm{C}(25)-\mathrm{C}(24)-\mathrm{C}(23)$ | 120.2(3) |
| $\mathrm{C}(25)-\mathrm{C}(24)-\mathrm{H}(24 \mathrm{~A})$ | 119.9 |
| $\mathrm{C}(23)-\mathrm{C}(24)-\mathrm{H}(24 \mathrm{~A})$ | 119.9 |
| $\mathrm{C}(26)-\mathrm{C}(25)-\mathrm{C}(24)$ | 119.7(3) |
| $\mathrm{C}(26)-\mathrm{C}(25)-\mathrm{H}(25 \mathrm{~A})$ | 120.2 |
| $\mathrm{C}(24)-\mathrm{C}(25)-\mathrm{H}(25 \mathrm{~A})$ | 120.2 |
| $\mathrm{C}(25)-\mathrm{C}(26)-\mathrm{C}(27)$ | 120.4(3) |
| $\mathrm{C}(25)-\mathrm{C}(26)-\mathrm{H}(26 \mathrm{~A})$ | 119.8 |
| $\mathrm{C}(27)-\mathrm{C}(26)-\mathrm{H}(26 \mathrm{~A})$ | 119.8 |
| $\mathrm{C}(26)-\mathrm{C}(27)-\mathrm{C}(22)$ | 121.2(3) |


| $\mathrm{C}(26)-\mathrm{C}(27)-\mathrm{H}(27 \mathrm{~A})$ | 119.4 |
| :---: | :---: |
| $\mathrm{C}(22)-\mathrm{C}(27)-\mathrm{H}(27 \mathrm{~A})$ | 119.4 |
| $\mathrm{C}(33)-\mathrm{C}(28)-\mathrm{C}(29)$ | 117.4(3) |
| $\mathrm{C}(33)-\mathrm{C}(28)-\mathrm{Sn}(1)$ | 119.44(19) |
| $\mathrm{C}(29)-\mathrm{C}(28)-\mathrm{Sn}(1)$ | 121.8(2) |
| $\mathrm{C}(30)-\mathrm{C}(29)-\mathrm{C}(28)$ | 121.0(3) |
| $\mathrm{C}(30)-\mathrm{C}(29)-\mathrm{H}(29 \mathrm{~A})$ | 119.5 |
| $\mathrm{C}(28)-\mathrm{C}(29)-\mathrm{H}(29 \mathrm{~A})$ | 119.5 |
| $\mathrm{C}(31)-\mathrm{C}(30)-\mathrm{C}(29)$ | 120.4(3) |
| $\mathrm{C}(31)-\mathrm{C}(30)-\mathrm{H}(30 \mathrm{~A})$ | 119.8 |
| $\mathrm{C}(29)-\mathrm{C}(30)-\mathrm{H}(30 \mathrm{~A})$ | 119.8 |
| $\mathrm{C}(30)-\mathrm{C}(31)-\mathrm{C}(32)$ | 119.8(3) |
| $\mathrm{C}(30)-\mathrm{C}(31)-\mathrm{H}(31 \mathrm{~A})$ | 120.1 |
| $\mathrm{C}(32)-\mathrm{C}(31)-\mathrm{H}(31 \mathrm{~A})$ | 120.1 |
| $\mathrm{C}(33)-\mathrm{C}(32)-\mathrm{C}(31)$ | 119.7(3) |
| $\mathrm{C}(33)-\mathrm{C}(32)-\mathrm{H}(32 \mathrm{~A})$ | 120.2 |
| $\mathrm{C}(31)-\mathrm{C}(32)-\mathrm{H}(32 \mathrm{~A})$ | 120.2 |
| $\mathrm{C}(32)-\mathrm{C}(33)-\mathrm{C}(28)$ | 121.8(3) |
| $\mathrm{C}(32)-\mathrm{C}(33)-\mathrm{H}(33 \mathrm{~A})$ | 119.1 |
| $\mathrm{C}(28)-\mathrm{C}(33)-\mathrm{H}(33 \mathrm{~A})$ | 119.1 |
| $\mathrm{C}(39)-\mathrm{C}(34)-\mathrm{C}(35)$ | 117.0(2) |
| $\mathrm{C}(39)-\mathrm{C}(34)-\mathrm{Sn}(1)$ | 120.42(19) |
| $\mathrm{C}(35)-\mathrm{C}(34)-\mathrm{Sn}(1)$ | 122.6(2) |
| $\mathrm{C}(36)-\mathrm{C}(35)-\mathrm{C}(34)$ | 121.6(3) |
| $\mathrm{C}(36)-\mathrm{C}(35)-\mathrm{H}(35 \mathrm{~A})$ | 119.2 |
| $\mathrm{C}(34)-\mathrm{C}(35)-\mathrm{H}(35 \mathrm{~A})$ | 119.2 |
| $\mathrm{C}(37)-\mathrm{C}(36)-\mathrm{C}(35)$ | 120.2(3) |
| $\mathrm{C}(37)-\mathrm{C}(36)-\mathrm{H}(36 \mathrm{~A})$ | 119.9 |
| $\mathrm{C}(35)-\mathrm{C}(36)-\mathrm{H}(36 \mathrm{~A})$ | 119.9 |
| $\mathrm{C}(38)-\mathrm{C}(37)-\mathrm{C}(36)$ | 119.5(3) |
| $\mathrm{C}(38)-\mathrm{C}(37)-\mathrm{H}(37 \mathrm{~A})$ | 120.2 |
| $\mathrm{C}(36)-\mathrm{C}(37)-\mathrm{H}(37 \mathrm{~A})$ | 120.2 |
| $\mathrm{C}(37)-\mathrm{C}(38)-\mathrm{C}(39)$ | 120.0(3) |
| $\mathrm{C}(37)-\mathrm{C}(38)-\mathrm{H}(38 \mathrm{~A})$ | 120.0 |
| $\mathrm{C}(39)-\mathrm{C}(38)-\mathrm{H}(38 \mathrm{~A})$ | 120.0 |
| $\mathrm{C}(34)-\mathrm{C}(39)-\mathrm{C}(38)$ | 121.7(3) |


| $\mathrm{C}(34)-\mathrm{C}(39)-\mathrm{H}(39 \mathrm{~A})$ | 119.2 |
| :--- | :--- |
| $\mathrm{C}(38)-\mathrm{C}(39)-\mathrm{H}(39 \mathrm{~A})$ | 119.2 |

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for d18124_a. The anisotropic displacement factor exponent takes the form: $-2 \pi^{2}\left[h^{2} a^{* 2} U^{11}+\ldots+2 h k a^{*} b^{*} U^{12}\right]$

|  | $\mathrm{U}^{11}$ | $\mathrm{U}^{22}$ | $\mathrm{U}^{33}$ | $\mathrm{U}^{23}$ | $\mathrm{U}^{13}$ | $\mathrm{U}^{12}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\operatorname{Ir}(1)$ | 15(1) | 12(1) | 20(1) | -2(1) | -1(1) | $0(1)$ |
| $\mathrm{Sn}(1)$ | 16(1) | 13(1) | 17(1) | -1(1) | -1(1) | $0(1)$ |
| $\mathrm{O}(1)$ | 21(1) | 22(1) | 20(1) | -1(1) | 2(1) | 4(1) |
| $\mathrm{O}(2)$ | 26(1) | 41(1) | 27(1) | 3(1) | 2(1) | 18(1) |
| N(1) | 16(1) | 16(1) | 20(1) | 1(1) | -2(1) | 3(1) |
| C(1) | 21(1) | 19(1) | 22(1) | -2(1) | 2(1) | -2(1) |
| C(2) | 28(2) | 32(2) | 20(2) | -3(1) | 3(1) | 10(1) |
| C(3) | 19(1) | 20(1) | 27(2) | -1(1) | $0(1)$ | 6 (1) |
| C(4) | 32(2) | 30(2) | 28(2) | 4(1) | -2(1) | 14(1) |
| C(5) | 19(1) | 19(1) | 21(1) | $0(1)$ | -2(1) | 3(1) |
| C(6) | 19(1) | 25(1) | 22(2) | $0(1)$ | 1(1) | -4(1) |
| C(7) | 27(2) | 27(2) | 23(2) | O(1) | -1(1) | -1(1) |
| C(8) | 32(2) | 30(2) | 29(2) | 5(1) | -3(1) | -1(1) |
| C(9) | 28(2) | 39(2) | 24(2) | 5(1) | -1(1) | -10(1) |
| C(10) | 27(2) | 39(2) | 24(2) | -4(1) | 7(1) | -4(1) |
| C(11) | 26(2) | 32(2) | 26(2) | -1(1) | 2(1) | 1(1) |
| C(12) | 29(2) | 45(2) | 29(2) | 15(1) | -2(1) | -2(1) |
| C(13) | 36(2) | 22(2) | 39(2) | -1(1) | -18(2) | 4(1) |
| C(14) | 26(2) | 12(1) | 47(2) | 1(1) | -4(1) | -2(1) |
| C(15) | 29(2) | 17(1) | 44(2) | -15(1) | -5(1) | $0(1)$ |
| C(16) | 46(2) | 26(2) | 45(2) | -10(1) | -18(2) | $0(1)$ |
| C(17) | 24(2) | 29(2) | 34(2) | -7(1) | -9(1) | 4(1) |
| C(18) | 13(1) | 18(1) | 30(2) | -3(1) | -4(1) | 1(1) |
| C(19) | 12(1) | 21(1) | 33(2) | -2(1) | 0(1) | 4(1) |
| C(20) | 24(2) | 35(2) | 50(2) | 13(2) | 7(2) | -2(1) |
| C(21) | 34(2) | 26(2) | 53(2) | 6(2) | 5(2) | -8(1) |
| C(22) | 18(1) | 13(1) | 29(2) | $0(1)$ | 1(1) | -1(1) |
| C(23) | 27(2) | 22(1) | 31(2) | $0(1)$ | 2(1) | 1(1) |
| C(24) | 36(2) | 29(2) | 41(2) | 5(1) | 15(2) | 2(1) |
| C(25) | 22(2) | 25(2) | 63(2) | 9(2) | 12(2) | 1(1) |
| C(26) | 20(2) | 19(1) | 58(2) | 3(1) | -6(2) | -1(1) |


| $\mathrm{C}(27)$ | $25(2)$ | $15(1)$ | $36(2)$ | $1(1)$ | $-3(1)$ | $1(1)$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{C}(28)$ | $21(1)$ | $17(1)$ | $18(1)$ | $-1(1)$ | $-4(1)$ | $4(1)$ |
| $\mathrm{C}(29)$ | $21(1)$ | $21(1)$ | $22(2)$ | $0(1)$ | $-2(1)$ | $2(1)$ |
| $\mathrm{C}(30)$ | $29(2)$ | $20(1)$ | $26(2)$ | $-8(1)$ | $-4(1)$ | $2(1)$ |
| $\mathrm{C}(31)$ | $32(2)$ | $31(2)$ | $20(2)$ | $-5(1)$ | $1(1)$ | $7(1)$ |
| $\mathrm{C}(32)$ | $31(2)$ | $31(2)$ | $22(2)$ | $4(1)$ | $3(1)$ | $0(1)$ |
| $\mathrm{C}(33)$ | $32(2)$ | $20(1)$ | $22(2)$ | $0(1)$ | $-2(1)$ | $-2(1)$ |
| $\mathrm{C}(34)$ | $16(1)$ | $14(1)$ | $22(1)$ | $1(1)$ | $-3(1)$ | $-3(1)$ |
| $\mathrm{C}(35)$ | $26(2)$ | $21(1)$ | $24(2)$ | $-2(1)$ | $0(1)$ | $1(1)$ |
| $\mathrm{C}(36)$ | $28(2)$ | $32(2)$ | $24(2)$ | $6(1)$ | $-6(1)$ | $-1(1)$ |
| $\mathrm{C}(37)$ | $23(2)$ | $26(2)$ | $43(2)$ | $2(1)$ | $-10(1)$ | $6(1)$ |
| $\mathrm{C}(38)$ | $27(2)$ | $34(2)$ | $33(2)$ | $-11(1)$ | $-5(1)$ | $11(1)$ |
| $\mathrm{C}(39)$ | $18(1)$ | $27(2)$ | $24(2)$ | $-5(1)$ | $-5(1)$ | $4(1)$ |
|  |  |  |  |  |  |  |

Table 5. Hydrogen coordinates ( $\times 10^{4}$ ) and isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for d18124_a.

|  | x | y | z | $\mathrm{U}(\mathrm{eq})$ |
| :---: | :---: | :---: | :---: | :---: |
| H(1IR) | 5350(20) | 1684(17) | 7960(20) | 39(9) |
| $\mathrm{H}(2 \mathrm{~A})$ | 7828 | 1060 | 5168 | 32 |
| H(4A) | 8880 | 691 | 8213 | 36 |
| H(4B) | 8049 | 71 | 7902 | 36 |
| H(7A) | 5636 | 2761 | 4154 | 31 |
| H(8A) | 5605 | 3066 | 2536 | 37 |
| H(9A) | 6522 | 2352 | 1481 | 36 |
| H(10A) | 7468 | 1333 | 2050 | 36 |
| H(11A) | 7527 | 1039 | 3667 | 34 |
| H(12A) | 6533 | 244 | 8626 | 52 |
| H(12B) | 6198 | 1037 | 9042 | 52 |
| H(12C) | 7182 | 626 | 9484 | 52 |
| H(13A) | 7305 | 2173 | 8780 | 49 |
| H(13B) | 8265 | 2085 | 8140 | 49 |
| H(13C) | 8270 | 1718 | 9182 | 49 |
| H(14A) | 5338 | 174 | 7416 | 34 |
| H(15A) | 5373 | 381 | 5874 | 36 |
| H(16A) | 4008 | 648 | 4924 | 47 |
| H(16B) | 3326 | 586 | 5832 | 47 |
| H(17A) | 3994 | 1883 | 4927 | 35 |
| H(17B) | 2935 | 1739 | 5389 | 35 |
| H(18A) | 4008 | 2694 | 6224 | 25 |
| H(19A) | 3767 | 2411 | 7724 | 26 |
| H(20A) | 2931 | 1385 | 8196 | 43 |
| H(20B) | 2738 | 1167 | 7098 | 43 |
| H(21A) | 4110 | 533 | 8436 | 45 |
| H(21B) | 3473 | 125 | 7593 | 45 |
| H(23A) | 7054 | 3320 | 5518 | 32 |
| H(24A) | 8625 | 3605 | 4943 | 42 |
| H(25A) | 9983 | 3855 | 6002 | 44 |


| $\mathrm{H}(26 \mathrm{~A})$ | 9757 | 3847 | 7639 | 39 |
| :--- | ---: | ---: | ---: | ---: |
| $\mathrm{H}(27 \mathrm{~A})$ | 8181 | 3589 | 8225 | 30 |
| $\mathrm{H}(29 \mathrm{~A})$ | 6741 | 4372 | 8889 | 26 |
| $\mathrm{H}(30 \mathrm{~A})$ | 6342 | 4818 | 10391 | 30 |
| $\mathrm{H}(31 \mathrm{~A})$ | 5251 | 4149 | 11325 | 33 |
| $\mathrm{H}(32 \mathrm{~A})$ | 4622 | 2989 | 10793 | 34 |
| $\mathrm{H}(33 \mathrm{~A})$ | 5041 | 2532 | 9310 | 29 |
| $\mathrm{H}(35 \mathrm{~A})$ | 5073 | 3718 | 5445 | 29 |
| $\mathrm{H}(36 \mathrm{~A})$ | 3976 | 4638 | 4851 | 33 |
| $\mathrm{H}(37 \mathrm{~A})$ | 3183 | 5443 | 5891 | 38 |
| $\mathrm{H}(38 \mathrm{~A})$ | 3505 | 5327 | 7533 | 38 |
| $\mathrm{H}(39 \mathrm{~A})$ | 4598 | 4399 | 8129 | 28 |
|  |  |  |  |  |

Table 6. Torsion angles [ ${ }^{\circ}$ ] for d18124_a.

| $\operatorname{Ir}(1)-\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(2)$ | -12.7(4) |
| :---: | :---: |
| $\operatorname{Ir}(1)-\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(6)$ | 168.62(16) |
| $\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)$ | -4.3(5) |
| $\mathrm{C}(6)-\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)$ | 174.3(3) |
| $\mathrm{C}(5)-\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{O}(2)$ | 6.9(3) |
| $\operatorname{Ir}(1)-\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{O}(2)$ | -175.93(17) |
| $\mathrm{C}(5)-\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{C}(2)$ | -172.0(3) |
| $\operatorname{Ir}(1)-\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{C}(2)$ | 5.2(4) |
| $\mathrm{C}(4)-\mathrm{O}(2)-\mathrm{C}(3)-\mathrm{N}(1)$ | 9.8(3) |
| $\mathrm{C}(4)-\mathrm{O}(2)-\mathrm{C}(3)-\mathrm{C}(2)$ | -171.1(2) |
| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)-\mathrm{N}(1)$ | 8.8(5) |
| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)-\mathrm{O}(2)$ | -170.0(3) |
| $\mathrm{C}(3)-\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{C}(5)$ | -21.6(3) |
| $\mathrm{C}(3)-\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(12)$ | -137.7(3) |
| $\operatorname{Ir}(1)-\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(12)$ | 45.3(3) |
| $\mathrm{C}(3)-\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(13)$ | 97.5(3) |
| $\operatorname{Ir}(1)-\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(13)$ | -79.4(3) |
| $\mathrm{C}(3)-\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(4)$ | -19.2(3) |
| $\operatorname{Ir}(1)-\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(4)$ | 163.85(18) |
| $\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{N}(1)$ | 24.0(3) |
| $\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{C}(12)$ | 144.7(2) |
| $\mathrm{O}(2)-\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{C}(13)$ | -91.9(3) |
| $\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(6)-\mathrm{C}(7)$ | 17.8(4) |
| $\mathrm{C}(2)-\mathrm{C}(1)-\mathrm{C}(6)-\mathrm{C}(7)$ | -161.0(3) |
| $\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(6)-\mathrm{C}(11)$ | -160.8(3) |
| $\mathrm{C}(2)-\mathrm{C}(1)-\mathrm{C}(6)-\mathrm{C}(11)$ | 20.4(4) |
| $\mathrm{C}(11)-\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{C}(8)$ | -1.2(4) |
| $\mathrm{C}(1)-\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{C}(8)$ | -179.8(3) |
| $\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{C}(8)-\mathrm{C}(9)$ | 0.9(4) |
| $\mathrm{C}(7)-\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{C}(10)$ | 0.1(4) |
| $\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(11)$ | -0.7(4) |
| $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(11)-\mathrm{C}(6)$ | 0.4(4) |
| $\mathrm{C}(7)-\mathrm{C}(6)-\mathrm{C}(11)-\mathrm{C}(10)$ | 0.5(4) |
| $\mathrm{C}(1)-\mathrm{C}(6)-\mathrm{C}(11)-\mathrm{C}(10)$ | 179.1(3) |


| $\mathrm{C}(21)-\mathrm{C}(14)-\mathrm{C}(15)-\mathrm{C}(16)$ | -1.3(4) |
| :---: | :---: |
| $\operatorname{Ir}(1)-\mathrm{C}(14)-\mathrm{C}(15)-\mathrm{C}(16)$ | -102.8(3) |
| $\mathrm{C}(21)-\mathrm{C}(14)-\mathrm{C}(15)-\operatorname{Ir}(1)$ | 101.5(3) |
| $\mathrm{C}(14)-\mathrm{C}(15)-\mathrm{C}(16)-\mathrm{C}(17)$ | 89.5(4) |
| $\operatorname{Ir}(1)-\mathrm{C}(15)-\mathrm{C}(16)-\mathrm{C}(17)$ | 8.3(4) |
| $\mathrm{C}(15)-\mathrm{C}(16)-\mathrm{C}(17)-\mathrm{C}(18)$ | -28.9(4) |
| $\mathrm{C}(16)-\mathrm{C}(17)-\mathrm{C}(18)-\mathrm{C}(19)$ | -47.0(4) |
| $\mathrm{C}(16)-\mathrm{C}(17)-\mathrm{C}(18)-\operatorname{Ir}(1)$ | 35.6(3) |
| $\mathrm{C}(17)-\mathrm{C}(18)-\mathrm{C}(19)-\mathrm{C}(20)$ | -2.9(4) |
| $\operatorname{Ir}(1)-\mathrm{C}(18)-\mathrm{C}(19)-\mathrm{C}(20)$ | -106.5(2) |
| $\mathrm{C}(17)-\mathrm{C}(18)-\mathrm{C}(19)-\operatorname{Ir}(1)$ | 103.6(3) |
| $\mathrm{C}(18)-\mathrm{C}(19)-\mathrm{C}(20)-\mathrm{C}(21)$ | 89.6(4) |
| $\operatorname{Ir}(1)-\mathrm{C}(19)-\mathrm{C}(20)-\mathrm{C}(21)$ | 8.0(4) |
| $\mathrm{C}(15)-\mathrm{C}(14)-\mathrm{C}(21)-\mathrm{C}(20)$ | -49.5(4) |
| $\operatorname{Ir}(1)-\mathrm{C}(14)-\mathrm{C}(21)-\mathrm{C}(20)$ | 33.1(3) |
| $\mathrm{C}(19)-\mathrm{C}(20)-\mathrm{C}(21)-\mathrm{C}(14)$ | -28.3(4) |
| $\mathrm{C}(27)-\mathrm{C}(22)-\mathrm{C}(23)-\mathrm{C}(24)$ | -0.3(4) |
| $\mathrm{Sn}(1)-\mathrm{C}(22)-\mathrm{C}(23)-\mathrm{C}(24)$ | -176.4(2) |
| $\mathrm{C}(22)-\mathrm{C}(23)-\mathrm{C}(24)-\mathrm{C}(25)$ | 0.9(4) |
| $\mathrm{C}(23)-\mathrm{C}(24)-\mathrm{C}(25)-\mathrm{C}(26)$ | -0.7(5) |
| $\mathrm{C}(24)-\mathrm{C}(25)-\mathrm{C}(26)-\mathrm{C}(27)$ | 0.0(4) |
| $\mathrm{C}(25)-\mathrm{C}(26)-\mathrm{C}(27)-\mathrm{C}(22)$ | 0.6(4) |
| $\mathrm{C}(23)-\mathrm{C}(22)-\mathrm{C}(27)-\mathrm{C}(26)$ | -0.4(4) |
| $\mathrm{Sn}(1)-\mathrm{C}(22)-\mathrm{C}(27)-\mathrm{C}(26)$ | 175.5(2) |
| $\mathrm{C}(33)-\mathrm{C}(28)-\mathrm{C}(29)-\mathrm{C}(30)$ | -1.0(4) |
| $\mathrm{Sn}(1)-\mathrm{C}(28)-\mathrm{C}(29)-\mathrm{C}(30)$ | 165.3(2) |
| $\mathrm{C}(28)-\mathrm{C}(29)-\mathrm{C}(30)-\mathrm{C}(31)$ | -0.7(4) |
| $\mathrm{C}(29)-\mathrm{C}(30)-\mathrm{C}(31)-\mathrm{C}(32)$ | 1.9(4) |
| $\mathrm{C}(30)-\mathrm{C}(31)-\mathrm{C}(32)-\mathrm{C}(33)$ | -1.3(4) |
| $\mathrm{C}(31)-\mathrm{C}(32)-\mathrm{C}(33)-\mathrm{C}(28)$ | -0.6(4) |
| $\mathrm{C}(29)-\mathrm{C}(28)-\mathrm{C}(33)-\mathrm{C}(32)$ | 1.7(4) |
| $\mathrm{Sn}(1)-\mathrm{C}(28)-\mathrm{C}(33)-\mathrm{C}(32)$ | -165.0(2) |
| $\mathrm{C}(39)-\mathrm{C}(34)-\mathrm{C}(35)-\mathrm{C}(36)$ | 0.2(4) |
| $\mathrm{Sn}(1)-\mathrm{C}(34)-\mathrm{C}(35)-\mathrm{C}(36)$ | 179.7(2) |
| C(34)-C(35)-C(36)-C(37) | -0.1(4) |
| $\mathrm{C}(35)-\mathrm{C}(36)-\mathrm{C}(37)-\mathrm{C}(38)$ | 0.2(5) |


| $\mathrm{C}(36)-\mathrm{C}(37)-\mathrm{C}(38)-\mathrm{C}(39)$ | $-0.4(5)$ |
| :--- | :---: |
| $\mathrm{C}(35)-\mathrm{C}(34)-\mathrm{C}(39)-\mathrm{C}(38)$ | $-0.4(4)$ |
| $\mathrm{Sn}(1)-\mathrm{C}(34)-\mathrm{C}(39)-\mathrm{C}(38)$ | $-179.9(2)$ |
| $\mathrm{C}(37)-\mathrm{C}(38)-\mathrm{C}(39)-\mathrm{C}(34)$ | $0.5(5)$ |

Symmetry transformations used to generate equivalent atoms:

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[^0]:    Name
    $\mathrm{Cu}\left(\mathrm{pMe} \mathrm{Cl}^{2}\right) 2$ - L7

[^1]:    Name
    Cu (nap) 2 - $\mathrm{L} 8 \quad-$

[^2]:    Name
    (COD) Ir (L2) HSnPh3

