THE DESIGN OF NEW LIGANDS AND TRANSITION METAL COMPOUNDS FOR THE OXIDATION OF ORGANIC COMPOUNDS

A Dissertation

by

JOSEPH MICHAEL GRILL

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

August 2006

Major Subject: Chemistry

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ABSTRACT

The Design of New Ligands and Transition Metal Compounds for the Oxidation of Organic Compounds.

(August 2006)

Joseph Michael Grill, B.S., University of Illinois at Urbana-Champaign

Chair of Advisory Committee: Dr. Stephen A. Miller

A review of metal-mediated epoxidation is given. Jacobsen's catalyst and the Sharpless asymmetric epoxidation catalyst are discussed. The origins of enantio-selectivity are explained using stereochemical models.

Several new salen-type ligands were synthesized based on biphenol and binaphthol. The synthesis of these ligands and their subsequent coordination to transition metals were described. The transition metal complexes were structurally characterized by X-ray diffraction of single crystals. The manganese (III) complexes were evaluated for catalytic activity in epoxidation reactions. Despite the fact that these many of these complexes were optically active, little asymmetric induction was observed in any of the epoxidation reactions.

The investigation of a soluble nickel salen complex for the epoxidation of olefins led to the discovery of a new heterogeneous catalyst for the epoxidation of α,β-unsaturated carboxylic acids. Nickel salen complexes, upon reaction with commercial bleach, yield a fine black powder, which we identified as nickel oxide hydroxide—a known but poorly characterized nickel peroxide containing species. The reaction of an aqueous nickel (II) source with commercial bleach also yields nickel oxide hydroxide. This material was characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). Extremely broad peaks in the X-ray diffraction pattern suggested that this material consisted of particles with a very small diameter and this was confirmed by TEM. This insoluble material was found to function as a heterogeneous catalyst for the epoxidation of α,β-unsaturated carboxylic acids in the presence of sodium hypochlorite. The high activity of this catalyst in the epoxidation of certain olefins is due in part to its small particle size, which increases the overall surface area of this heterogeneous catalyst. Large particles of nickel oxide hydroxide were prepared and the catalytic activity was comparatively less.

The oxidation of several other organic substrates was also explored using this catalyst. Both primary and secondary alcohols can be oxidized with our nickel-based system. Primary alcohols go through an aldehyde intermediate which is then in turn oxidized to the carboxylic acid.

For Sue Krystof who taught my first chemistry class and to whom I am greatly indebted for the knowledge she bestowed.

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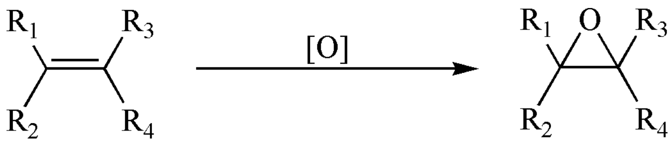
CHAPTER I

INTRODUCTION: AN OVERVIEW OF METAL MEDIATED EPOXIDATION CHEMISTRY

The epoxide is an important synthon in organic chemistry and a great deal of research has been devoted to the efficient, often asymmetric, synthesis of epoxides from olefins. Conceptually this reaction involves adding an oxygen atom across a carbon-carbon double bond (Scheme 1.1). Epoxides can be derived from olefins through several routes but one of the most attractive ways to accomplish this reaction is through the transition metal mediated oxidation of olefins, generally using a catalytic amount of a transitional metal and a terminal oxidant. This fact is evidenced in the explosion in the number of papers dealing with transition metal mediated epoxidation in the past 25 years. Despite the common misconception among many chemists that the epoxidation of olefins is a “solved” problem, each epoxidation system is has its own set of advantages and disadvantages. Certain types of substrates, electron deficient olefins for example, are still challenging to epoxidize via transition metal mediated catalysis. Furthermore, many of the epoxidation reactions are sensitive to 1) the geometry of the olefin, 2) the electronic environment of the olefin and 3) the presence of directing groups near the olefin.

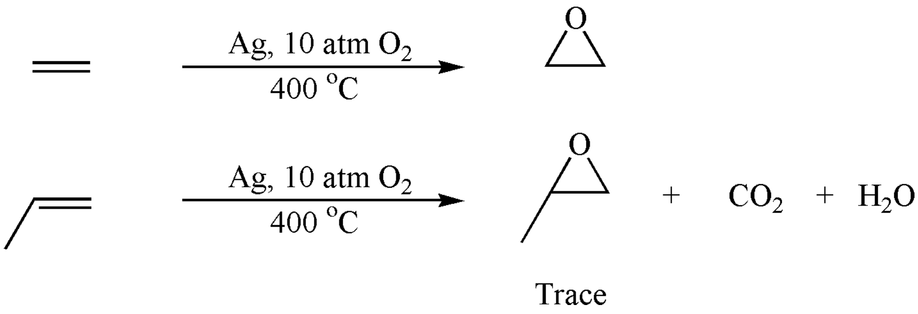
This dissertation follows the style and format of the *Journal of the American Chemical Society.*

Scheme 1.1. Olefin epoxidation



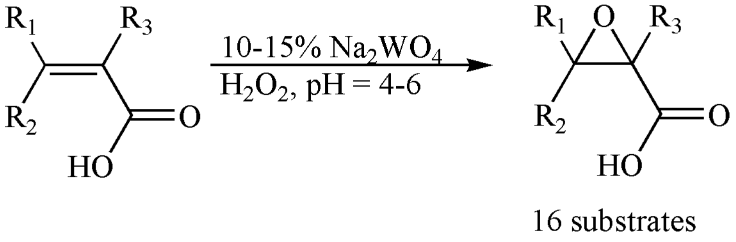
Samuel Lehner reported the first example of a catalytic oxidation of an olefin with a metal catalyst in 1931 (Scheme 1.2).[1,2] In these two papers, Lehner reported the oxidation ethylene to ethylene oxide using a silver metal catalyst with a large surface area. This continuous feed process devised by Lehner became a major industrial route to ethylene oxide, and is still used today. Quite unfortunately, this method is only useful for the epoxidation of ethylene and attempts to epoxidize larger olefins fail giving trace amounts of product, plus carbon dioxide and water.

Scheme 1.2. Reaction of olefins with oxygen and silver



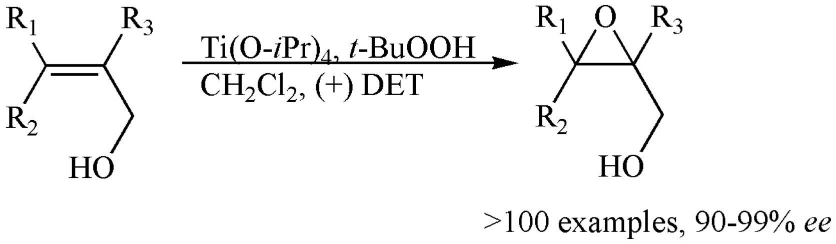
In 1959 George Payne reported the epoxidation of three α,β-unsaturated carboxylic acids (maleic acid, fumaric acid, and crotonic acid) using hydrogen peroxide and a catalytic amount sodium tungstate.[3] Generally α,β-unsaturated carboxylic acids are slow to epoxidize with the standard peroxide reagents that were available at the time and side products would often be produced at elevated temperatures. By carefully controlling the pH of the reaction, Payne was able to isolate the epoxide products in modest to good yields (50-77%). This reaction was reexamined and optimized by K. Barry Sharpless in 1985.[4] Sharpless used catalyst loadings of 10-15% sodium tungstate and kept the pH at 4-6 depending on the substitution pattern of the olefin. He was able to epoxidize 16 different α,β-unsaturated carboxylic acids with varying degrees of success (Scheme 1.3). Unfortunately, he was not able to accomplish this reaction asymmetrically and the epoxidation of α,β-unsaturated carboxylic acids has received only sparse attention since Sharpless' paper in 1985.

Scheme 1.3. Epoxidation of α,β-unsaturated carboxylic acids with catalytic sodium tungstate and hydrogen peroxide



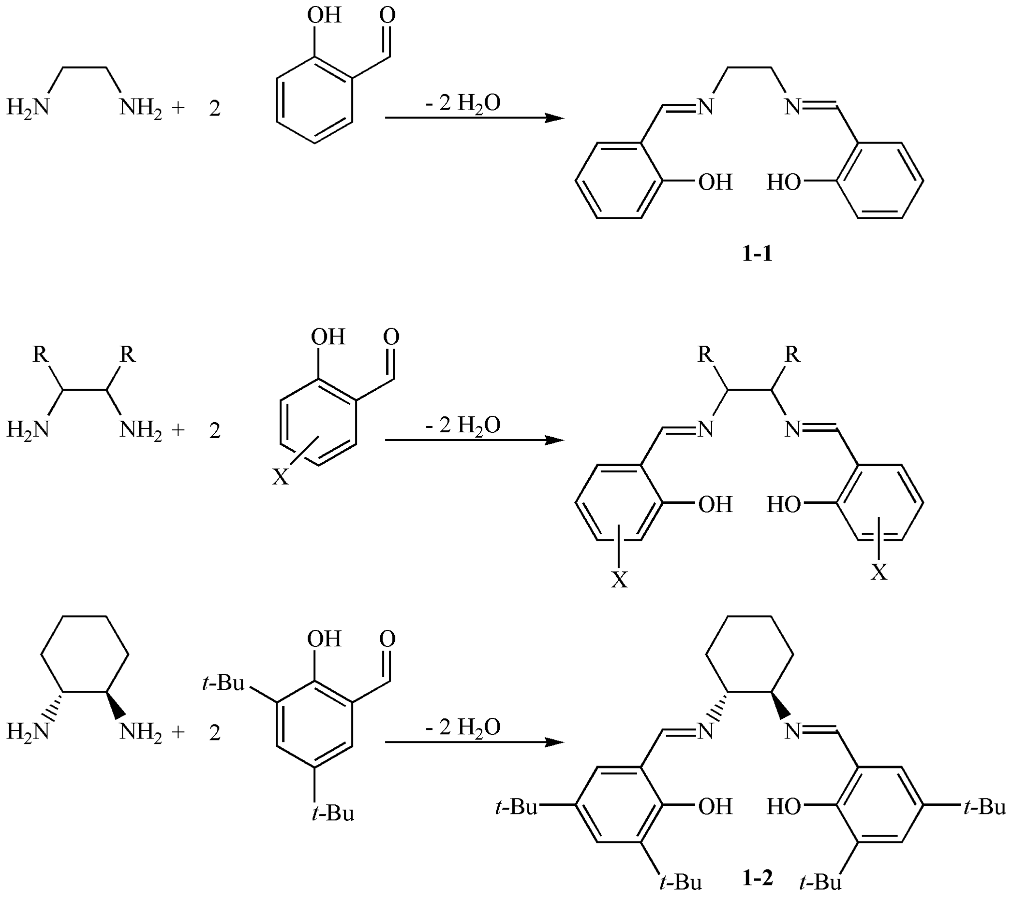
In 1980 Sharpless reported what is now known as the Sharpless asymmetric epoxidation reaction.[5] Using this new reaction, Sharpless was able to epoxidize several allylic alcohols with titanium isopropoxide, (-) or (+) diethyl tartrate, and an organic peroxide (Scheme 1.4). With the addition of molecular sieves to remove trace amounts of water, the reaction becomes catalytic in titanium operating at 5-10 mol% catalyst loading for most substrates.[6] This reaction was the first example of a highly enantioselective, transition metal mediated epoxidation of an olefin and Sharpless received the Nobel Prize in chemistry in 2001 for this discovery. Sharpless' system is attractive because 1) it uses an inexpensive catalyst, 2) it uses an inexpensive chiral pool reagent readily available in either enantiomer, and 3) it can asymmetrically epoxidize a prochiral olefin of any geometry in high enantiomeric excess (*ee*) with a high degree of predictibility. However, the system requires a proximal alcohol for enantionselectivity as it functions as a directing group. Nonetheless, the Sharpless asymmetric epoxidation reaction has been used in several hundred total syntheses of natural products and is a standard tool for synthetic organic chemists.[7,8,9,10,11]

Scheme 1.4. The Sharpless asymmetric epoxidation reaction



Since the discovery of an efficient asymmetric epoxidation system, a multitude of researchers have been finding new catalysts to efficiently epoxidize a wider range of olefins, particularly relatively unfunctionalized olefins. To this end, researchers have been increasingly turning to soluble transition metal catalysts. Many of these catalysts are based on using the chelating salen ligand which can be synthesized from the addition of 2 equivalents of salicylaldehyde to 1 equivalent of ethylene diamine (Scheme 1.5). This simple ligand, **1-1,** can be easily modified by changing either the diamine or the aldehyde to include chirality, steric bulk and/or electronic modifications. Eric Jacobsen published several early papers where he investigated the effects of using chiral diamines and modified aldehydes for the epoxidation of olefins using manganese (III) salen complexes.[12,13,14,15,16,17,18,19] Eventually **1-2** was found to be an ideal ligand for asymmetric induction. Jacobsen demonstrated that several different unfunctionalized olefins could be epoxidized using what is now known as Jacobsen's catalyst **1-3** but generally only olefins with *cis* geometry or trisubstituted olefins are epoxidized in high *ee*.

Scheme 1.5. Salen ligands

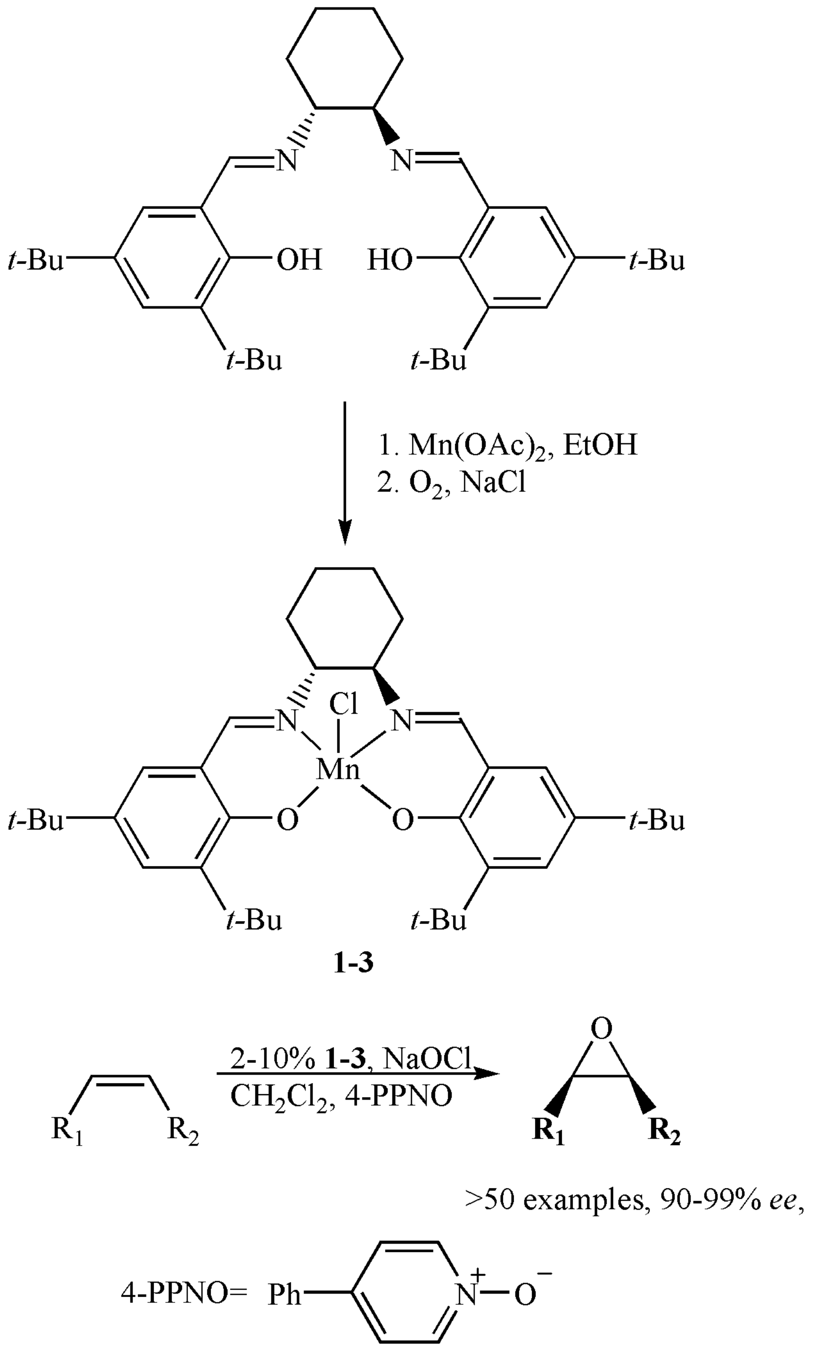


1-1

1-2

A crystallographic study of these catalysts provides valuable insight into their enantioselectivity.[20] The olefin substrate is hypothesized to approach the manganese complex with a side-on approach. The ligand structure effectively blocks one enantioface of the incoming substrate allowing for high enantioselectivity in the product. Jacobsen's catalyst is commercially available and has a variety of uses in synthetic organic chemistry, such as in the production of Taxol, an anti-cancer drug.[15] The catalyst does have several drawbacks, however. First, an additive is required to act as an axial ligand. This additive usually takes the form of a pyridine N-oxide compound (Scheme

Scheme 1.6. Jacobsen's epoxidation catalyst, **1-3**

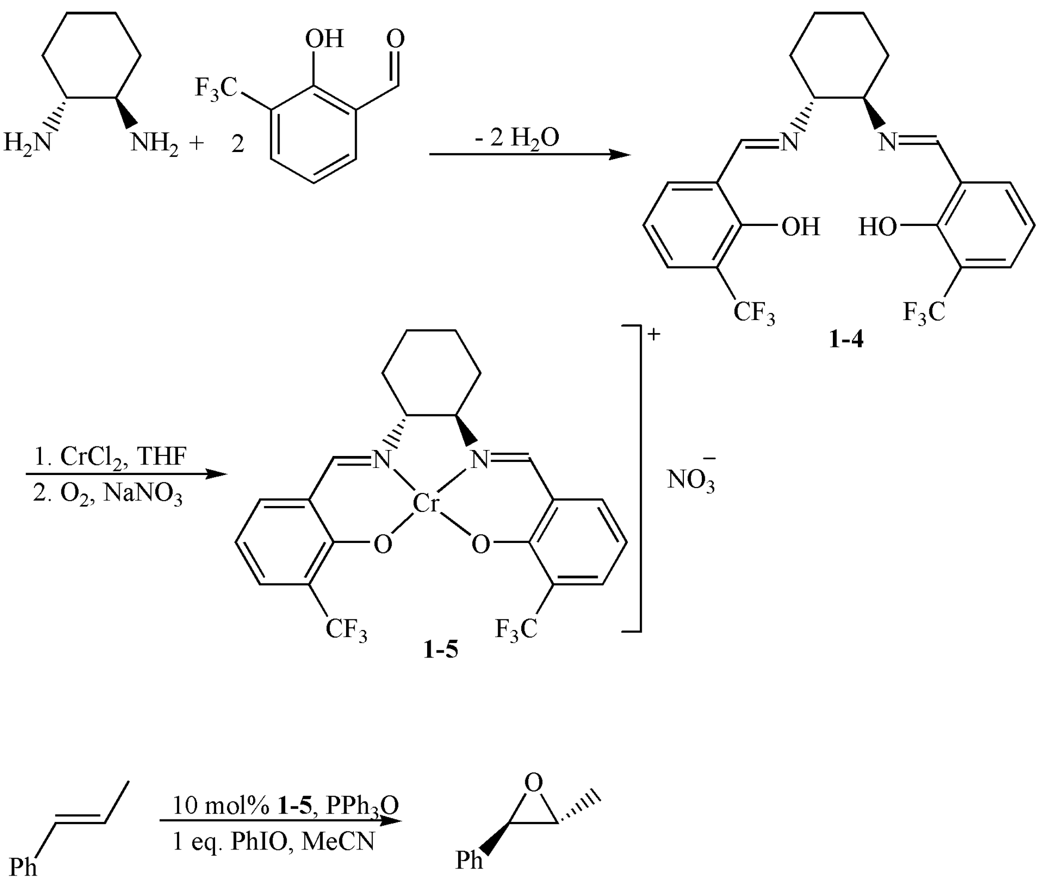


1.6). Without this additive, diminished enantioselectivity is observed.[12,13,14,15] The exact role of this additive is of interest because Jacobsen's catalyst is currently one of the most effective means of epoxidizing unfunctionalized olefins. Jacobson confirmed that this additive does not transfer oxygen to the olefin through a series of control experiments.[15] In fact, the importance of an axial ligand in similar epoxidation catalysts had already been reported by Samsel et al. and by Katsuki et al.[21,22] In these reports, chromium was used as the catalyst. While the isolated Mn (V) oxo salen species had not yet been reported, Cr(V) oxo salen species were known. It was observed that an axial ligand such as a hydrophobic pyridine N-oxide stabilized the high oxidation state of the chromium. Jacobsen presumed that the manganese complexes epoxidize through a similar mechanism where the Mn (III) is oxidized to Mn (V) and then delivers an oxygen atom to the olefin. Thus, an axial ligand could help stabilize a relatively short-lived Mn (V) oxo species. This hypothesis is supported by observed enantiomeric excesses with and without the additive,[12,13,14,15,16,17,18,19] calculations,[23] and recent isolated examples of Mn (V) oxo species which have been shown to act as effective oxygen transfer agents.[24,25]

Jacobsen's catalyst is also incapable of epoxidizing *trans* olefins in high *ee*, giving only a 27% *ee* in the direct epoxidation of *trans*-stilbene.[26] Jacobsen did find a partial solution to this problem. Through the use of a quaternary ammonium salt, the *trans* epoxides can be obtained in good *ee*'s (80-91%) by an isomerization reaction after the epoxidation of the *cis* olefin but the ammonium salt is expensive and must be separated from the product. Furthermore enantiopurity is not fully maintained in the isomerization resulting in the loss of 10-18% *ee* for the six examples reported.[26] Jacobsen's system is attractive because 1) the ligand uses *trans*-1,2-diaminocyclohexane, a cheap chiral reagent readily available in either enantiomer, 2) it uses an aldehyde that is cheap and easy to synthesize, 3) the epoxidation reaction uses bleach as the oxidant, 4) the epoxidation usually occurs smoothly with high yields at low catalyst loading (2-10 mol%), and 5) it uses a very inexpensive transition metal.

Jacobsen's catalyst is one of the most successful catalysts for asymmetric epoxidations since it is capable of epoxidizing many substrates in high *ee* but it has two key weaknesses: 1) Jacobsen's catalyst is not capable of epoxidizing *trans* olefins in high *ee*; and 2) Jacobsen's catalyst is not capable of epoxidizing electron deficient olefins as these substrates are highly deactivated. Little success has been had in the past 10 years in addressing these two issues. Declan Gilheany has had some limited success in epoxidizing a few *trans* olefins in high *ee* using a modified salen ligand coordinated to chromium (III) (Scheme 1.7).[27,28,29,30,31,32] Gilheany explored the electronic and steric modification of the salen ligand and devised a system that could epoxidize *trans* olefins enantioselectively. In particular, Gilheany studied salen complexes that had electron-withdrawing groups attached to the phenyl rings. Gilheany et al. found that complexes that contained electron-withdrawing groups on the phenyl rings gave good *ee*'s in the epoxidation of *trans* olefins and ones with electron donating groups on the phenyl rings gave poor *ee*'s. However, the scope of the reaction is rather limited. The catalyst used is only effective (>90% *ee*) for a single substrate, (*E*)-β-methylstyrene, making this approach less than ideal. Further, the system uses a very expensive oxidant, PhIO, in order to obtain good *ee*'s and activity. Additionally, this system uses a ligand that is difficult to synthesize, making this approach to enantioselective epoxidation unattractive.

Scheme 1.7. Gilheany's epoxidation catalyst



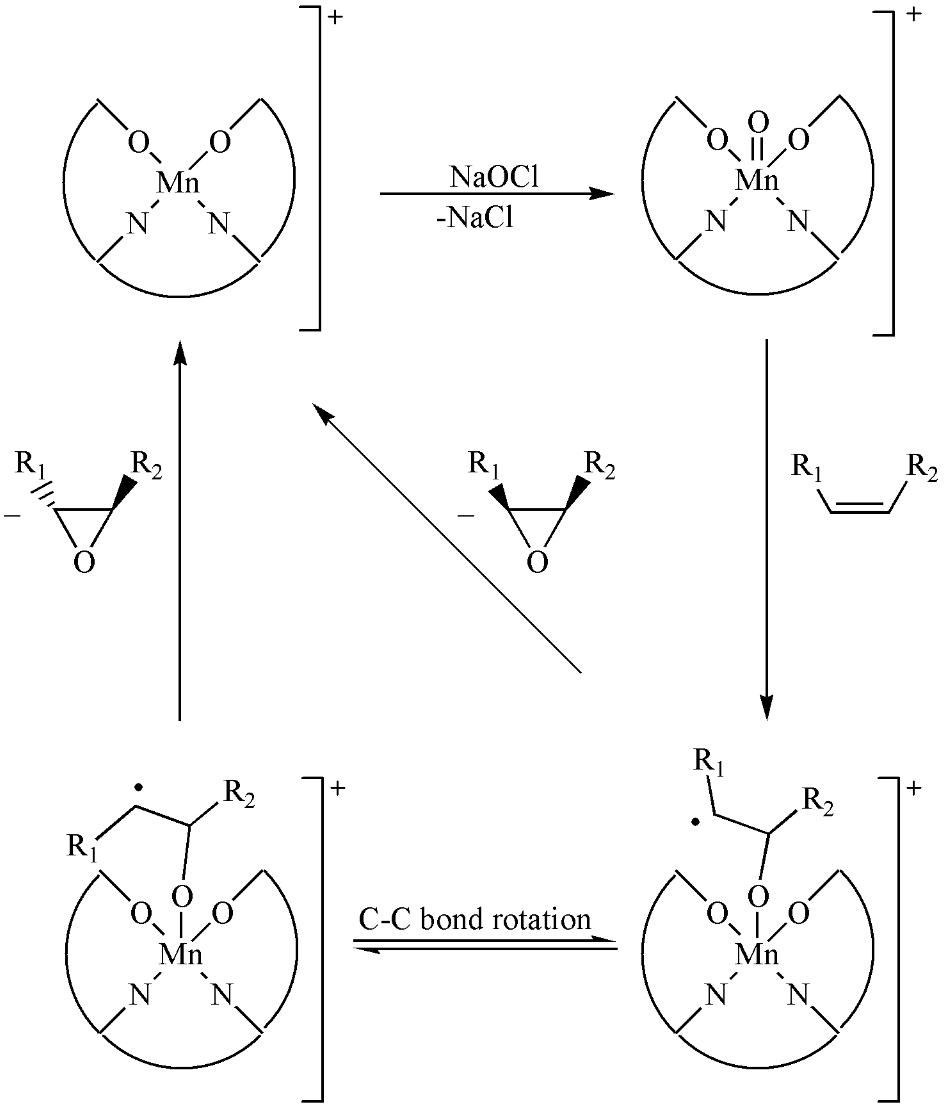
1-4

1-5

45% yield, 92 % *ee*

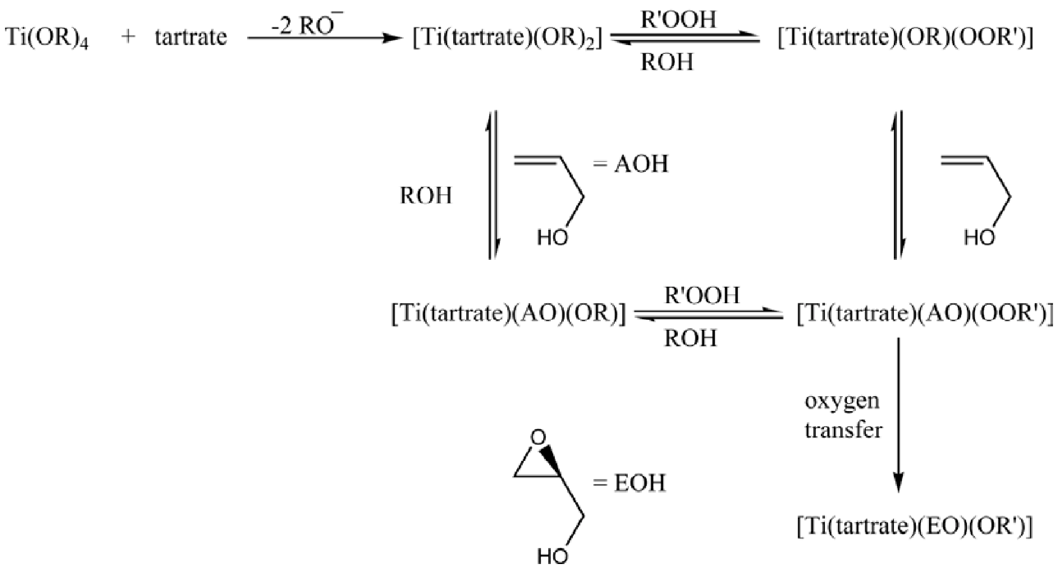
The key to understanding the asymmetric epoxidation lies in the mechanism of the epoxidation. For the most part, two general mechanisms persist in the literature for asymmetric epoxidation—a precoordination mechanism and a radical mechanism. It is generally thought that Sharpless' titanium system (and incidentally many enzymatic systems) proceeds through the precoordination mechanism and Jacobsen's catalyst proceeds through the radical mechanism. There was some debate in the literature as to the exact mechanism of the Jacobsen's catalyst. Some claimed that this reaction went through an oxymetallacyclic intermediate after attack of the substrate at the oxo ligand and this species' viability in the catalytic cycle is generally supported by calculations for other transitional metal systems such as osmium and ruthenium.[33,34,35,36] A manganese oxymetallacyclic intermediate was somewhat supported by calculation[37] and experiment as well. However, recent evidence suggests that an oxymetallacyclic intermediate is not likely in the case of chromium and manganese systems. In the generally accepted radical mechanism, oxidation of manganese (III) to manganese (V) occurs, followed by addition of an olefin to form a C-O bond and a carbon radical. Collapse of the radical species t then gives the epoxide (Scheme 1.8).[38] This mechanism allows for the possibility of getting both the *trans* and *cis* epoxide; however, this requires a rotation before collapse. In most reactions involving Jacobsen's catalyst, both isomers are observed with the major product resulting form a direct collapse of the radical and the minor product arising from rotation before collapse. Thus *cis* olefins give *cis* epoxides as the major product and *trans* olefins give *trans* epoxides as the major product. In most cases the intermediate manganese (V) oxo species is not isolable, but in a few rare cases the manganese (V) oxo species can be isolated and characterized.[39,24,25,40] However, these examples do not use a salen ligand; rather, they use amide based ligands or corrolazine ligands. Chromium (V) oxo salen complexes, on the other hand, are much more stable and can be isolated and characterized easily.[27,28,29,30,31,32] These manganese (V) and chromium (V) oxo species are competent stoichiometric reagents for the delivery of oxygen lending credibility to the invocation of such intermediates for manganese-salen complexes. This radical mechanism is further supported for the manganese and chromium systems in the literature through both experiment[41,42,] and calculations.[23,43,44]

Scheme 1.8. Radical epoxidation mechanism using manganese[38]



The mechanism of the Sharpless asymmetric epoxidation contrasts sharply with the mechanism for Jacobsen's catalyst and explains why a proximal alcohol is required for asymmetric induction in his system. Sharpless published several papers in which he conclusively showed that the epoxidation using his titanium system relied on precoordination of one enantioface of the olefin to the catalyst, followed by delivery of the oxygen atom to the exposed enantioface (Scheme 1.9).[45,46,47] Though the exact solid state structure of the titanium catalyst was not known, a structure was proposed that was consistent with the observed catalytic results and with the structures of several related compounds. Several key observations were made to elucidate a probable mechanism for this reaction. First, the *ee* excess is not dependent on the identity of the titanium alkoxide used. Second, the *ee* is heavily dependent on the identity of the tartaric ester used with bulkier esters giving better activity and selectivity. Finally, the *ee* and activity of the catalyst is heavily influenced by the presence or absence of water in the reaction.

Scheme 1.9. Mechanism of the Sharpless asymmetric epoxidation[46]



In our efforts to epoxidize electron deficient substrates using a soluble nickel-salen complex we discovered a heterogeneous system that is capable of epoxidizing α,β-unsaturated carboxylic acids with very low catalyst loadings. This system consists of nickel oxide hydroxide, which is easily synthesized by the addition of bleach to aqueous nickel (II) sources. Nickel oxide hydroxide has been known for some time and has been studied as a stoichiometric oxidant for many organic compounds such as alcohols, phenols, aldehydes, amines, and others.[48] Previously, this material had been poorly characterized but it is suspected that this material 1) has a large surface area, 2) contains nickel oxides, and 3) oxidizes organic substrates through a free radical mechanism.[49,50] One of the major reasons that it has been poorly characterized is because the material is insoluble in all common solvents except acidic solvents, but acidic solvents lead to rapid decomposition of this material. The X-ray powder diffraction of this material has very broad peaks, making the solid-state structure difficult to determine. However, it was suspected that this material was actually β-NiOOH, a well-known and better-characterized material. M. Wyn Roberts published a paper in 1983 that confirmed this hypothesis using X-ray photoelectron spectroscopy and by analyzing the gaseous products of the decomposition of this material by mass spectroscopy.[51] This material has never been previously known to epoxidize olefins. However, we have shown it to be quite active for the catalytic epoxidation of α,β-unsaturated carboxylic acids, thus expanding the set of reagents available for this important reaction in organic chemistry.

CHAPTER II

NEW SALEN LIGANDS BASED ON 2,2'-BIPHENOL AND BINAPHTHOL[*]

SYNOPSIS

Several new salen-type ligands have been synthesized by performing a facile nucleophilic aromatic substitution reaction with either 2,2'-biphenol or chiral binaphthol, followed by reduction of the nitro group and subsequent reaction of the resulting diamine with 2 equivalents of a salicylaldehyde. Coordination of these ligands to metals results in unusual salen complexes in which the nitrogen atoms are *trans* to each other in the solid state. These complexes were studied by X-ray diffraction on single crystals to unambiguously determine the molecular structure. The manganese containing complexes are active catalysts for the epoxidation of olefins. With the chiral ligands, very little asymmetric induction is observed for the epoxidation of styrene using the manganese catalyst.

INTRODUCTION

The salen ligand is a versatile, widely-used ligand for homogeneous transition metal mediated catalysis.[14,28,26,52] The simple salen ligand is synthesized by the condensation of two equivalents of salicylaldehyde with one equivalent of ethylene diamine (Scheme 1.5). Transition metal salen complexes have been known since at least

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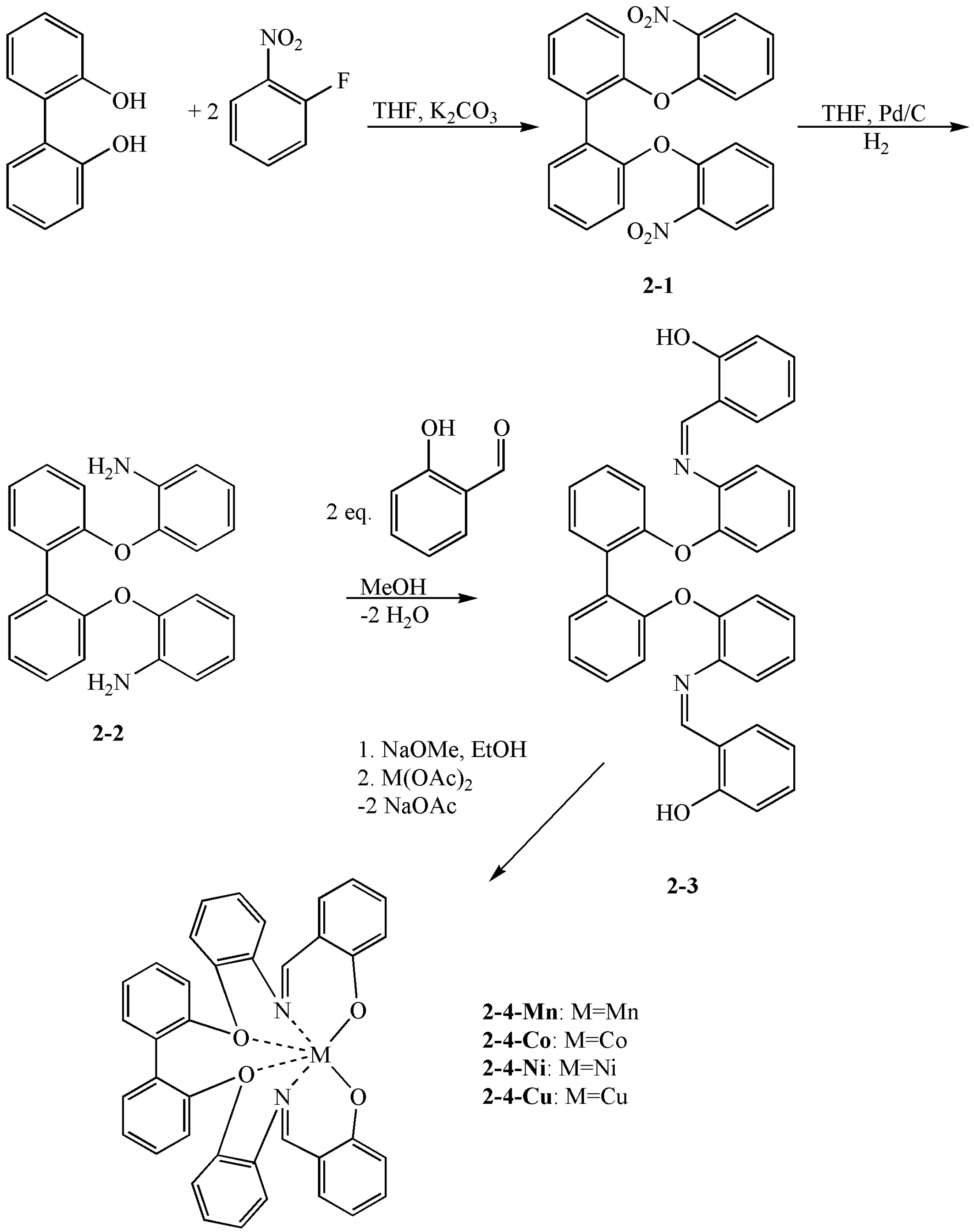
1931.[12,13,14,15] Modified salen complexes derived from other diamines and/or salicylaldehyde derivatives have been used in reactions such as asymmetric epoxidation,[14] the copolymerization of carbon dioxide with epoxides,[52] and the hydrolytic kinetic resolutions of racemic epoxides,[53] depending on the metal employed.

Jacobsen and coworkers reported the synthesis of a very successful chiral salen-type ligand (Scheme 1.6). The corresponding manganese catalyst is useful for the epoxidation of *cis*-disubstituted olefins in the presence of commercial bleach.[15] Overall the asymmetric epoxidation of *cis*-olefins with Jacobsen's catalyst is effective but the epoxidation requires a large catalyst loading (6%) and an expensive pyridine-N-oxide derivative in order to obtain high enantiomeric excesses (*ee*'s). Gilheany and coworkers reported the synthesis of a series of chiral chromium-salen complexes capable of epoxidizing *trans*-disubstituted olefins with poor to good *ee*'s, but the system suffers from limited substrate tolerance and high catalyst loading (10 mol%) (Scheme 1.6).[27,28,29,30,31] Furthermore, it requires an expensive additive and an expensive oxidant. The *ee*'s obtained by Gilheany range from poor to good (10%-92%) depending on the specific catalyst, the conditions, and the substrate, but the isolated yields in most cases are poor. The need for new catalysts that are more efficient, less expensive and more selective is evident.

RESULTS AND DISCUSSION

2-fluoronitrobenzene reacts readily with a variety of mildly nucleophilic species, such as alcohols or amines, to generate a new carbon-nucleophile bond and hydrofluoric acid.[54] In order to synthesize new salen-type ligands, we took advantage of this facile nucleophilic aromatic substitution reaction (Scheme 2.1). 2,2'-biphenol reacts readily with 2-fluoronitrobenzene in refluxing THF to give the expected product **2-1**. Reduction of **2-1** with hydrogen using a palladium on carbon catalyst gives the previously unknown diamine **2-2** in excellent overall yield (97%). Reaction of **2-2** with two equivalents of salicylaldehyde gives the corresponding dialdimine, **2-3** (Scheme 2.1). This ligand is an "expanded salen ligand" because it has the usual chelating atoms of salen plus an additional two neutral donor atoms. The expanded salen ligand, **2-3** (SalbipH$_2$), is readily deprotonated with sodium methoxide in ethanol and coordinated to transition metals (Scheme 2.1). The X-ray structures of the complexes containing Mn, Co, Ni, and Cu were obtained (Figure 2.1). Crystallographic data are given in appendix A and selected bond lengths and angles are given in Table 2.1. The complexes containing Mn, Co, and Ni have distorted octahedral geometries with *trans* nitrogen atoms. The N-M-N angle increases as we move from manganese to nickel (Mn=158.9°, Co=167.2°, Ni= 167.6°) as a consequence of the decreasing ionic radius of the metal. The fact that the complexes have trans nitrogen atoms is quite unusual. For the simple salen complexes, *trans* coordination of nitrogen atoms is geometrically impossible. In the structures of the Mn, Co, and Ni containing species, the ethereal oxygen atoms are coordinated to the metal in the solid state, with average metal-oxygen distances of 2.36 Å, 2.23 Å and 2.19 Å, respectively (Figure 2.1). As the ethereal oxygen atoms get closer to the metal, we observe the expected increase in N-M-N angle. The copper complex is distorted square planar. In the copper complex, the oxygen atoms do not seem to be bound as tightly to the metal as in the cases of the Mn, Co, and Ni complexes as the metal-oxygen distance is quite large (2.79 Å and 2.80 Å) (Figure 2.1). A N-M-N angle of only 164.6° is also observed.

Scheme 2.1. Synthesis of a new salen-type ligand and its coordination to metals



2-1

2-2

2-3

2-4-Mn: M=Mn
2-4-Co: M=Co
2-4-Ni: M=Ni
2-4-Cu: M=Cu

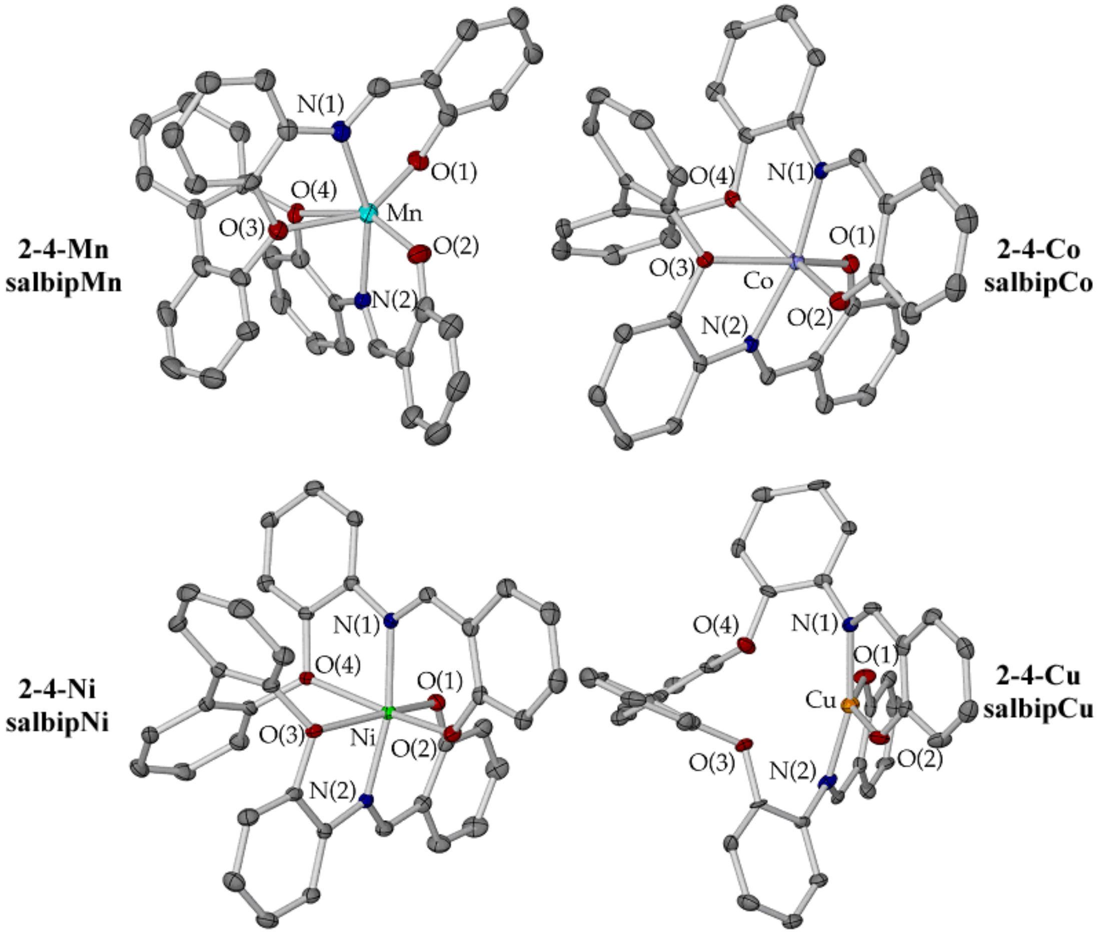


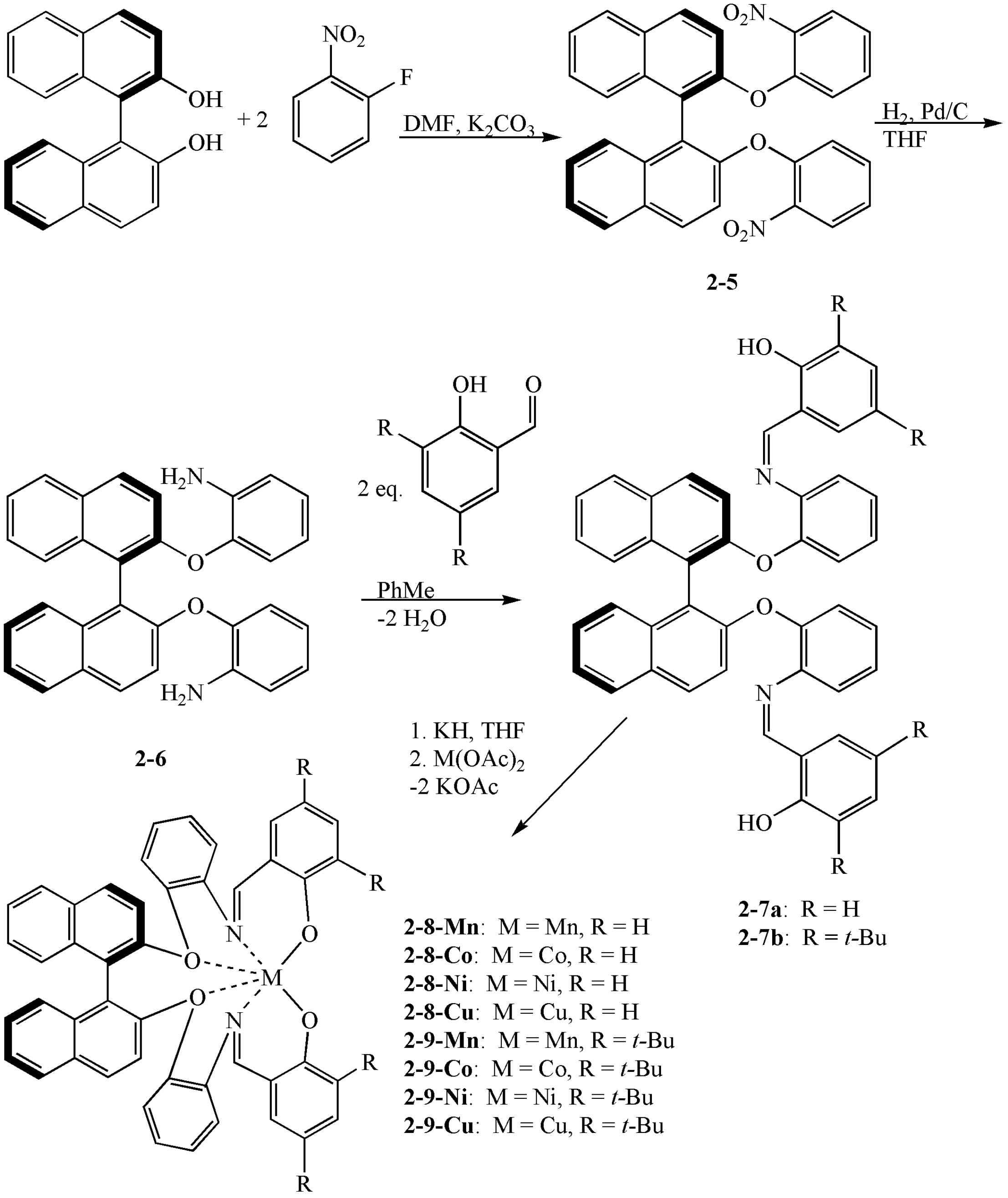
Figure 2.1. X-ray structures of **2-4-Mn**, **2-4-Co**, **2-4-Ni**, and **2-4-Cu** with 50% probability ellipsoids and hydrogen atoms omitted for clarity.

Table 2.1. Selected bond lengths and angles for **2-4-Mn**, **2-4-Co**, **2-4-Ni**, **2-4-Cu**, **2-8-Co** and **2-8-Cu**

	2-4-Mn	**2-4-Co**	**2-4-Ni**	**2-4-Cu**	**2-8-Co**	**2-8-Cu**
N(1)-M-N(2) <	159.9°	167.2°	167.6°	164.6°	164.8°	160.5°
O(1)-M-O(2) <	109.5°	110.5°	103.5°	149.3°	106.1°	156.9°
O(1)-M-(O3) <	152.1°	159.2°	165.2°	127.4°	161.5°	125.6°
O(1)-M-(O4) <	90.9°	88.8°	89.2°	82.3°	87.4°	84.48°
O(2)-M-O(3) <	94.7°	88.1°	89.5°	81.9°	87.0°	74.4°
O(2)-M-O(4) <	149.2°	158.0°	165.2°	126.6°	81.7°	117.6°
O(3)-M-O(4) <	74.2°	75.0°	79.0°	57.4°	64.3°	61.6°
M-O(1)	2.02 Å	1.97 Å	1.96 Å	1.91 Å	1.96 Å	1.90 Å
M-O(2)	2.02 Å	1.97 Å	1.96 Å	1.91 Å	1.95 Å	1.89 Å
M-O(3)	2.37 Å	2.23 Å	2.18 Å	2.80 Å	2.31 Å	3.22 Å
M-O(4)	2.35 Å	2.24 Å	2.20 Å	2.79 Å	2.25 Å	2.76 Å
M-N(1)	2.22 Å	2.08 Å	2.01 Å	1.97 Å	2.07 Å	1.98 Å
M-N(2)	2.22 Å	2.07 Å	2.01 Å	1.98 Å	2.10 Å	1.99 Å

Given the facility of the salbipH_2 ligand synthesis, we sought to synthesize a chiral version of our expanded salen ligand using (*R*)-binaphthol. Unfortunately (*R*)-binaphthol reacts very slowly with 2-fluoronitrobenzene in refluxing THF, taking up to two weeks for complete reaction. However, the reaction proceeds quite rapidly in DMF, affording the expected product **2-5** in high yield after several hours (Scheme 2.2). Reduction of **2-5** in THF with hydrogen using a palladium on carbon catalyst gives the previously unknown chiral diamine **2-6** in excellent overall yield (90.1%). Reaction of **2-6** with two equivalents of salicylaldehyde or a substituted salicylaldehyde affords the expected chiral expanded salen ligand **2-7a** or **2-7b** (Scheme 2.2). These are termed salbinH_2 and salbin(t-Bu)$_4H_2$ because they are derived from *sal*icylaldehyde and *bin*aphthol. Ligands **2-7a** and **2-7b** are readily deprotonated in THF with potassium hydride and coordinated to transition metals (Scheme 2.2). The complexes are very difficult to crystallize and in many cases crystals suitable for X-ray diffraction could not be grown. Nonetheless, we were able to obtain crystals of **2-8-Co** (Figure 2.2). Its structure is similar to that of **2-4-Co** (Figure 2.1) with minor differences. For example, the N-Co-N angle is 164.8° in **2-8-Co**, compared to the N-Co-N angle of 167.2° in **2-4-Co**. Also, the ethereal oxygen atoms in **2-8-Co** are 2.31 Å and 2.25 Å from the cobalt atom. This compares well to distances of 2.23 Å and 2.24 Å in **2-4-Co**. Figure 2.3 shows the similarities in the core structures of **2-4-Co** and **2-8-Co.** Additionally, X-ray quality crystals of **2-8-Cu** were obtained (Figure 2.2). Its structure is similar to that of **2-4-Cu** (Figure 2.1) with minor differences. The N-Cu-N angle in **2-8-Cu** is 160.5°, whereas the N-Cu-N angle in **2-4-Cu** is 164.6°. Also, the ethereal oxygen atoms in **2-8-Cu** are 3.22 Å and 2.76 Å from the copper atom. This contrasts with the nearly identical copper-ethereal oxygen distances of 2.80 Å and 2.79 Å in **2-4-Cu**. Figure 2.4 shows the similarities in the core structures of **2-4-Cu** and **2-8-Cu**.

Scheme 2.2. Synthesis of an expanded chiral salen-type ligand (2-7a, salbinH$_2$; 2-7b, salbin(t-Bu)$_4$H$_2$) and its coordination to metals



2-5

2-6

2-7a: R = H
2-7b: R = t-Bu

2-8-Mn: M = Mn, R = H
2-8-Co: M = Co, R = H
2-8-Ni: M = Ni, R = H
2-8-Cu: M = Cu, R = H
2-9-Mn: M = Mn, R = t-Bu
2-9-Co: M = Co, R = t-Bu
2-9-Ni: M = Ni, R = t-Bu
2-9-Cu: M = Cu, R = t-Bu

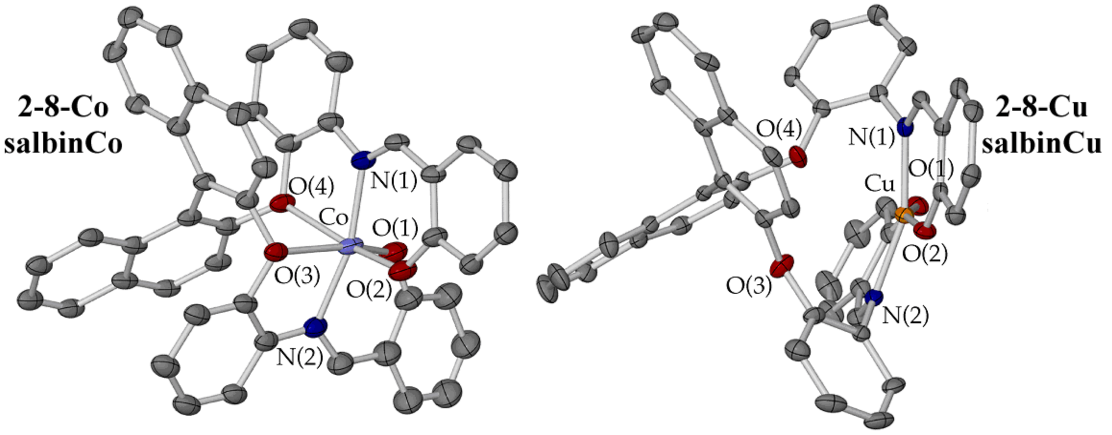


Figure 2.2. X-ray structures of **2-8-Co** and **2-8-Cu** with 50% probability ellipsoids and hydrogen atoms omitted for clarity.

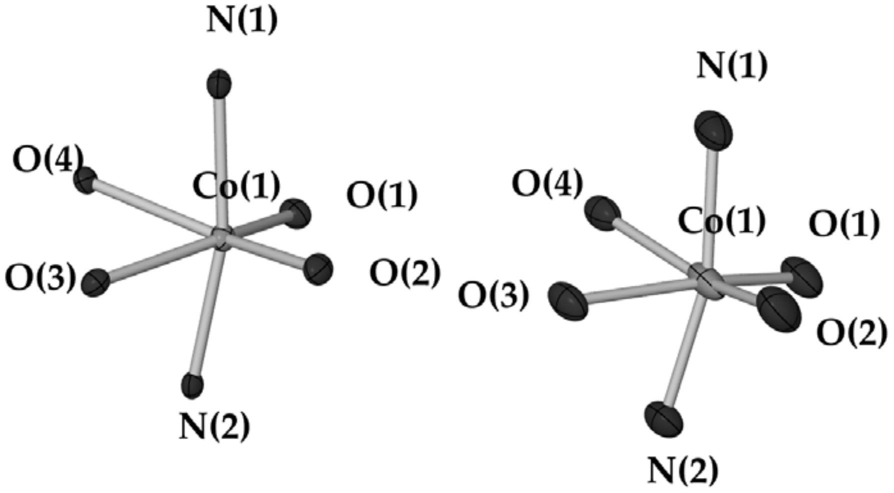


Figure 2.3. Coordination sphere of **2-4-Co** and **2-8-Co** with 50% probability ellipsoids.

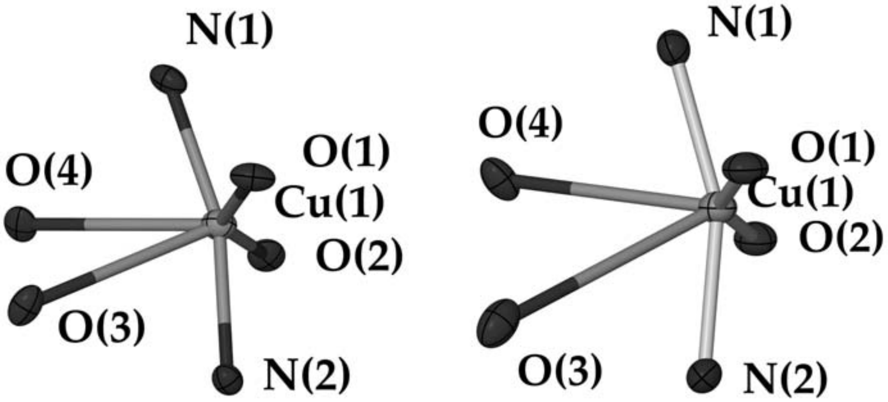


Figure 2.4. Coordination sphere of **2-4-Cu** and **2-8-Cu** with 50% probability ellipsoids.

Both Salbip and Salbin ligands bind to the metal in a similar fashion, in that starting from a given terminus of the ligand, the heteroatoms wrap around the metal center in the same way. Let us consider the ligand to be like a tether with oxygen and nitrogen atoms attached (Figure 2.5). Once could envision a few reasonable isomers of the resulting transition metal complex. Let us impose the condition that any two consecutive heteroatoms must be in a *cis* rather than a *trans* arrangement. This is a reasonable condition since any *trans* arrangement of adjacent heteroatoms would require much more flexibility than this ligand affords. Given this constraint, consider the stepwise chelation of this ligand to a metal. The first three atoms have two reasonable options for binding-- they can either bind in a facial or meridional geometry (*fac*-1,2,3 and *mer*-1,2,3). If we start with the *mer*-1,2,3 isomer as an intermediate, there is only one possible isomer that can be observed in the final product, given the restraint that each consecutive heteroatom must have a *cis* relationship to the one that preceded it. This isomer happens to be the only isomer that is observed in any of the solid state molecular structures. None of the isomers that begin with facial arrangement of the first three atoms (O1, N2, O3) is ever observed.

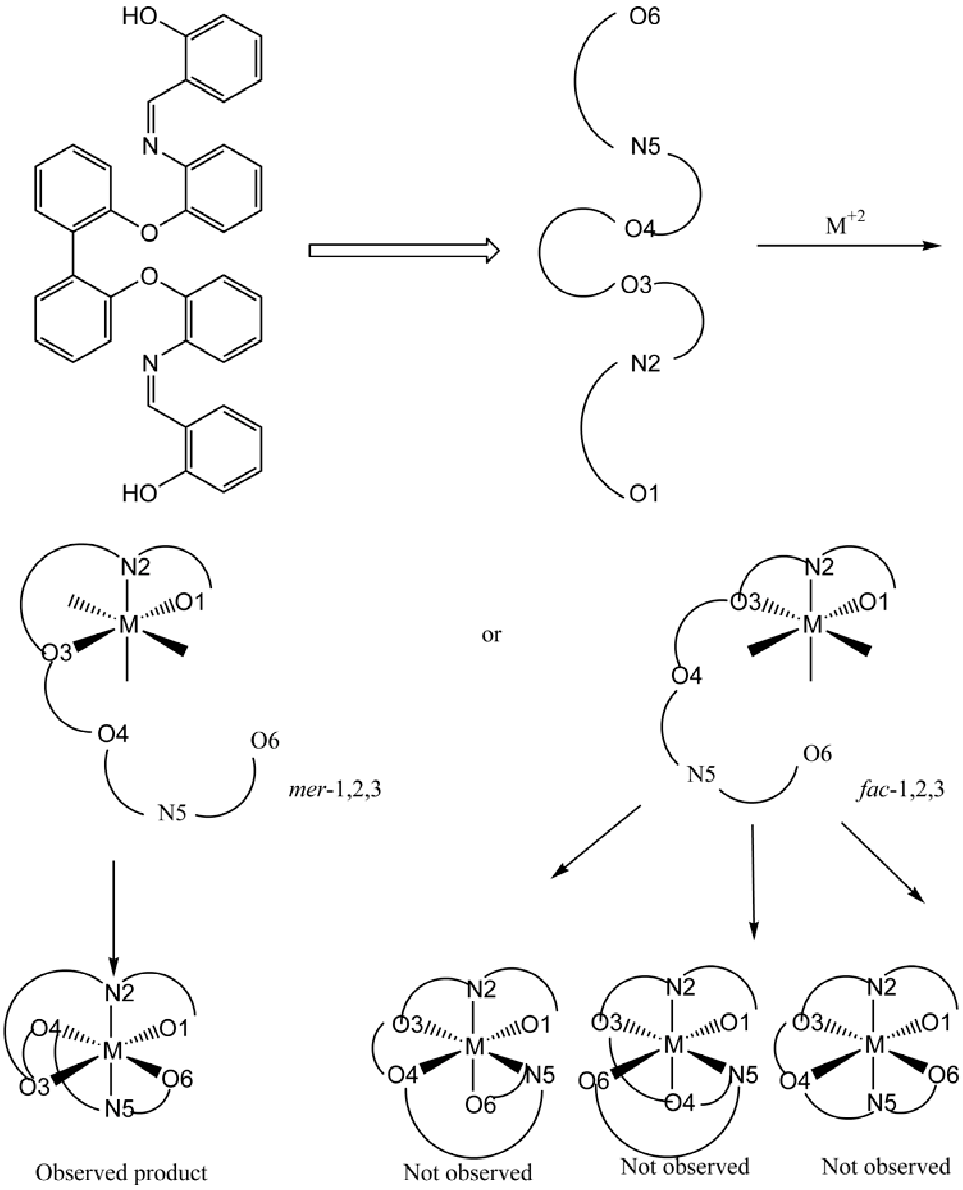


Figure 2.5. Possible binding geometries for Salbip and Salbin.

Using commercially available Mn(III) Jacobsen's catalyst, it is possible to obtain high *ee's* for the epoxidation of many *cis* olefins. However, a pyridine-*N*-oxide derivative (or other additive) is required, usually with a 25 mol% loading relative to the olefin substrate. Jacobsen asserts that this additive acts as an axial ligand to the manganese center.[15,26] Our initial hope that the ethereal oxygen atoms of **2-4** or **2-8** may supplant this additive was not realized; an additive is indeed required to obtain reasonable catalytic activity. The ether oxygen atom, along with its persistence by chelation, does not mimic the net electronic effects of the pyridine-*N*-oxide additive.

The octahedral manganese complex **2-4**-Mn catalyzes the epoxidation of various olefins under the standard conditions used by Jacobsen[15] with 5 mol% catalyst loading (Scheme 2.3). The results are listed in Table 2.1. Overall, the performance of the achiral catalyst **2-4-Mn** is comparable to other salen-manganese complexes with regard to turnover numbers and rates.[15,26,29]

Scheme 2.3. Catalytic epoxidation of olefins with [Mn] = **4-Mn**, **8-Mn**, or **9-Mn**

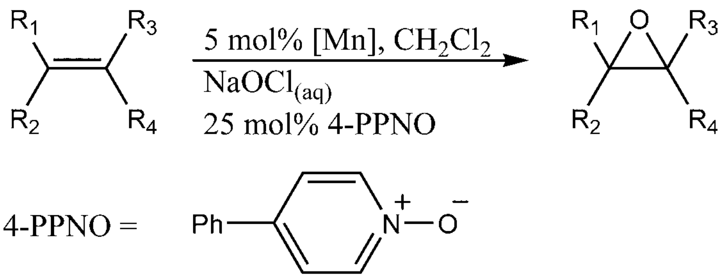
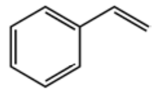
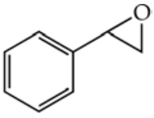
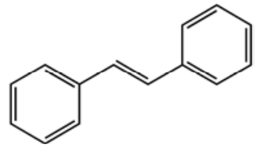
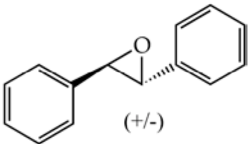
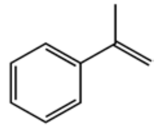
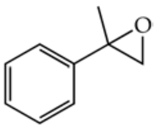
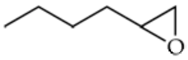
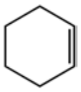
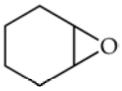


Table 2.2. Substrates, epoxidation products, and isolated yields for catalyst **2-4-Mn**

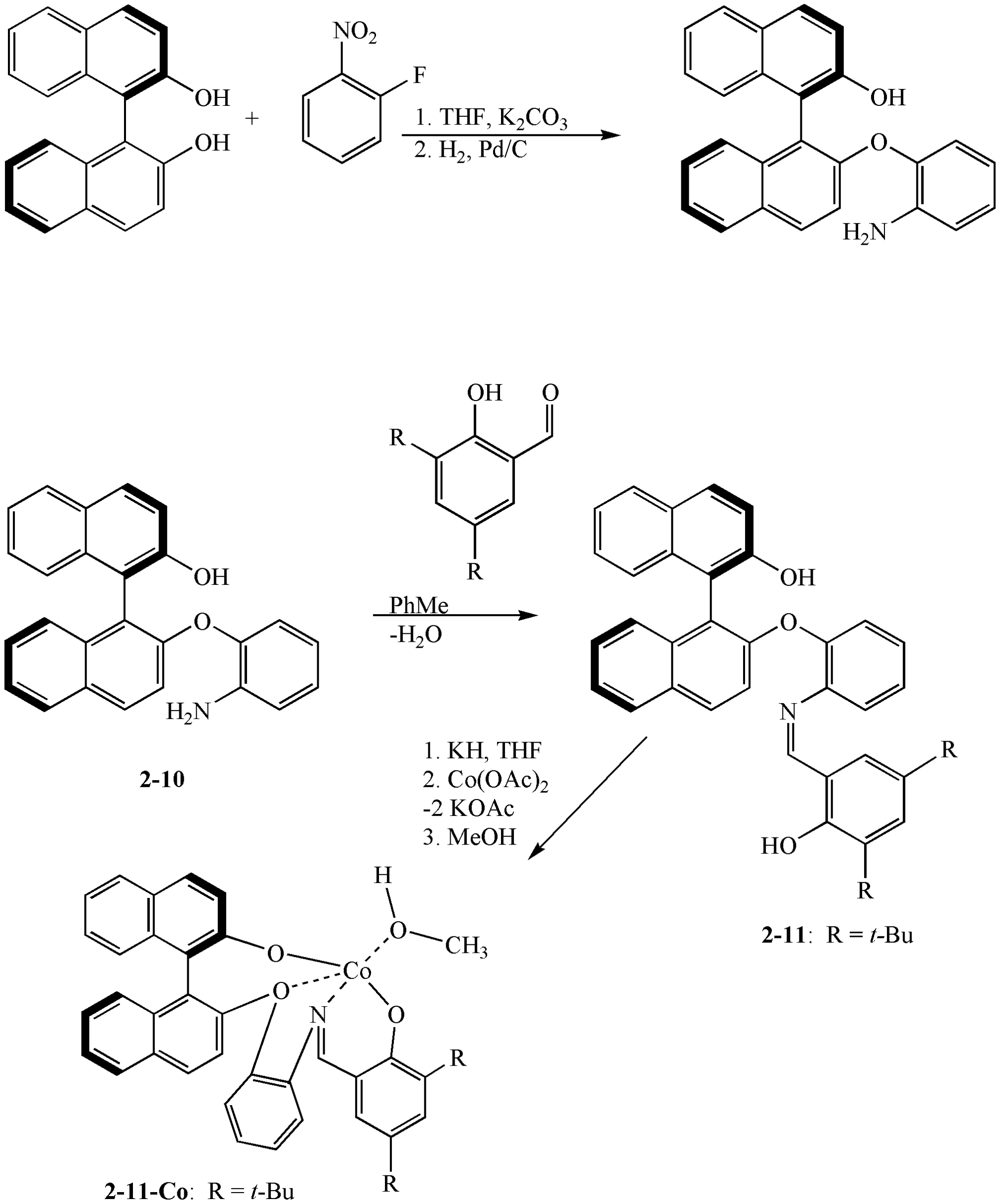
Olefin	Epoxide	Yield (%)
		83%
		56%
		78%
		85%
		77%

Encouraged by the results with racemic **2-4-Mn**, we sought to employ our chiral manganese complexes to obtain enantiomerically enriched epoxides (also under the standard conditions outlined in Scheme 2.3). (*R*)-binaphthol-based complex **2-8-Mn** is capable of epoxidizing olefins with an activity comparable to that of **2-4-Mn**. Unfortunately, the *ee* for the epoxidation of styrene is quite low at 11%. Thus, we turned to the *tert*-butylated complex **2-9**-Mn in the pursuit of higher *ee*'s. Complex **2-9-Mn** is capable of epoxidizing olefins; however, the activity is lower. In order to obtain complete conversion of styrene to styrene oxide, 10 mol% catalyst loading was required. Furthermore, the addition of *tert*-butyl groups to the catalyst only increased the *ee* in the case of styrene oxide to 22%. In the epoxidation of *trans*-stilbene, the reaction does not reach completion even with 10% catalyst loading. The GC yield of epoxide is only 15% and the *ee* is only 18%.

The initial testing of **2-4-Co**, **2-8-Co**, and **2-9-Co** for the hydrolytic kinetic resolution of racemic epoxides[53] was unfruitful. This is not wholly unexpected because the ethereal oxygen atoms (Figure 2.1, Figure 2.2, O(3) and O(4)) seemingly prevent the creation of an open coordination site, a prerequisite for coordination and activation of the epoxide substrate.

Our hypothesis was that the chirality of the ligand was not close enough to the metal in order to effect enantioselectivity. In order to synthesize a complex that had the binaphthol rings closer to the metal center, we synthesized an unsymmetrical version of our ligand by reacting one equivalent of 2-fluoronitrobenzene with one equivalent of binaphthol. Reduction using palladium on carbon and hydrogen gave compound **2-10**. Subsequent reaction with a salicylaldehyde resulted in the formation of ligand **2-11** (Scheme 2.4). The synthesis of the ligand is accomplished in only 21% overall yield from binaphthol, due to modest selectivity in the first step. However, **2-10** can be separated easily from any unreacted binaphthol and any amounts compound **2-5** formed during the reaction by taking advantage of the desired compound's high solubility in methanol. Since the ligand was difficult to synthesize, we decided to focus our efforts on the manganese and cobalt complexes of this ligand. This ligands can be easily coordinated to cobalt or manganese using the usual route. Single crystals of **2-11-Co** were obtained from methanol. The geometry of the cobalt complex **2-11-Co** is distorted trignal bipyramidal with a molecule of methanol occupying the fifth coordination site on the cobalt atom (Figure 2.6). There are many some similarities between this complex and the semetrical salbip and salbin cobalt complexes **2-4-Co** and **2-8-Co**. For example the Co-ether oxygen distance in **2-11-Co** is 2.40 Å compared to average Co-ether oxygen distances of 2.24 Å in **2-4-Co** and 2.28 Å in **2-8-Co**. Crystallographic data for **2-11-Co** are given in appendix A. Unfortunately this compound crystallized in a non-chiral space group. This means that either the compound was racemized during the course of one of the reactions in the sequence or that the crystal that formed contained the small amount of the opposite enantiomer derived from the small amount of *S*-binaphthol present in the starting material (99% *ee* starting material). Nevertheless, we tested both the manganese and cobalt compounds for epoxidation activity. Much to our surprise we found that the manganese complex **2-11-Mn** was completely inactive in the epoxidation of our test substrate, styrene. On the other hand, our cobalt complex, **2-11-Co**, showed high activity for the epoxidation of olefins under our standard reaction conditions. We did not observe any significant enantiomeric excess (~2%) in the resulting styrene oxide. Cobalt complexes that are capable of olefin epoxidation are rare[55,56] so we were surprised by these results since generally manganese complexes will epoxidize olefins and cobalt complexes usually will not.

Scheme 2.4. Synthesis of an unsymmetrical ligand derived from binaphthol



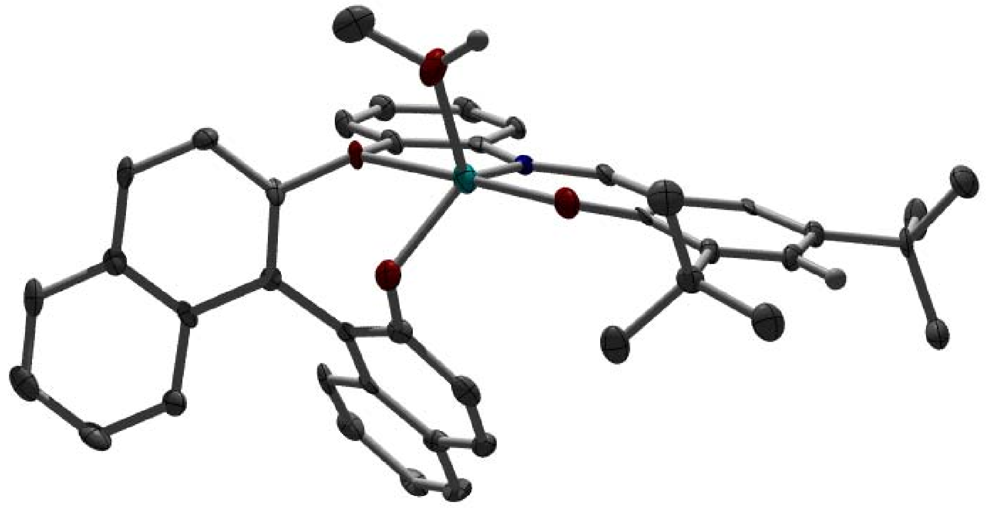


Figure 2.6. X-ray structure of **2-11-Co** with 50% probability ellipsoids and hydrogen atoms omitted for clarity (except MeOH).

CONCLUSIONS

Novel racemic and chiral expanded salen ligands were synthesized and readily coordinated to Mn, Co, Ni, and Cu to yield complexes with unique structural motifs. Catalytically, the manganese-based complexes generally behaved comparably to their salen analogues for the epoxidation of olefins. While asymmetric induction was minimal with **2-8-Mn** and **2-9-Mn**, a variety of other asymmetric catalytic reactions could be explored using these readily synthesized and inexpensive transition metal complexes derived from chiral binaphthol.

The cobalt complex derived from the unsymmetrical version of our ligand shows activity for olefin epoxidation in the presence of commercial bleach, but ultimately does not yield large enantiomeric excesses. The corresponding manganese complex displays no catalytic activity for the epoxidation of olefins.

EXPERIMENTAL

General remarks

All air sensitive procedures were conducted under a purified atmosphere of nitrogen in a glove box or using standard Schlenk line techniques. Solvents were distilled under nitrogen using standard techniques. Manganese (II) acetate tetrahydrate (Acros, 99+%), cobalt (II) acetate tetrahydrate (Acros, 99+%), nickel (II) acetate tetrahydrate (Acros, 99+%), and copper (II) acetate tetrahydrate (Acros, 99+%), were each dehydrated by heating under dynamic vacuum at 150°C for 3 hours. The anhydrous materials were stored in a dry box under nitrogen. (*R*)-binaphthol was obtained from ABCR Chemical and 3,5-di-*tert*-butyl salicylaldehyde was obtained from Advanced Asymmetrics. All other reagents were used as received. All NMR chemical shifts are given in ppm and were recorded on a Mercury-300BB spectrometer (^{1}H, 299.91 MHz; ^{13}C {^{1}H} 75.41 MHz) using the solvent as an internal standard ($CDCl_3$ (or residual $CHCl_3$): ^{1}H 7.27 ppm; ^{13}C 77.0 ppm). Chiral phase gas chromatography was performed on an Agilent 6850 gas chromatograph with a 30 meter 3-*o*-trichloracetyl-2,6-di-*o*-pentyl β-cyclodextrin column. X-ray crystallographic data were obtained using a Bruker SMART 1000 three-circle diffractometer operating at 50 kV and 40mA, Mo Kα (λ = 0.71073 Å) with a graphite monochromator and a CCD-PXL-KAF2 detector or a

Bruker GADPS instrument operating at 40 kV and 40 mA, Cu Kα (λ = 1.54578 Å) with a graphite monochromator and a CCD-PXL-KAF2 detector.

Synthesis of 2,2'-bis-(2-nitrophenoxy)-biphenyl (2-1)

2,2'-biphenol (10.00 g, 53.7 mmol) and potassium carbonate (16.33 g, 118.2 mmol) were added to a 500 mL round bottom flask with THF (200 mL). The reaction was refluxed for 72 hours. Removal of the insoluble potassium salts by filtration, followed by removal of the THF by rotary evaporation and high vacuum gave the product as a white solid: 22.36 g (97.2%). Note: THF removal is not necessary as it is a suitable solvent for the next reaction. ^{1}H NMR ($CDCl_3$): δ 6.85 (d, *J*=8.4 Hz, 2H, Ar*H*), 6.97 (d, *J*=9.3 Hz, 2H, Ar*H*), 7.05 (t, *J*=6.3 Hz, 2H, Ar*H*), 7.19 (t, *J*=6.9 Hz, 2H, Ar*H*), 7.26-7.39 (m, 4H, Ar*H*), 7.45 (d, *J*=6.8 Hz, 2H, Ar*H*), 7.80 (d, *J*=4.1 Hz, 2H, Ar*H*). ^{13}C {^{1}H} NMR ($CDCl_3$) δ 119.8, 122.7, 125.0, 125.8, 129.3, 129.8, 132.7, 135.4, 137.5, 140.7, 151.8, 152.7. TOF MS/ESI: *m/z* 429 $(M+H)^+$.

Synthesis of 2,2'-bis-(2-aminophenoxy)-biphenyl (2-2)

A solution of **2-1** (10.00 g, 23.3 mmol) in THF (200 mL) was placed into a hydrogenation vessel with 10% Pd/C (0.25 g) and one drop of concentrated sulfuric acid. The vessel was purged for several minutes with hydrogen and then pressurized to 40 psi. The slurry was stirred for 8 hours at room temperature. The pressure was released and the solution was then filtered to remove the palladium catalyst. Removal of the solvent by rotary evaporation and high vacuum gave the product as an off-white solid which was sufficiently pure for characterization and further use: 8.55 g (99.6%) ^{1}H NMR ($CDCl_3$): δ 3.749 (broad, 4H, N*H*), 6.66 (t, *J*=7.2 Hz, 2H, Ar*H*), 6.75 (m, 4H, Ar*H*), 6.87 (d, *J*=7.8 Hz, 2H, Ar*H*), 6.95 (t, *J*=7.8 Hz, 2H, Ar*H*), 7.12 (t, *J*=7.5 Hz, 2H, Ar*H*), 7.25 (t, *J*=7.5 Hz, 2H, Ar*H*), 7.40 (d, *J*=7.2 Hz, Ar*H*). ^{13}C {^{1}H} NMR ($CDCl_3$) δ 115.5, 116.6, 118.8, 121.4, 122.6, 125.4, 128.6, 129.2, 132.0, 139.3, 142.7, 155.3. TOF MS/ESI: *m/z* 369 $(M+H)^+$.

Synthesis of salbipH_2 (2-3)

A quantity of **2-2** (10.00 g, 25.9 mmol) was added to a round bottom flask with methanol (250 mL). Salicylaldehyde (6.32 g, 51.8 mmol) was added to the flask. A yellow precipitate formed almost instantly. The slurry was stirred for 3 hours to ensure reaction completion. The slurry was then cooled in an ice bath. The solid was collected by filtration and washed with cold methanol (3 x 100 mL). The yellow power was dried by vacuum: 14.1 g (91.6%). ^{1}H NMR ($CDCl_3$): δ –1.95 (s, 2H, O*H*), 6.78 (d, *J*=9.6 Hz, 2H, Ar*H*), 6.85-6.94 (m, 6H, Ar*H*), 7.00-7.13 (m, 8H, Ar*H*), 7.20-7.35 (m, 6H, Ar*H*), 7.45 (d, *J*=7.8 Hz, 2H, Ar*H*), 8.47 (s, 2H, Ar-N=C*H*-Ar). ^{13}C {^{1}H} NMR ($CDCl_3$) δ 117.5, 118.0, 118.9, 119.5, 120.2, 121.4, 123.5, 124.0, 127.7, 129.1, 129.2, 132.5, 132.6, 133.2, 139.8, 149.8, 154.4, 161.5, 164.1. TOF MS/ESI: *m/z* 577 $(M+H)^+$.

Typical procedure for the metallation of ligand 2-3 (2-4-Mn, 2- 4-Co, 2-4-Ni, 2-4-Cu)

A quantity of **2-3** (1.00 g, 1.7 mmol) and sodium methoxide (0.18 g, 3.3 mmol) were placed into a swivel frit. The vessel was evacuated and dry, degassed ethanol (~40 mL) was vacuum transferred into the frit. The solution was warmed to 50°C for 4 hours. All solvent was removed by vacuum. The frit was brought into the glove box and anhydrous $M(OAc)_2$ (1.8 mmol) was added. Ethanol (~30 mL) was vacuum transferred into the frit. The reaction was heated to 50°C for 4 hours during which time a precipitate formed. This precipitate was filtered, washed with ethanol and dried under vacuum.

Synthesis of salbipMn (2-4-Mn)

M = Mn: red-orange micro crystals, 0.87 g (79.9%). Crystals (needles) for X-ray diffraction were grown by cooling a saturated dichloromethane solution to –35°C.

Synthesis of salbipCo (2-4-Co)

M = Co: red micro crystals, 0.94 g (85.8%). Crystals (needles) for X-ray diffraction were grown by cooling a saturated dichloromethane solution to –35°C.

Synthesis of salbipNi (2-4-Ni)

M = Ni: yellow powder, 0.62 g (56.6%). Crystals (needles) for X-ray diffraction were grown by cooling a saturated dichloromethane solution to –35°C.

Synthesis of salbipCu (2-4-Cu)

M = Cu: green-brown micro crystals, 0.79 g (71.8%). Crystals (needles) for X-ray diffraction were grown by cooling a saturated dichloromethane solution to –35°C.

Synthesis of (R)-2,2'-bis-(2-nitrophenoxy)-[1,1']binaphthalenyl (2-5)

R-binaphthol (10.00 g, 34.9 mmol) and potassium carbonate (10.14 g, 73.3 mmol) were dissolved in DMF (120 mL). 2-fluoronitrobenzene (9.85 g, 69.8 mmol) was added to the solution. The obtained solution was stirred at 80°C for 6 hours and then poured over ice water (250 mL). A white precipitate formed immediately. The white precipitate was collected by filtration, washed with hot water (3 x 50 mL) and dried under vacuum: 18.0 g (97.8%) ^{1}H NMR ($CDCl_3$): δ 7.00-7.04 (m, 4H, Ar*H*), 7.23 (d, *J*=9.0 Hz, 2H, Ar*H*), 7.21-7.37 (m, 6H, Ar*H*), 7.44 (t, *J*=6.2 Hz, 2H, Ar*H*), 7.72 (d, *J*=8.4 Hz, 2H, Ar*H*), 7.89 (d, *J*=8.1 Hz, 2H, Ar*H*), 7.941 (d, *J*=9.0 Hz, 2H, Ar*H*). ^{13}C {^{1}H} NMR ($CDCl_3$) δ 119.1, 120.7, 122.4, 122.9, 125.5, 125.8, 126.1, 127.3, 128.3, 130.8, 131.1, 134.1, 134.3, 141.0, 150.8, 151.2. TOF MS/ESI: *m/z* 529 $(M+H)^+$.

Synthesis of (R)-2,2'-bis-(2-aminophenoxy)-[1,1']binaphthalenyl (2-6)

A quantity of **2-5** (10.00 g, 18.9mmol) was dissolved in THF (200 mL) and the solution was added to a hydrogenation vessel containing 10% Pd/C (0.25 g). One drop of concentrated sulfuric acid was added. The vessel was flushed for several minutes with hydrogen and then pressurized to 40 psi. The slurry was stirred for 8 hours at room temperature. The pressure was released and the solution was then filtered to remove the palladium catalyst. Removal of the solvent by rotary evaporation and high vacuum gave the product was an off-white solid, which was sufficiently pure for characterization and further use (14.83 g, 90.6%): ^{1}H NMR ($CDCl_3$): δ 3.55 (broad, 4H, N*H*), 6.61 (t, *J*= 8.7 Hz, 2H, Ar*H*), 6.66 (d, *J*=6.6 Hz, 2H, Ar*H*), 6.82 (d, J=7.8 Hz, 2H, Ar*H*), 6.90 (t, *J*=7.5 Hz, 2H, Ar*H*), 7.20 (d, *J*=9.0 Hz, 2H, Ar*H*), 7.31-7.43 (m, 6H, Ar*H*), 7.87-7.91 (m, 4H, Ar*H*). ^{13}C {^{1}H} NMR ($CDCl_3$) δ 116.4, 117.5, 118.7, 120.6, 120.7, 124.7, 124.9, 125.6, 127.0, 128.5, 130.0, 130.5, 134.4, 138.9, 143.5, 153.0. TOF MS/ESI: *m/z* 469 $(M+H)^+$.

Synthesis of salbinH$_2$ (2-7a)

A quantity of **2-6** (10.00 g, 21.3 mmol) was dissolved in toluene (200 mL) in a round bottom flask with a few crystals of *p*-toluenesulfonic acid (0.05 g). Salicylaldehyde (5.21 g, 42.7 mmol) was added and a Dean-Stark trap was attached. The solution was refluxed for 3 hours during which time approximately 0.75 mL of water were collected. The toluene was then removed by rotary evaporation followed by high vacuum to give a yellow glass: 13.69 g (98.4%). This glass was sufficiently pure for characterization and further use. A powder could be obtained by adding 100 mL of methanol to the glass and stirring the slurry for 2 hours. ^{1}H NMR ($CDCl_3$): δ –2.24 (s, 2H, O*H*), 6.706-6.821 (m, 6H, Ar*H*), 6.890-7.11 (m, 10H, Ar*H*), 7.19-7.35 (m, 8H, Ar*H*), 7.85-7.95 (m, 4H, Ar*H*), 8.17 (s, 2H, Ar-N=C*H*-Ar). ^{13}C {^{1}H} NMR ($CDCl_3$) δ 117.2, 118.3, 118.8, 119.4, 120.3, 123.0, 124.1, 124.9, 125.8, 125.9, 127.1, 127.3, 128.2, 130.1, 130.5, 132.7, 133.1, 134.4, 140.0, 149.2, 152.1, 161.2, 165.4. TOF MS/ESI: *m/z* 677 $(M+H)^+$.

Synthesis of salbin(*t*-Bu)$_4$H$_2$ (2-7b)

A quantity of **2-6** (10.00 g, 21.3 mmol) was dissolved in toluene (200 mL) in a round bottom flask with a few crystals of *p*-toluenesulfonic acid (0.05 g). 3,5-di-*tert*-butyl salicylaldehyde (10.00 g, 42.7 mmol) was added and a Dean-Stark trap was attached. The solution was refluxed for 3 hours during which time approximately 0.75 mL of water were collected. The toluene was then removed by rotary evaporation followed by high vacuum to give a yellow glass: 27.32 g (93.5%). This glass was sufficiently pure for characterization and further use. A powder could be obtained by adding 100 mL of methanol to the glass and stirring the slurry for 2 hours. ^{1}H NMR ($CDCl_3$): δ –1.99 (s, 2H, O*H*), 1.26 (s, 18H, Ar-C(CH_3)$_3$), 1.32 (s, 18H, Ar-C(CH_3)$_3$), 6.74 (t, *J*=6.9 Hz, 2H, Ar*H*), 6.82 (d, *J*=8.1 Hz, 2H, Ar*H*), 6.89-6.99 (m, 6H, Ar*H*), 7.17-7.28 (m, 6H, Ar*H*), 7.39 (d, *J*=2.7 Hz, 2H, Ar*H*), 7.80 (d, *J*=8.1 Hz, 2H, Ar*H*), 7.88 (d, *J*=9.0 Hz, 2H, Ar*H*), 8.25 (s, 2H, Ar-N=C*H*-Ar). ^{13}C {^{1}H} NMR ($CDCl_3$) δ 29.5, 31.8, 34.4, 35.2, 118.6, 120.3, 121.6, 122.0, 123.9, 124.6, 126.1, 126.6, 127.0, 127.2, 127.9, 128.0, 128.5, 129.9, 130.6, 134.4, 137.1, 140.3, 140.5, 149.6, 152.5, 158.3, 165.5. TOF MS/ESI: *m/z* 901 $(M+H)^+$.

Typical procedure for the metallation of ligand (2-7a) or (2-7b)

The ligand **2-7a** or **2-7b** (2.2 mmol) was placed into a swivel frit with potassium hydride (0.18 g, 4.4 mmol) under an atmosphere of nitrogen. THF (~40 mL) was transferred into the swivel frit. The reaction was stirred for 2 hours at room temperature open to a bubbler during which time the color changed from yellow to red-orange. The THF was removed under high vacuum. The frit was brought into the glove box and anhydrous $M(OAc)_2$ (2.3 mmol) was added. THF (~40 mL) was transferred into the swivel frit. The reaction was stirred at 50°C for 6 hours. The THF was removed by vacuum and toluene (~40 mL) was transferred into the frit. The solution was filtered to remove the potassium acetate salt. The salt cake was washed several times with toluene to extract the product. The volume of toluene was reduced to 10 mL and the solution was allowed to stand until precipitate formed. The precipitate was collected by filtration and dried under high vacuum.

Synthesis of salbinMn (2-8-Mn)

M = Mn: red-orange powder, 1.78 g (82.5%).

Synthesis of salbinCo (2-8-Co)

M = Co: red powder, 1.24 g (77.1%). Crystals (needles) for X-ray diffraction were grown by cooling a saturated ethyl acetate solution to –35°C.

Synthesis of salbinNi (2-8-Ni)

M = Ni: yellow powder, 1.41 g (87.2%).

Synthesis of salbinCu (2-8-Cu)

M = Cu: green-brown micro crystals, 1.90 g (87.1%). Crystals (needles) for X-ray diffraction were grown by cooling a saturated dichloromethane solution to –35°C.

Synthesis of salbin(*t*-Bu)$_4$Mn (2-9-Mn)

M = Mn: red-orange powder, 1.83 g (84.0%).

Synthesis of salbin(*t*-Bu)$_4$Co (2-9-Co)

M = Co: red powder, 1.33 g (62.1%).

Synthesis of salbin(*t*-Bu)$_4$Ni (2-9-Ni)

M = Ni: yellow powder, 1.98 g (90.9%).

Synthesis of salbin(*t*-Bu)$_4$Cu (2-9-Cu)

M = Cu: green-brown micro crystals, 1.49 g (68.4%). Crystals (needles) for X-ray diffraction were grown by cooling a saturated dichloromethane solution to –35°C.

Synthesis of ligand 2-11

R-binaphthol (10.00 g, 34.9 mmol) and potassium carbonate (10.14 g, 73.3 mmol) were dissolved in THF (200 mL). 2-fluoronitrobenzene (4.93 g, 34.9 mmol) was added to the solution. The obtained solution was stirred at reflux for 24 hours and then the insoluble potassium salts were filtered off. The THF solution was placed in a hydrogenation vessel with 10% Pd/C (0.25 g) and 1 drop of concentrated sulfuric acid and the vessel was flushed with hydrogen for several minutes. The vessel was flushed for several minutes with hydrogen and then pressurized to 40 psi. The slurry was stirred for 8 hours at room temperature. The pressure was released and the solution was then filtered to remove the palladium catalyst. Removal of the solvent by rotary evaporation and high vacuum gave the product was an off-white glass. Methanol (100 mL) was added to this glass and it was allowed to stand in an ice bath. The solid that formed was filtered off and discarded. The mother liquor was placed in a round-bottom flask and the solvent was removed by rotary evaporation. Removal of the residual methanol by high vacuum gave an off-white glass which contained mostly **2-10**. To this glass was added 1 equivalent of 3,5-di-*t*-butylsalicylaldehyde. Toluene (100 mL) was added, and a few crystals of *p*-toluenesulfonic acid (0.05 g). A Dean-Stark trap was attached and the solution was refluxed for 3 hours during which time water was collected. The toluene was then removed by rotary evaporation followed by high vacuum to give a yellow glass. This yellow glass could be crystallized from ethyl acetate to give the product. ^{1}H NMR ($CDCl_3$): δ 1.13 (s, 9H), 1.33 (s, 9H), 5.07 (s, broad, 2H), 7.00-7.45 (m, 10H), 7.78-7.87 (m, 2H), 7.91-8.04 (m, 6H), 8.49 (s, 1H). TOF MS/ESI: *m/z* 594 $(M+H)^+$.

Synthesis of 2-11-Co

The ligand **2-11** (2.2 mmol) was placed into a swivel frit with potassium hydride (0.18 g, 4.4 mmol) under an atmosphere of nitrogen. THF (~40 mL) was transferred into the swivel frit. The reaction was stirred for 2 hours at room temperature open to a bubbler during which time the color changed from yellow to red-orange. The THF was removed under high vacuum. The frit was brought into the glove box and anhydrous $Co(OAc)_2$ (2.3 mmol) was added. THF (~40 mL) was transferred into the swivel frit. The reaction was stirred at 50°C for 6 hours. The THF was removed by vacuum and toluene (~40 mL) was transferred into the frit. The solution was filtered to remove the potassium acetate salt. The salt cake was washed several times with toluene to extract the product. The volume of toluene was reduced to 10 mL and the solution was allowed to stand until precipitate formed. The precipitate was collected by filtration and dried under high vacuum.

Typical procedure for epoxidation of olefins with 2-4-Mn, 2- 8-Mn, 2-9-Mn or 2-11-Co

An olefin (9.6 mmol), 4-phenylpyridine-*N*-oxide (0.41 g, 2.4 mmol), the manganese catalyst **2-4-Mn**, **2-8-Mn**, **2-9-Mn** or **2-11-Co** (0.48 mmol), and dichloromethane (30 mL) were placed into a round bottom flask. This solution was cooled to 0°C in an ice bath. Commercial bleach (*circa* 5% aqueous NaOCl, 100 mL) was cooled to 0°C in an ice bath and added in one portion to the flask. The reaction was stirred for 3 hours at 0°C and then allowed to stir for 3 hours at room temperature. The reaction was transferred into a separatory funnel with 100 mL of diethyl ether. The organic layer was removed and set aside. The aqueous layer was extracted with diethyl ether (2 x 50 mL). The combined organic extracts were washed with water (2 x 20 mL) and brine (10 mL). The organic layer was then dried over anhydrous magnesium sulfate and filtered. Removal of the ether by rotary evaporation gave the crude product. The product was purified by fractional distillation. Isolated yields for catalyst **2-4-Mn** are given in Table 2.3. When applicable, the enantiomeric excess of the epoxide was determined by chiral phase GC.

CHAPTER III

EPOXIDATIONS USING NICKEL OXIDE HYDROXIDE

SYNOPSIS

Nickel oxide hydroxide nanoparticles were prepared by precipitation upon reacting various nickel (II) solutions with commercial bleach. We isolated this material and characterized it by XRD, DSC/TGA, and TEM. This material, either prepared *in situ* or isolated, is an active heterogeneous catalyst for the epoxidation of several α,β-unsaturated carboxylic acids. This catalyst displays high reactivity and requires remarkably low catalyst loading (2.5 mol%) for the complete conversion of α,β-unsaturated carboxylic acids to products. This catalyst surpasses the activity of existing tungsten systems by 400-600%. Furthermore, this catalyst is inexpensive, environmentally benign, and readily prepared. The unusually high activity of this heterogeneous catalyst is due to its small particle size and thus high surface area. Larger particles of this material were prepared and found to have greatly diminished catalytic activity.

INTRODUCTION

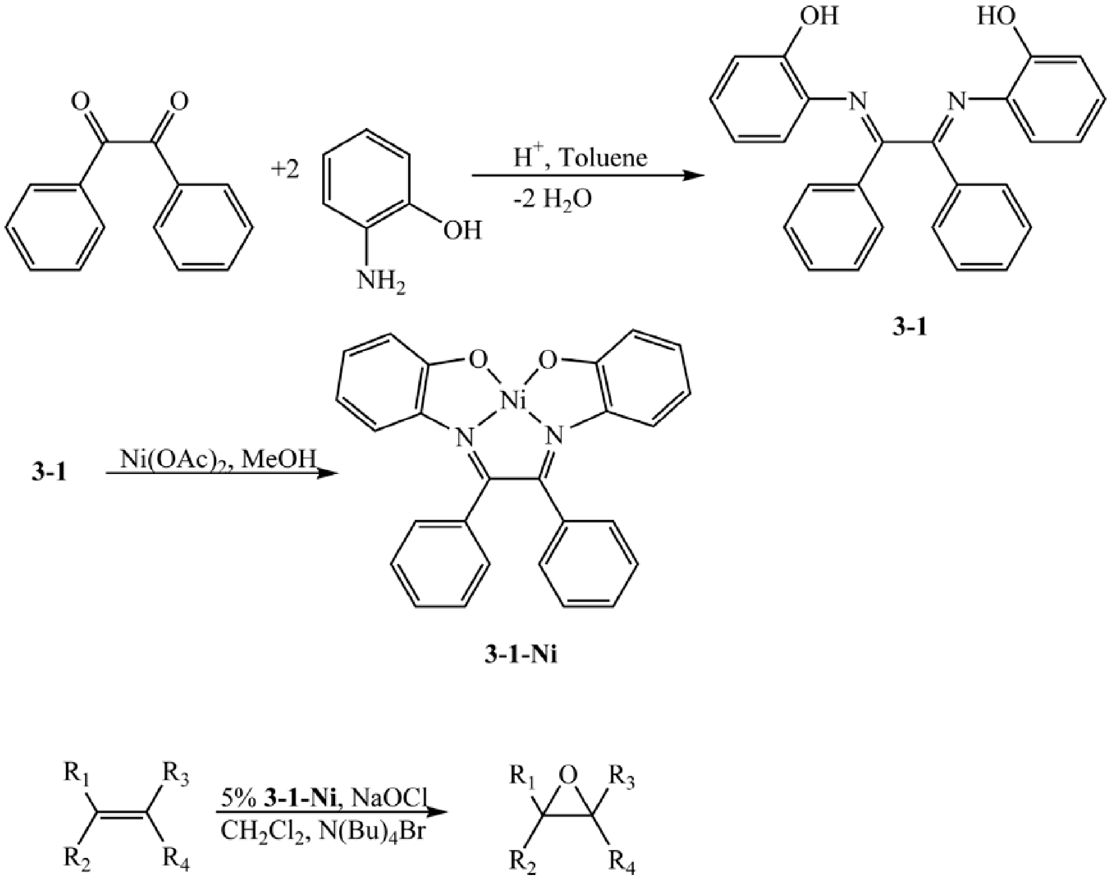
Nickel oxide hydroxide has been known to oxidize a host of organic molecules when used stiochiometrically.[48] Among the substrates that can be oxidized using nickel oxide hydroxide are alcohols, aldehydes, phenols, amines, and oximes. These reactions all use 1.5-2.0 equivalents of nickel and varied reaction conditions depending on the substrate. However, there are only two reports in the literature that use nickel catalytically with excess bleach.[57,58] The earliest report of a catalytic oxidation using these reaction conditions was in 1945 wherin Weijlard demonstrated the oxidation of nicotine and vitamin C using catalytic nickel and excess bleach.[57] Since that time, however, there has been surprisingly little work done with this system and the oxidations that were reported were generally limited to alcohols.

We discovered that this system is also capable of mediating the epoxidation of α,β-unsaturated carboxylic acids. This discovery was coincident with the investigation of a series of soluble nickel-salen catalysts for olefin epoxidation. We found that upon decomposition of these complexes and expulsion of the nickel (II) ion from the ligand, nickel oxide hydroxide is formed *in situ* and acts as a heterogeneous catalyst. The catalyst was characterized and found to consist of nanoparticles with an average diameter of approximately 4 nm by transition electron microscopy (TEM). This catalyst was also characterized by X-ray diffraction (XRD) and thermal gravimetric analysis/differential scanning calorimetry (TGA/DSC). A range of substrates was epoxidized with this catalyst and it was found to be far more active and cost effective when compared to an existing tungsten system.[3,4]

RESULTS AND DISCUSSION

Our work in this area began with the investigation of a nickel-salen complex (Scheme 3.1). We had become interested in using nickel as a catalytic route to olefin epoxidation since there were only a few reports of nickel-salen catalyzed epoxidations. We hypothesized that since nickel is a late transition metal, the nickel containing catalysts would be more tolerant of the electron deficient olefins, especially ones that contain oxygen. Among the scattered reports of nickel-salen catalyzed epoxidations, there were no reports wherein nickel was used to epoxidize an α,β-unsaturated carboxylic acid. Upon testing our nickel complex, **3-1-Ni**, we discovered that under our catalytic conditions, methacrylic acid could be epoxidized. This was somewhat surprising since most catalytic routes to epoxides do not work for highly electron deficient olefins such as α,β-unsaturated carboxylic acids.

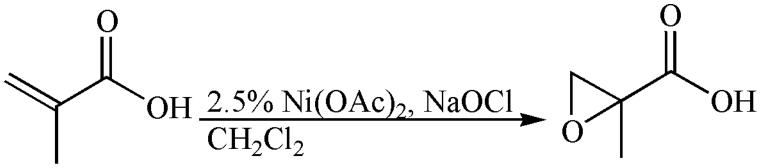
Scheme 3.1. Synthesis of 3-1-Ni and catalytic epoxidation



In 1988, Burrows et al. reported the use of similar salen-catalysts for olefin epoxidation, demonstrating that Ni-salen complexes were able to epoxidize a variety of electron rich olefins.[59] During the course of this reaction, Burrows and coworkers noticed a black precipitate forming. The precipitate was isolated, and identified as nickel oxide hydroxide. Burrows determined that this species was catalytically unimportant over the course of several experiments.[59,60] By isolating this precipitate, and combining it with an electron rich olefin, she observed that there was no reaction with any of the electron rich olefins subjected to epoxidation conditions.

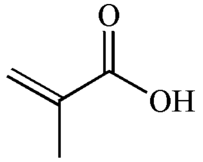
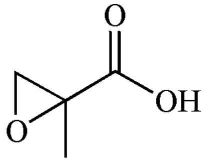
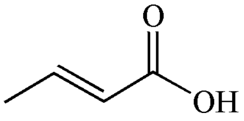
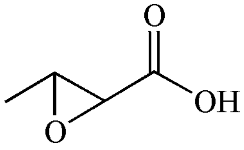
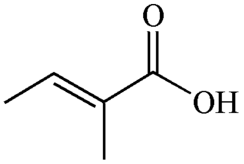
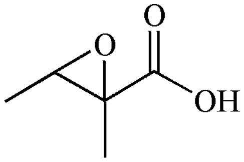
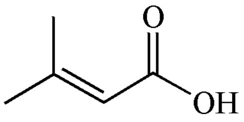
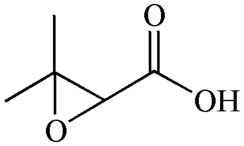
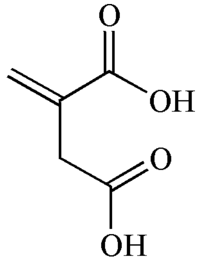
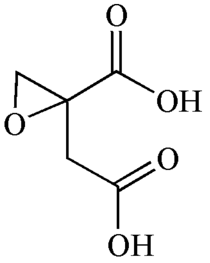
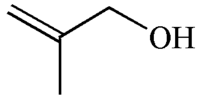
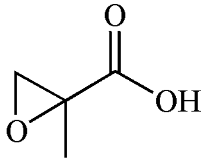
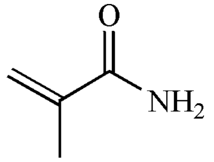
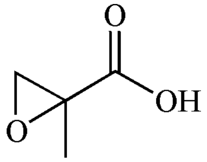
In order to support the hypothesis that the transition metal complex is important for catalytic activity, a control experiment using nickel acetate was called for (Scheme 3.2). Much to our surprise we observed the epoxidation of methacrylic acid with only 2.5% nickel acetate catalyst loading and excess bleach. This result seemed to refute the conclusions made by Burrows, who asserted the importance of the ligand to epoxidation. Further probing of this reaction demonstrated that several α,β-unsaturated carboxylic acids could be epoxidized by simply combining a water soluble nickel (II) source and bleach with the chosen olefin in dichloromethane (Table 3.1). Furthermore, primary amides were hydrolyzed under the reaction conditions. In the case of methacrylamide, the amide was hydrolyzed and the resulting carboxylic acid was epoxidized. Primary alcohols were also oxidized to carboxylic acids under the reaction conditions. In the case of β-methyl allylalcohol, the alcohol was oxidized to the acid and then epoxidized under the reaction conditions. However, ordinary olefins such as 1-hexene and styrene are not epoxidized by using nickel acetate as the catalyst. Since these substrates can be epoxidized by Burrows' catalyst, it is reasonable to conclude that styrene and 1-hexene are being oxidized through a different mechanism than the α,β-unsaturated carboxylic acids. Consistent with Burrows' conclusion, electron rich olefins require a Ni-salen complex to achieve epoxidation. However, with α,β-unsaturated carboxylic acids the salen ligand actually retards the reaction relative to using nickel acetate.

Scheme 3.2. Epoxidation of methacrylic acid



72% isolated yield
97.5% purity

Table 3.1. Epoxidation of olefins with catalytic nickel

Entry	substrate	product	yield (%)[b]
1			97
2			45
3			75
4			70
5			31
6			82
7			81

[a] Reaction conditions: 2.5 mol% NiOOH, CH_2Cl_2, aq. NaOCl, 1 eq. NaOH, 2 hours at 0°C then 2 hours at 25°C. [b] GC yield.

Since this reaction occurs without the use of a salen ligand, we sought to isolate and characterize the relevant catalyst in this reaction. If bleach is added to aqueous nickel acetate, a fine black precipitate is formed instantly. This material can be isolated through the use of a centrifuge and characterized by XRD, TGA/DSC and TEM. The

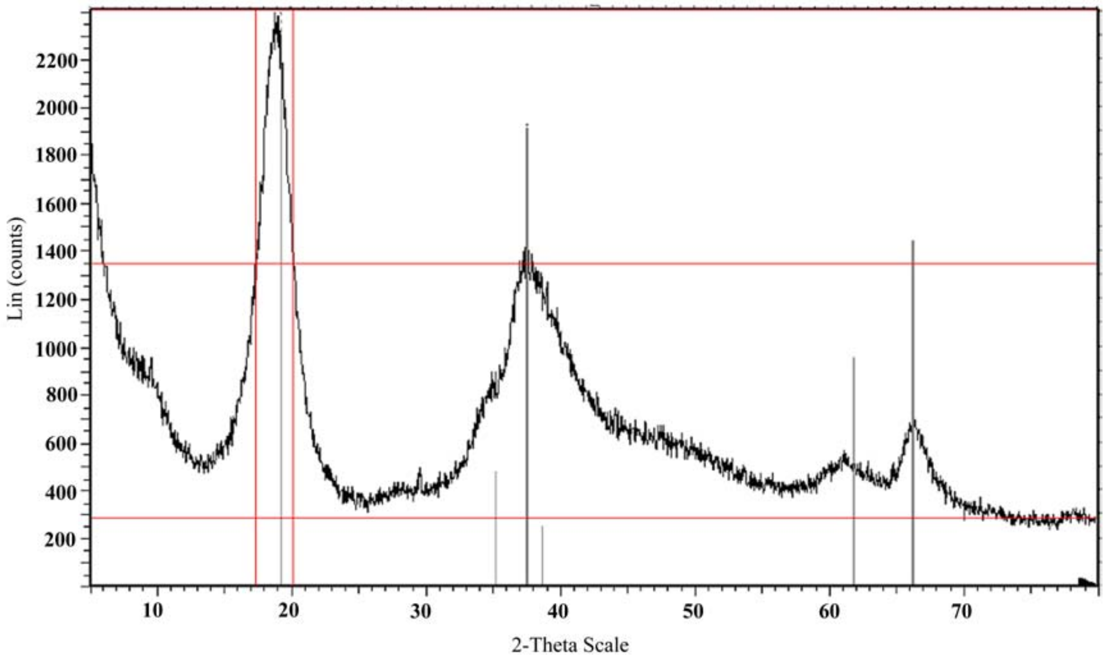


Figure 3.1. XRD spectrum of nickel oxide hydroxide catalyst.

$D = k\lambda/(\beta\cos\theta)$ (Equation 3.1)

D = average particle diameter, $k = 1.0$ (this shape constant can be approximated as 1.0, but can vary between 0.89 and 1.39), $\lambda = 1.5417$ Å (wavelength of radiation), $\beta = \Delta(2\theta) = ((20.1°-17.4°)/360°)*2\pi = 0.04712$ radians (peak width at half height), $\theta = 9.4°$ (the Bragg angle, $2\theta = 18.8°$), $D = 33.2$ Å ≈ 3.3 nm.

XRD was found to have extremely broad peaks which is usually indicative of a very small particle size (Figure 3.1). A Debye-Scherrer calculation, which estimates the particle sized based on this peak broadening, gave an average particle size of approximately 3.3 nm (Equation 3.1).[61]

Examination of the catalyst by TEM confirmed the dimensions of the catalyst particles as being approximately 3-5 nm in diameter (Figure 3.2). DSC/TGA analysis of this material showed the decomposition to nickel oxide (Figure 3.3). The nickel oxide was also characterized by XRD and TEM and was found to consist of very small particles (Figure 3.4, 3.5, Equation 3.2). We hypothesized that the small particle size was critical for good catalyst performance.

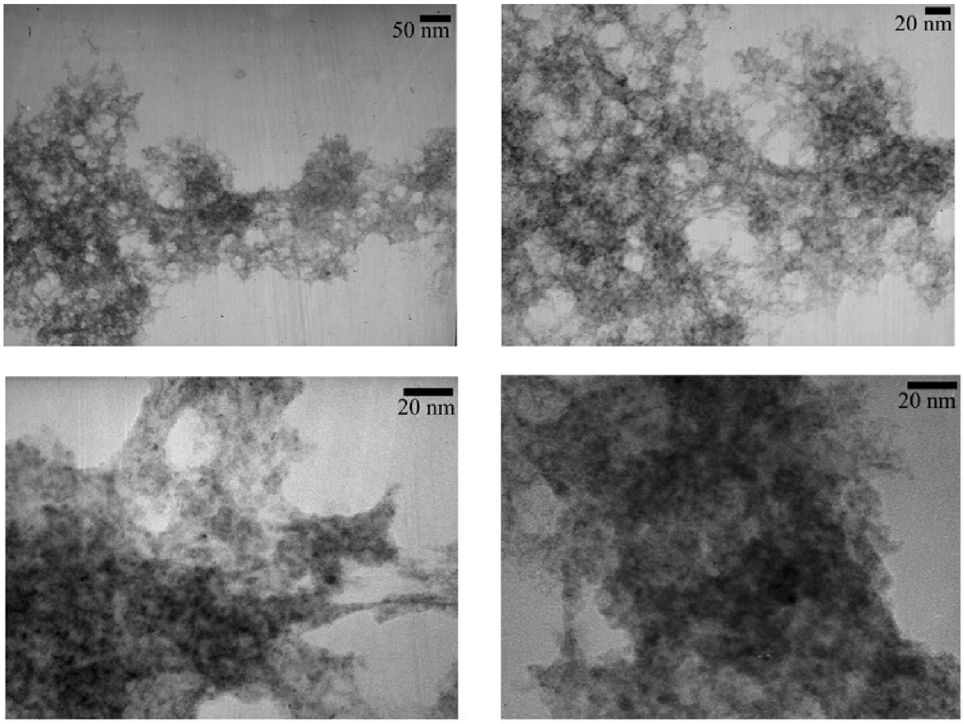


Figure 3.2. TEM images of nickel oxide hydroxide catalyst.

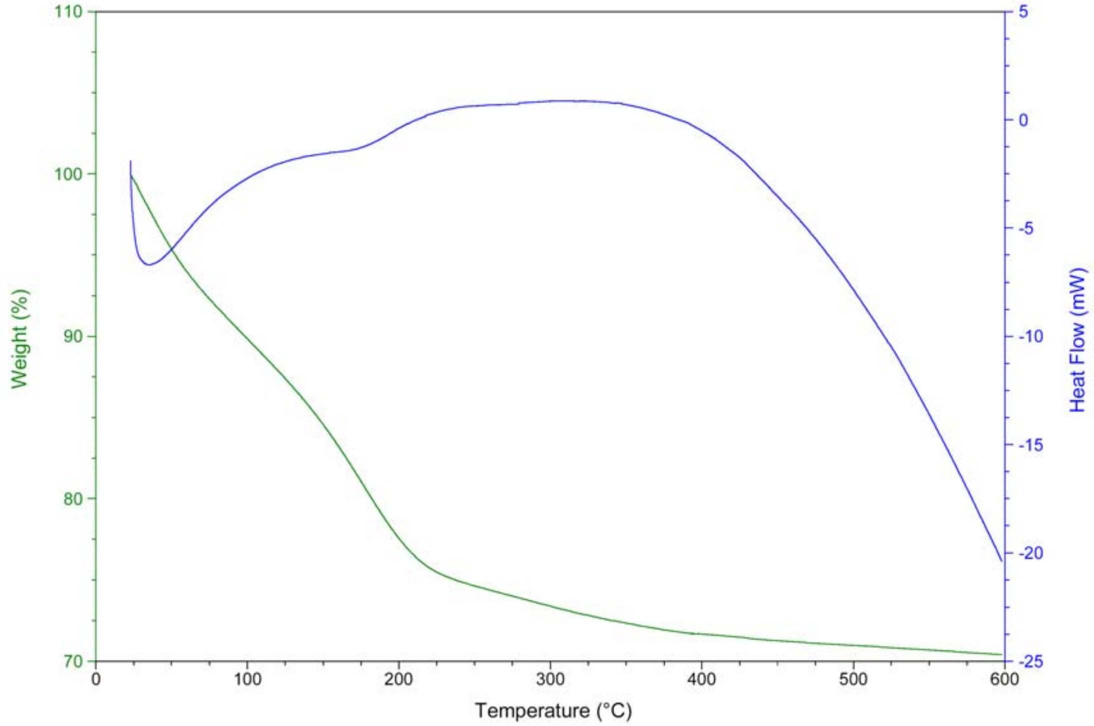


Figure 3.3. DSC/TGA data for nickel oxide hydroxide.

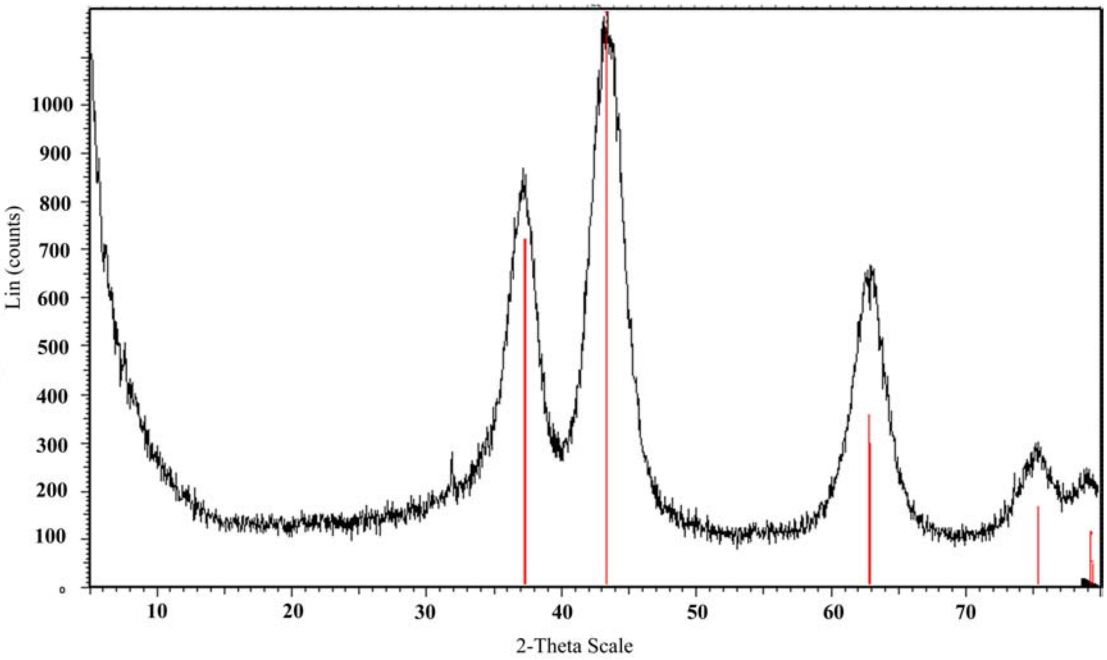


Figure 3.4. XRD spectrum of nickel oxide prepared from the decomposition of nickel oxide hydroxide.

$L = k\lambda/(B\cos\theta)$ (Equation 3.2)

L = average particle diameter, k = 1.0 (usually taken as unity), λ = 1.5417 Å (wavelength of radiation), B = (((64.3°-61.5°)/2)/360°)*2 = 0.02443 radians (peak width at half height), θ = 31.4° (the Bragg angle, usually the most isolated peak is chosen, 2θ = 62.8°), L = 73.9 Å ≈ 7.4 nm. For this calculation we assumed that line broadening due to the instrument was negligible.

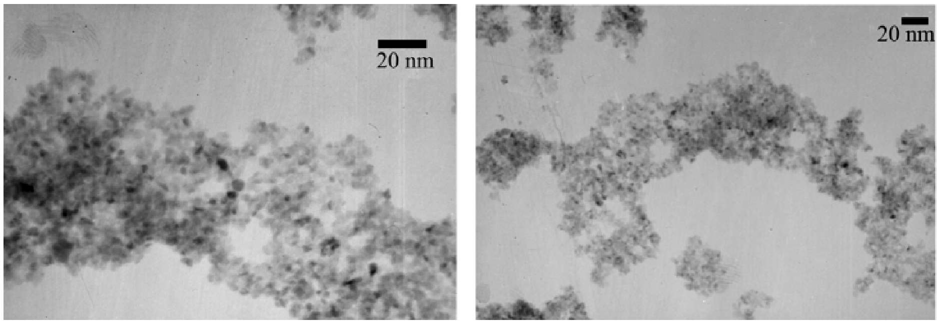


Figure 3.5. TEM images of nickel oxide particles derived from the decomposition of nickel oxide hydroxide.

One of the key features of this catalyst is its small particle size. In order to achieve good catalyst activity and selectivity, this seems to be a requirement. To demonstrate this fact, we tested nickel oxide hydroxide with a particle size of approximately 100 nm which was prepared independently according to a literature method.[62] Examination by TEM revealed crystallites of approximately 50-150 nm in diameter (Figure 3.6). We chose methacrylic acid as our test substrate and we compared several different samples of catalyst. The results are summarized in Table 3.2. We found that preisolated nickel oxide hydroxide is an effective epoxidation catalyst and that small particle size and good catalyst dispersion are critical for activity. This is not particularly surprising; however, it does support our claim that nickel oxide hydroxide is an important species in this reaction. Nickel hydroxide, a commercially available water insoluble nickel species, is a poor catalyst due to the fact that the particle size is approximately 100 nm in diameter and that it is oxidized to the active catalyst in a heterogeneous reaction that does not alter the particle size.

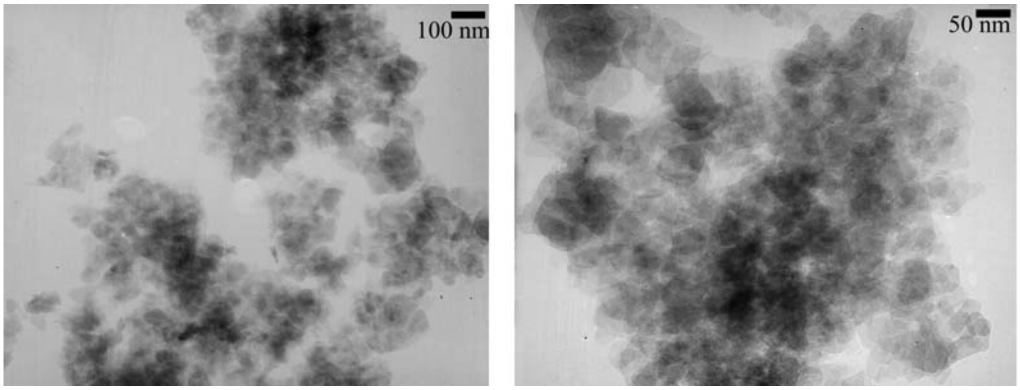


Figure 3.6. TEM images of nickel oxide hydroxide prepared from ozone and nickel hydroxide.

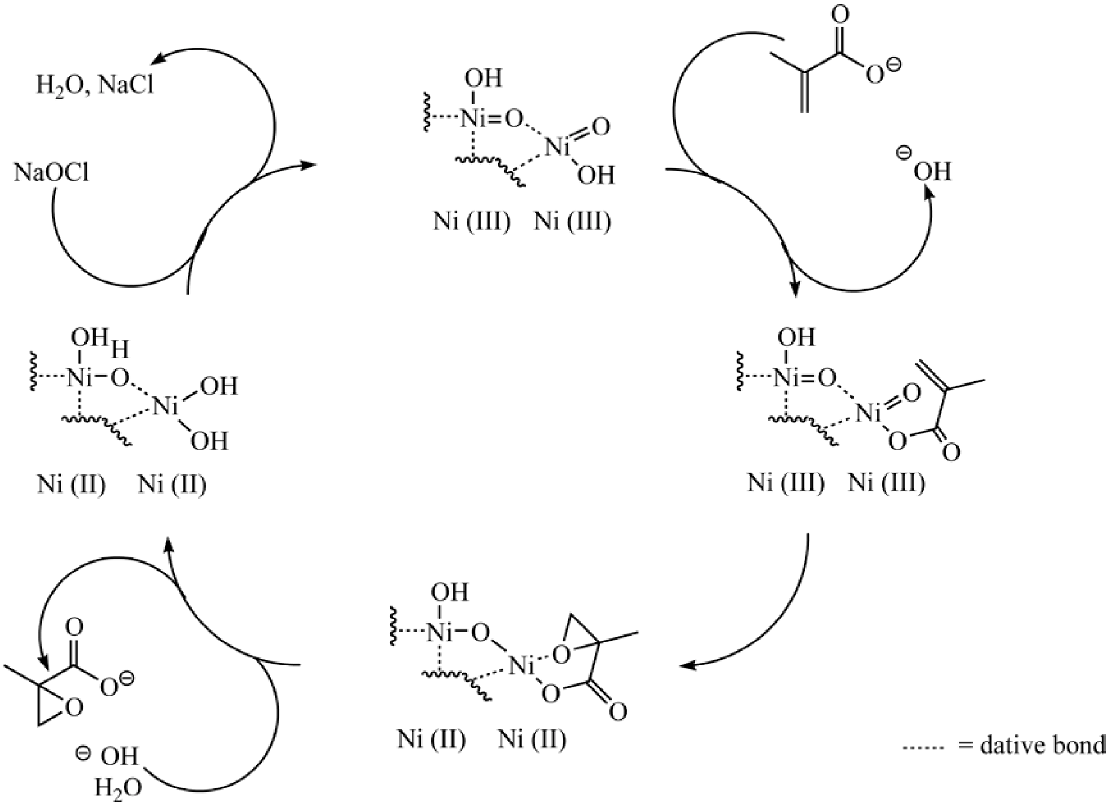
Table 3.2. Catalyst turnovers and epoxide yields for the epoxidation of methacrylic acid with NaOCl using several nickel species

[Ni]	size	form	turnover number	% epoxide
NiOOH	4 nm	*in situ*	39.4	97.2
NiOOH	4 nm	*in situ*[b]	39.2	96.7
NiOOH	4 nm	isolated	21.8	54.5
NiOOH	4 nm	isolated[b]	25.0	62.5
NiOOH	100 nm	isolated[b]	1.8	4.5
$Ni(OH)_2$	100 nm	commercial	1.6	4.0
$Ni(OH)_2$	100 nm	commercial[b]	3.0	7.4

[a] Yield after 10 hours, determined by GC. The balance was identified as starting material and/or chlorinated byproducts by ^{1}H NMR. [b] The catalyst was dispersed by brief sonication before use.

It is curious that olefins lacking a carboxylic acid are inert to this catalyst. This observation actually gives insight into the mechanism of this reaction. Since non-acidic substrates are inert, the reaction likely involves using the carboxylic acid as a directing group, much like alcohols act as directing groups in the Sharpless asymmetric epoxidation reaction. The mechanism outlined in Scheme 3.3 is proposed for this reaction. This reaction invokes a Ni(III) intermediate which is consistent with the photoelectron spectrum reported by M. W. Roberts et al in 1983.[63] Since this reaction is heterogeneous, it is most likely occurring on the surface of the catalyst. The reaction is run at pH 12, so the carboxylic acids are fully deprotonated. First, a deprotonated acid replaces one of the hydroxide ligands on a nickel (III) ion. Next, the oxygen is delivered to the olefin, which causes two one-electron reductions in adjacent metal centers to give a μ-oxo Ni (II)- Ni-(II) species. The oxo bridge is then hydrolyzed and the acid is displaced by hydroxide. The Ni (II)-Ni (II) species is then oxidized back to a Ni (III)-Ni (III) species and the cycle repeats.

Scheme 3.3. Proposed mechanism for epoxidation



CONCLUSIONS

In conclusion we have demonstrated the synthesis nickel oxide hydroxide nanoparticles by direct precipitation from aqueous nickel (II) acetate upon the addition of commercial bleach. We have demonstrated that this material is an efficient catalyst for the epoxidation of α-β unsaturated carboxylic acids and that nickel-salen complexes are not likely catalytically responsible for the oxidation of these olefins. Multi-gram quantities of methacrylic acid oxide can be obtained using low catalyst loading (2.5 mol %) of an inexpensive catalyst with commercial bleach as the oxidant.

EXPERIMENTAL

General considerations and instrumentation

Solvents were used as received. Commercial bleach (ca. 5-6% aqueous NaOCl) was degassed with nitrogen for 5 minutes immediately before use. All NMR chemical shifts are given in ppm and were recorded on a Mercury-300BB or an Inova-300 spectrometer (^{1}H, 299.91 MHz; ^{13}C{^{1}H} 75.41 MHz) using the solvent as an internal standard (residual proton in $CDCl_3$: ^{1}H 7.26 ppm; ^{13}C 77.0 ppm; or residual proton in DMSO-d_6: ^{1}H 2.49 ppm). X-Ray Diffraction (XRD) data was collected with a Bruker 4x5 D8 powder wide angle X-ray diffractometer with CuK radiation operating at 40kV and 40 mA. Transmission Electron Microscopy (TEM) micrographs were acquired with a JEOL 2010 instrument operating at 200kV (analytical resolution = 0.23 nm, +/- 30 degrees tilt) equipped with an Oxford Instruments eXL EDS system. Samples were prepared for TEM by dispersing the sample in water by sonication, then depositing the dilute suspension on a copper grid with holey carbon film support. Thermal Gravimetric Analysis (TGA) data were collected on a TA Instruments Q600 SDT under an argon purge. GC data were obtained with an Agilent 6850 gas chromatograph with helium carrier gas and an FID detector. The column employed was a J&W Scientific column, model 19091Z-413E with a 30 m length, an inner diameter of 0.32 mm, and a film thickness of 0.25 μm.

Standard procedure for epoxidation of olefins

A 500 mL flask was charged with sodium hydroxide (1.80 g, 45.0 mmol, 1.0 eq.) and water (10.0 mL). Upon dissolution of the sodium hydroxide, an olefin (45.0 mmol, 1.0 eq.) and nickel acetate tetrahydrate (0.27 g, 1.13 mmol, 0.025 eq.) were added to the flask. The solution was cooled to 0°C in an ice bath and dichloromethane (30 mL) was added. Commercial bleach (300 mL) was placed in an ice bath and degassed with nitrogen for 5 minutes. The bleach was placed in an addition funnel and added at the rate of 1 drop per second. A fine black precipitate formed immediately upon addition of the bleach. The reaction slurry was stirred for 2 hours in an ice bath and then at room temperature for 2 hours. The reaction was transferred to a separatory funnel with diethyl ether (100 mL) and the layers were allowed to separate. The aqueous layer was acidified with 2 M aqueous hydrochloric acid until it was strongly acidic by pH paper. The organic layer was then collected and set aside. The aqueous layer was saturated with sodium chloride and then extracted with diethyl ether (3 x 100 mL). The combined organic extracts were dried over anhydrous magnesium sulfate and filtered. The solvent was removed by rotary evaporation. Purification was achieved through distillation or sublimation, depending on the substrate.

2-methyl-oxirane-2-carboxylic acid ($C_4H_6O_3$) (Table 3.1, entry 1)

The crude product was obtained in 97% purity by ^{1}H NMR and GC. The compound could be distilled into a liquid nitrogen cooled bump trap remove the impurity. Yield: 3.31 g (72.1 %). ^{1}H NMR ($CDCl_3$): δ 1.58 (s, 3H), 2.82 (d, $^2J_{HH}$ = 6.0 Hz, 1H), 3.14 (d, $^2J_{HH}$ = 6.0 Hz, 1H), 9.58 (broad s, 1H). ^{13}C NMR ($CDCl_3$): δ 17.1, 53.6, 53.9, 176.0. MS (ESI) *m/z* = 101 $[M-H]^-$.

3-methyl-oxirane-2-carboxylic acid ($C_4H_6O_3$) (Table 3.1, entry 2)

This product was sublimed and recrystallized from hexanes. Yield: 1.00 g (21.5%). ^{1}H NMR ($CDCl_3$): δ 1.45 (d, $^3J_{HH}$ = 5.1 Hz, 3H), 3.25-3.33 (m, 2H), 11.10 (broad s, 1H). ^{13}C NMR ($CDCl_3$): δ 17.4, 53.7, 55.4, 175.3. MS (ESI) *m/z* = 101 $[M-H]^-$.

2,3-dimethyl-oxirane-2-carboxylic acid ($C_5H_8O_3$) (Table 3.1, entry 3)

The product was purified by sublimation 1.62 g (31.1%). ^{1}H NMR ($CDCl_3$): δ 1.38 (d, $^3J_{HH}$ = 5.5 Hz, 3H), 1.53 (s, 3H), 3.34 (q, $^3J_{HH}$ = 5.5 Hz, 1H), 8.43 (broad s, 1H). ^{13}C NMR ($CDCl_3$): δ 12.9, 13.6, 58.0, 58.9, 175.4. MS (ESI) *m/z* = 115 $[M-H]^-$.

3,3-dimethyl-oxirane-2-carboxylic acid ($C_5H_8O_3$) (Table 3.1, entry 4)

The product was not isolated as it decomposes rapidly upon removal of the ether. ^{1}H NMR ($CDCl_3$): δ 1.43-1.46 (m, 6H), 2.39 (s, 1H), 9.80 (broad s, 1H). MS (ESI) *m/z* = 115 [M-H]$^-$.

2-carboxymethyl-oxirane-2-carboxylic acid ($C_5H_6O_5$) (Table 3.1, entry 5)

Note: In this case, 2.0 eq. of sodium hydroxide were used instead of 1.0. The crude product was determined to be a mixture of product (31%) and starting material by GC. ^{1}H NMR (DMSO-*d*$_6$): δ 2.86 (d, $^2J_{HH}$ = 6.0 Hz, 1H), 2.92 (d, $^2J_{HH}$ = 5.8 Hz, 1H), 2.92 (d, $^2J_{HH}$ = 5.8 Hz, 1H), 2.96 (d, $^2J_{HH}$ = 6.0 Hz, 1H), 12.40 (s, 2H). MS (ESI) *m/z* = 145 [M-H]$^-$.

Oxidation and epoxidation of 2-methylallyl alcohol (Table 3.1, entry 6)

A 500 mL flask was charged with sodium hydroxide (1.8 g, 45.0 mmol, 1.0 eq.) and water (10.0 mL). Upon dissolution of the sodium hydroxide, 2-methylallyl alcohol (3.25 g, 45.0 mmol, 1.0 eq.) and nickel acetate tetrahydrate (0.27 g, 1.13 mmol, 0.025 eq.) were added to the flask. The solution was cooled to 0°C in an ice bath and dichloromethane (30 mL) was added. Commercial bleach (300 mL) was placed in an ice bath and degassed with nitrogen for 5 minutes. The bleach was placed in an addition funnel and added at the rate of 1 drop per second. A fine black precipitate formed immediately upon addition of the bleach. The reaction slurry was stirred for 6 hours in an ice bath and then at room temperature for 4 hours. The reaction was transferred to a separatory funnel with diethyl ether (100 mL) and the layers were allowed to separate. The aqueous layer was acidified with 2 M hydrochloric acid until it was strongly acidic by pH paper. The organic layer was then collected and set aside. The aqueous layer was saturated with sodium chloride and then extracted with diethyl ether (3 x 100 mL). The combined organic extracts were dried over anhydrous magnesium sulfate and filtered. The solvent was removed by rotary evaporation. The product 2-methyl-oxirane-2-carboxylic acid was recovered in 48% isolated yield after short-path vacuum distillation into a liquid nitrogen cooled trap. Its identity was confirmed by comparison (NMR, MS) to an authentic sample.

Epoxidation and hydrolysis of methacrylamide (Table 3.1, entry 7)

A 500 mL flask was charged with sodium hydroxide (1.8 g, 45.0 mmol, 1.0 eq.) and water (10.0 mL). Upon dissolution of the sodium hydroxide, methacrylamide (3.83 g, 45.0 mmol, 1.0 eq.) and nickel acetate tetrahydrate (0.27 g, 1.13 mmol. 0.025 eq.) were added to the flask. The solution was cooled to 0°C in an ice bath and dichloromethane (30 mL) was added. Commercial bleach (300 mL) was placed in an ice bath and degassed with nitrogen for 5 minutes. The bleach was placed in an addition funnel and added at the rate of 1 drop per second. A fine black precipitate formed immediately upon addition of the bleach. The reaction slurry was stirred for 6 hours in an ice bath and then at room temperature for 4 hours. The reaction was transferred to a separatory funnel with diethyl ether (100 mL) and the layers were allowed to separate. The aqueous layer was acidified with 2 M hydrochloric acid until it was strongly acidic by pH paper. The organic layer was then collected and set aside. The aqueous layer was saturated with sodium chloride and then extracted with diethyl ether (3 x 100 mL). The combined organic extracts were dried over anhydrous magnesium sulfate and filtered. The solvent was removed by rotary evaporation. The product 2-methyl-oxirane-2-carboxylic acid was recovered in 35% isolated yield after short-path vacuum distillation into a liquid nitrogen cooled trap. Its identity was confirmed by comparison (NMR, MS) to an authentic sample.

Control experiment

The epoxidation of methacrylic acid was attempted under the standard epoxidation conditions, omitting the nickel. No reaction was observed.

Hydrolysis of primary amides

The standard procedure for the epoxidation of olefins was used, but the sodium hydroxide was omitted.

Hydrolysis of acetamide

Acetic acid was obtained as the product. GC yield (92%), isolated yield: 2.16 g (80%)

Hydrolysis of propionamide

Propanic acid was obtained as the product. GC yield (74%), isolated yield: 1.84 g (55%).

N-methyl methacrylamide and N,N-dimethyl methacrylamide

These two substrates were inert to the reaction conditions. Attempts to oxidize these materials resulted in the recovery of starting material.

GC analysis

The crude product of each epoxidation was assayed by gas chromatography. Approximately 30 mg of each crude product was dissolved in 3 mL of diethyl ether. The GC trace was then compared to the GC trace of a pure epoxide standard (prepared with *m*-chloroperbenzoic acid; see below) to determine purity. Each epoxidation reaction (Table 1, entries 1-6) was performed twice under identical conditions and the reported results are the averages of the two runs.

NiOOH nanoparticles, circa 4 nm

Nickel acetate tetrahydrate (0.25 g, 1.0 mmol, 1.0 eq.) was dissolved in water (20 mL). The solution was cooled to 0°C in an ice bath and commercial bleach (10 mL) was slowly added with constant stirring. A black precipitate formed immediately. The solution was transferred to a vial and subjected to centrifugation. The black powder was rinsed with water (4 x 10 mL) to remove traces of sodium chloride and NaOCl. The black powder was dried under high vacuum and was subsequently characterized by XRD and TEM. Yield: 0.18 – 0.20 g. The reaction is readily scaled up to 10 g, but isolation of the product using a standard laboratory centrifuge is impractical. Note: This material decomposes to NiO under ambient conditions after several weeks. All characterization was done within 72 hours of synthesis.

NiO nanoparticles

NiOOH nanoparticles (0.10 g, 0.46 mmol) were placed in an open vial and heated in an oven at 230°C for 24 hours. The nickel oxide was characterized by XRD. (0.07 g, 0.92 mmol).

NiOOH, circa 100 nm

$Ni(OH)_2$ (2.00 g, 21.6 mmol, 1.0 eq.) was placed on a glass frit with sodium hydroxide powder (0.50 g, 12.5 mmol, 0.58 eq.). Ozone gas was bubbled through water and then passed over the solid $Ni(OH)_2$/NaOH mixture. Over the course of 4 hours, the light green $Ni(OH)_2$ turned black. The black powder was rinsed with water and dried under high vacuum. The powder was characterized by TEM. Yield: 1.93 g (82.5%).

Typical epoxidation procedure using insoluble nickel sources as catalysts (Table 3.2)

A 500 mL flask was charged with sodium hydroxide (1.80 g, 45.0 mmol, 1.0 eq.) and water (10.0 mL). Upon dissolution of the sodium hydroxide, methacrylic acid (3.87 g, 45.0 mmol, 1.0 eq.) was added to the flask. A nickel source (see Table 3.2; *e.g.*, 4 nm NiOOH, 100 nm NiOOH, or commercial $Ni(OH)_2$) (1.13 mmol, 0.025 eq.) was dispersed in water (3 mL) and subjected to sonication for 3 minutes when denoted. The nickel source was then added to the flask and the slurry was cooled to 0°C in an ice bath. Dichloromethane (30 mL) was added. Commercial bleach (300 mL) was placed in an ice bath and degassed with nitrogen for 5 minutes. The bleach was placed in an addition funnel and added at the rate of 1 drop per second. The reaction slurry was stirred for 6 hours in an ice bath and then at room temperature for 4 hours. The reaction was transferred to a separatory funnel with diethyl ether (100 mL) and the layers were allowed to separate. The aqueous layer was acidified with 2 M hydrochloric acid until it was strongly acidic by pH paper. The organic layer was then collected and set aside. The aqueous layer was saturated with sodium chloride and then extracted with diethyl ether (3 x 100 mL). The combined organic extracts were dried over anhydrous magnesium sulfate. Filtration and removal of the solvent by rotary evaporation and high vacuum gave the products, which were analyzed by ^1H NMR to obtain the reaction conversion. Note: In the case of all reactions using NiOOH as the nickel catalyst, the NiOOH was prepared less than 4 hours prior to use in order to minimize decomposition. In order to ensure accurate catalyst loading of NiOOH, the NiOOH was prepared from a known mass of nickel acetate and excess bleach. The reaction to form NiOOH was assumed to proceed quantitatively. The precipitate was collected by centrifugation, rinsed with water and then transferred to the reaction flask. The centrifuge tube was rinsed with water to ensure nearly quantitative transfer of the catalyst to the reaction flask.

Synthesis of epoxide standards using *m*-chloroperbenzoic acid (*m*-CPBA)

The five unique products listed in Table 1 were prepared independently to obtain "authentic samples" for NMR and GC standards. An olefin (10.0 mmol, 1.0 eq.) was dissolved in dichloromethane (25 mL) in a flask. Solid *m*-CPBA (77% maximum peroxide content, 6.0 g, 26.8 mmol, 2.68 eq.) was added and the reaction was stirred for 24 hours at reflux. The solution was cooled to room temperature and any solid that formed was filtered off and discarded. The dichloromethane was then removed by rotary evaporation and the resulting residue was rinsed with cold water. The slurry was filtered and the solid was discarded. The water was removed by rotary evaporation and the resulting residue was distilled or sublimed into a liquid-nitrogen cooled trap under high vacuum. ^{13}C NMR, ^{1}H NMR, and GC standards were prepared from these materials.

CHAPTER IV

OTHER OXIDATIONS USING NICKEL OXIDE HYDROXIDE

SYNOPSIS

Nickel oxide hydroxide was used as a catalyst for the oxidation of several organic substrates. This catalyst was utilized for the oxidation of primary alcohols and aldehydes to carboxylic acids and for the oxidation of secondary alcohols to ketones. Several unusual reactions of this catalyst with olefin substrate are also described. The epoxidation of α,β-unsaturated carboxylic acids without the use of organic solvent is also discussed.[64]

INTRODUCTION

Nickel oxide hydroxide has been known to oxidize a host of organic substrates for quite some time. Among the substrates that can be oxidized using nickel oxide hydroxide are alcohols, aldehydes, phenols, amines, and oximes. However, early reports demonstrated oxidations of organic compounds using 1-1.5 equivalents of nickel. In 1975 M. V. George and K. S. Balachandran published an extensive review covering the major reactions that can be carried out using stoichiometric nickel oxide hydroxide.[48] We were aware of two reports in the literature wherein nickel oxide hydroxide is used catalytically with excess bleach to oxidize an organic product. Weijlard reported the first example of using nickel catalytically to oxidize organic molecules in the presence of bleach in which he oxidized nicotine and vitamin C using a catalytic amount of a nickel

(II) salt (3-5 mol%) and excess sodium hypochlorite.[57] Bekkum et al. published a report in 1996 in which they used a large amount of nickel (15-120 mol%) and excess bleach to cleave the diols in several sugars to give carboxylic acids.[58] Oddly, Bekkum et al. did not reference the original work by Weijlard. Our group recently reported the only other published example of preparing nickel oxide hydroxide in situ and then catalytically oxidizing an organic compound in the presence of excess bleach. In this report we utilized a nickel (II) salt (2.5 mol%) and excess bleach to oxidize several α,β-unsaturated carboxylic acids to epoxy acids.[65]

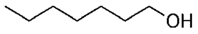
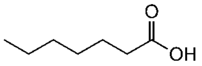
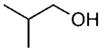
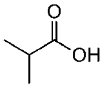
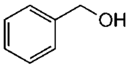
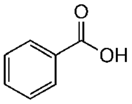
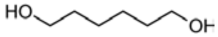
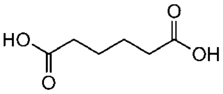
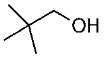
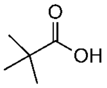
We hypothesized that many of the reactions that can be carried out using stoichiometric nickel oxide hydroxide could be carried out instead with a catalytic amount of nickel in the presence of excess sodium hypochlorite, since this reaction has literature precedent, but a relatively unexplored scope.[57,58] Of particular interest to our group is the facile oxidation of alcohols using benign, inexpensive catalysts. Typically this reaction can be accomplished in the lab through the stoichiometric use of Collins reagent[66], Jones reagent[67], pyridinium chlorochromate (PCC)[68] or potassium permanganate. These routes are generally undesirable due to the large amounts of heavy-metal containing waste that they produce. They do, however, tend to be selective and very reliable. Industrially these oxidations can be accomplished with oxygen using heterogeneous catalysts but the reaction conditions often lead to the over oxidation of some of the substrate.[69] This route is quite useful for synthesizing small molecules from an abundant industrial feedstock because the lack of selectivity for the ketones or acids is outweighed by the low cost of oxidant, oxygen gas. Thus some of the starting material is sacrificed to carbon dioxide and water to obtain a moderate yield of the desired product. With more complex, expensive alcohols, a more selective route is required that does not destroy portions of the substrate. Herein we report the facile oxidation of several primary and secondary alcohols to give carboxylic acids and ketones, respectively, using extremely inexpensive, commonly available reagents. The oxidation proceeds rapidly in the presence of nickel oxide hydroxide and excess bleach under ambient conditions and appears to be quite general and predictable giving high yields (70-95%) and high purities (90-100%) in most cases. With a few exceptions, these oxidations can be run without the use of an organic solvent. In the reactions involving the oxidation of water-insoluble organic solids, a small amount of dichloromethane or diethyl ether was added and the reaction proceeded smoothly.

RESULTS AND DISCUSSION

In order to obtain relevant data for activity and selectivity comparisons, we decided to run each oxidation reaction under our standard conditions, which called for a small amount of dichloromethane to dissolve the organic and then we ran a separate set of experiments excluding all organic solvent from the reaction. The results could then be compared to determine what, if any, role the organic solvent was playing in the reaction. Since our catalyst in active form, NiOOH, is insoluble under our reaction conditions it is reasonable to assume that this reaction is occurring on the catalyst surface. Thus we hypothesized that alcohols that are liquids under the reaction conditions could be oxidized without the use of an organic solvent whereas alcohols that are solid, or otherwise insoluble in the aqueous reaction medium would require dissolution in an organic solvent. In most cases, this seems to be true. An organic substrate that is either liquid or water-soluble can be oxidized without the use of organic solvents. This is particularly advantageous because it reduces the amount of waste generated and it eliminates the need for a toxic solvent. This reaction appears to be quite general, oxidizing aliphatic and aromatic alcohols quite cleanly. Aldehydes are also readily oxidized to carboxylic acids using this catalytic system.

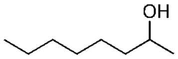
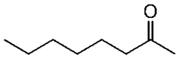
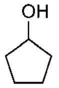
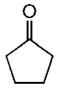
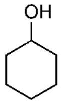
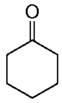
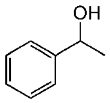
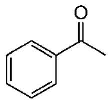
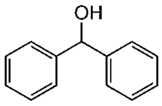
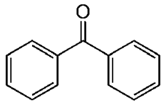
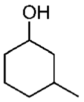
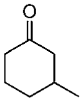
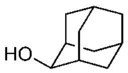
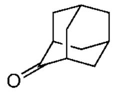
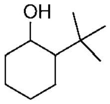
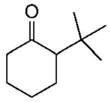
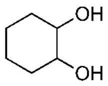
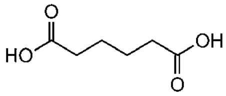
The oxidation of primary alcohols proceeds smoothly under the standard reaction conditions to give the corresponding carboxylic acids after acidic workup. Isolated yields for these reactions were generally good ranging from 68-93% and purities were high (91-98% by GC), indicating that the reaction proceeds smoothly generating few byproducts (Table 4.1). Since these alcohols are all liquids or water soluble, similar results were expected when the organic solvent was excluded from the reaction. Indeed, these substrates seem to all be readily oxidized to the carboxylic acids without the need for organic solvent (Table 4.1). The yields using the two different reaction conditions did not differ significantly.

Table 4.1. Oxidation of primary alcohols

entry	substrate	product	% crude yield	% GC purity	% isolated yield[c]	% crude yield	% GC purity	% isolated yield[c]
			standard conditions[a]			no organic solvent[b]		
1			93	91	87	91	92	86
2			95	95	89	96	95	89
3			87	93	75	87	95	75
4			68	*n.d.*	68	72	*n.d.*	72
5			88	98	88	81	97	81

a. Standard reaction conditions: 2.5 mol% $NiCl_2$, 45 mmol alcohol, 15 mL CH_2Cl_2, 300 mL bleach, 2 hours at 0 °C then 2 hours at 20 °C . b. CH_2Cl_2 was omitted. c. Isolated yields were ≥96% pure. *n.d.*= not determined.

Table 4.2. Oxidation of secondary alcohols

entry	substrate	product	% crude yield	% GC purity	% isolated yield[c]	% crude yield	% GC purity	% isolated yield[c]
			standard conditions[a]			no organic solvent[b]		
1			71	>99	71	70	>99	70
2			65	94	59	66	97	66
3			87	90	84	89	92	75
4			33	90	29	55	33	*n.d.*
5			90	>99	90	*n.r.*	*n.r.*	*n.r.*
6			78	>99	78	*n.r.*	*n.r.*	*n.r.*
7[d]			98	>99	98	*n.r.*	*n.r.*	*n.r.*
8			*n.r.*	*n.r.*	*n.r.*	*n.r.*	*n.r.*	*n.r.*
9			90	*n.d.*	90	88	*n.d.*	88

a. Standard reaction conditions: 2.5 mol% $NiCl_2$, 45 mmol alcohol, 15 mL CH_2Cl_2, 300 mL bleach, 2 hours at 0 °C then 2 hours at 20 °C . b. CH_2Cl_2 was omitted. c. Isolated yields were ≥96% pure. d. Diethyl ether was substituted for dichloromethane for this substrate because the alcohol shows very little solubility in the latter. *n.r*=no reaction, *n.d.*= not determined.

Secondary alcohols are likewise oxidized to ketones in high yields and purities in most cases (Table 4.2). Again, in the case of liquid alcohols or water-soluble alcohols, no organic solvent is required (Table 4.2). There was one notable exception to this general trend. The oxidation of DL-sec-phenethyl alcohol reached only 33% conversion after the 4-hour reaction time in the absence of organic solvent (Table 4.2, entry 4). The balance of the material was determined to be starting material by GC. Curiously, running this reaction for longer periods of time did not improve the yield or the conversion. Even with organic solvent, a low yield of the corresponding ketone is obtained but with high purity (Table 4.2, entry 4). 1,2-diols are cleaved by this catalyst. For example, 1,2-dihydroxycyclohexane is converted to adipic acid by this catalyst (Table 4.2, entry 9).

We chose to study the oxidation of benzyl alcohol more carefully. In order to accomplish this, an oxidation reaction was performed under our organic solvent free conditions at 20 ºC. Aliquots were taken every 5 minutes and quenched using saturated solutions of sodium thiosulfate. The aliquots were acidified and extracted with ether. The relative abundances of benzoic acid, benzyl alcohol and benzaldehyde were then determined using gas chromatography. There were no other species present in the GC traces. Figure 4.1 is a graph of the mole fraction of each component at various times. The concentration of benzaldehyde can be seen increasing over time and reaches a maximum at approximately 45 minutes and then drops off rapidly. The concentraion of benzoic acid stays fairly low in the first 40 minutes of the reaction and then climbs rapidly implying that there is an induction period for this reaction. It is clear, however, that the benzyl alcohol is first oxidized to benzaldehyde and that the benzaldehyde is then in turn oxidized to benzoic acid. The oxidation of benzaldehyde proceeds smoothly to give benzoic acid in 20 minutes under the same reaction conditions (Figure 4.2). Alaphatic alcohols are oxidized extremely rapidly; the oxidation of 1-propanol is complete after only 15 minutes at room temperature (Figure 4.3).

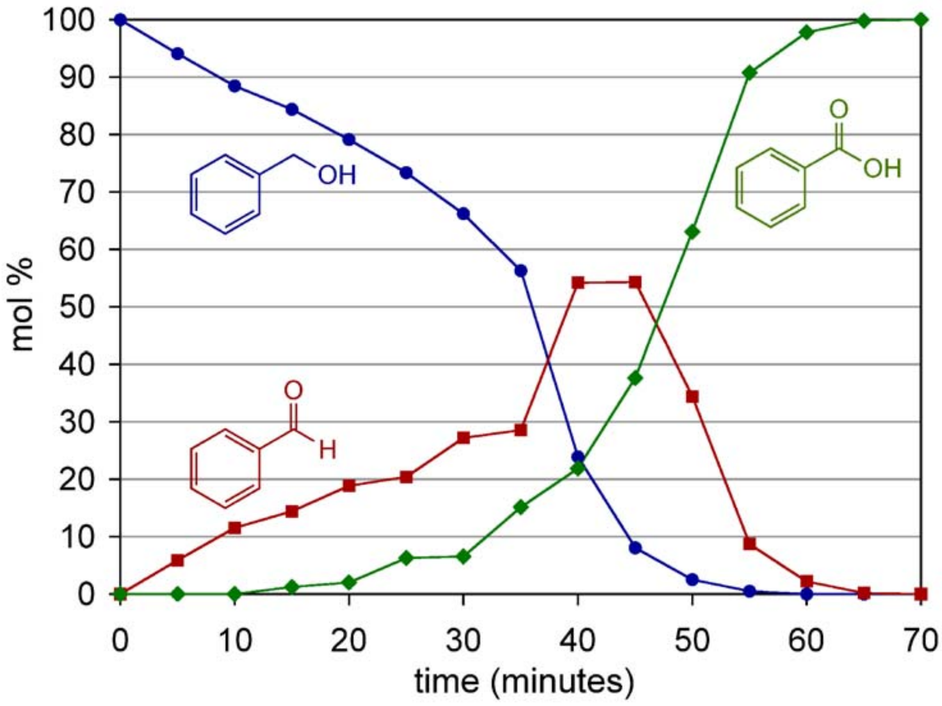


Figure 4.1. Kinetic data for the oxidation of benzyl alcohol.

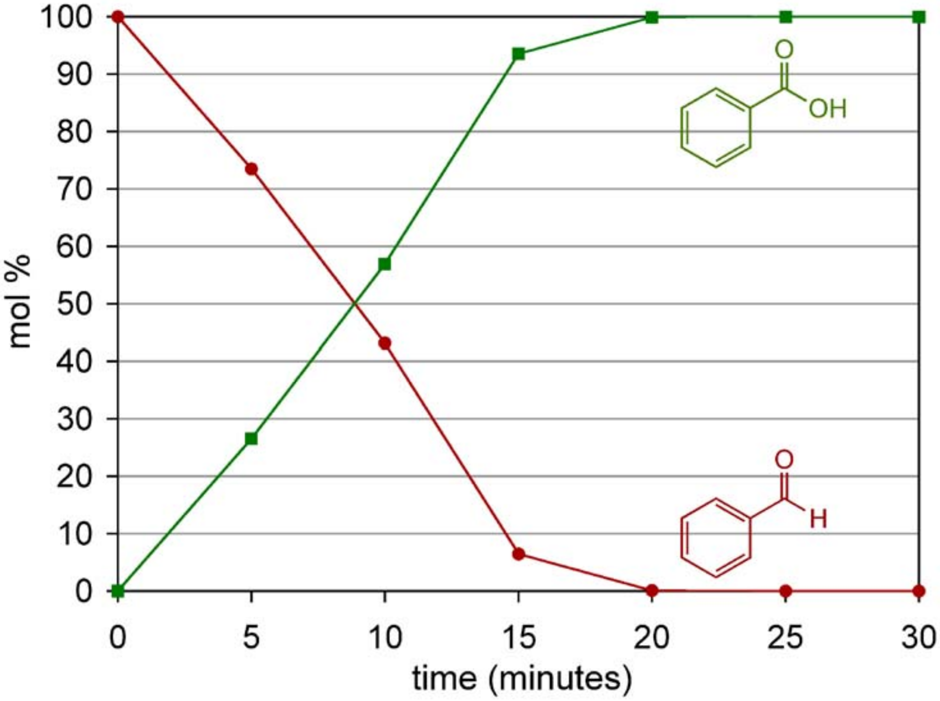


Figure 4.2. Kinetic data for the oxidation of benzaldehyde.

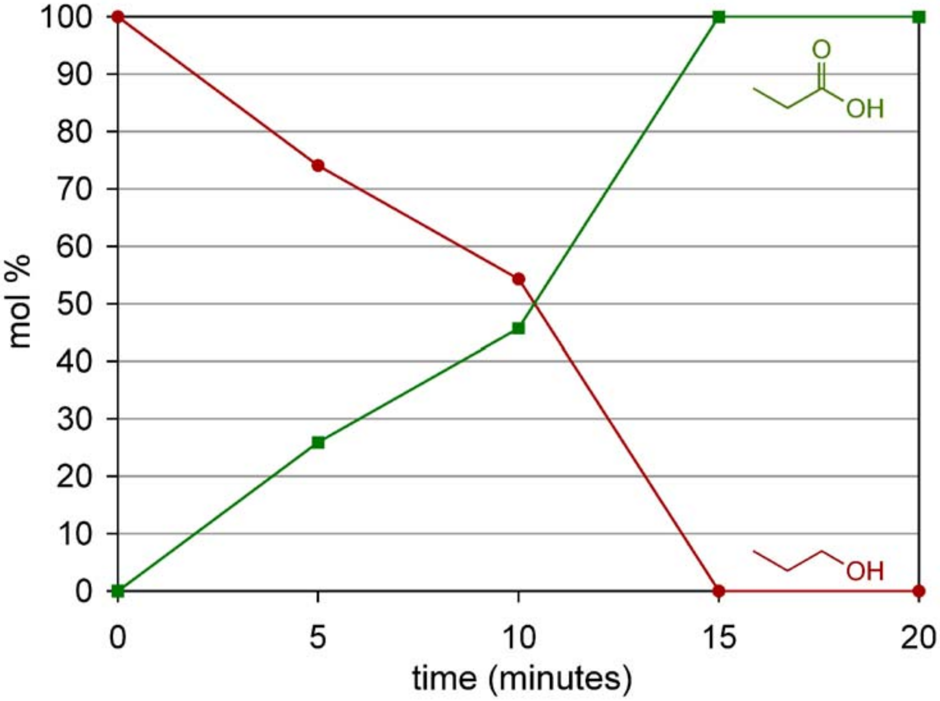
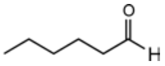
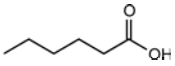
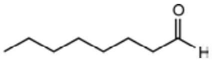
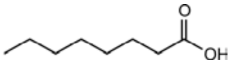
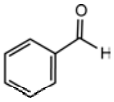
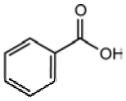
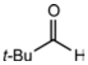
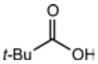


Figure 4.3. Kinetic data for the oxidation of 1-propanol.

Aldehydes can be readily oxidized to the corresponding carboxylic acids using this system, which is not surprising. Three aldehydes were oxidized to demonstrate this point (Table 4.3). Acids were obtained in both high yield and high purity using this system.

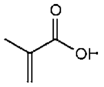
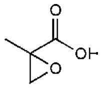
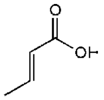
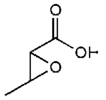
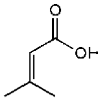
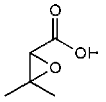
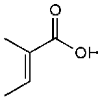
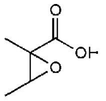
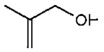
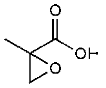
Table 4.3. Oxidation of aldehydes[a]

entry	substrate	Product	Isolated yield (%)	GC purity (%)
1			82	92
2			80	94
3			96	>99
4			85	97

a. Standard reaction conditions: 2.5 mol% $NiCl_2$, 45 mmol aldehyde, 15 mL CH_2Cl_2, 300 mL bleach, 2 hours at 0 °C then 2 hours at 20 °C

We recently published several examples of the epoxidation of α,β-unsaturated carboxylic acids using our standard reaction conditions.[65] We decided to explore the possibility of epoxidizing these olefins without the use of organic solvent. All of our substrates dissolved readily in our reaction medium and not surprisingly, the α,β-unsaturated carboxylic acids were readily epoxidized in comparable yields and purities to those we reported with the use of dichloromethane as a solvent (Table 4.4).

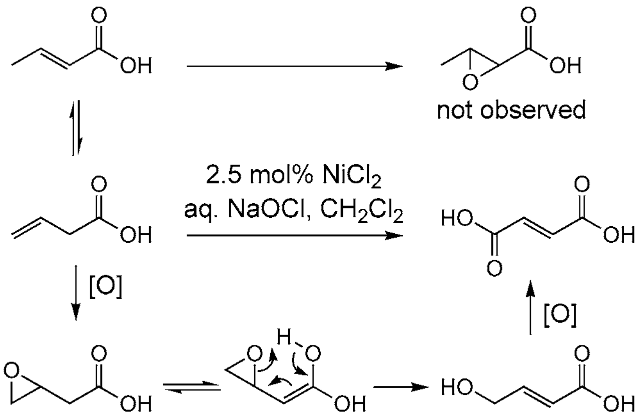
Table 4.4. Epoxidation of α,β-unsaturated carboxylic acids without organic solvent[a]

entry	substrate	product	GC yield (%)
1			95
2			42
3			71
4			85
5			89

a. Solvent-free reaction conditions: 2.5 mol% $NiOAc_2$, 45 mmol acid, 45 mmol NaOH, 300 mL bleach, 2 hours at 0 °C then 2 hours at 20 °C

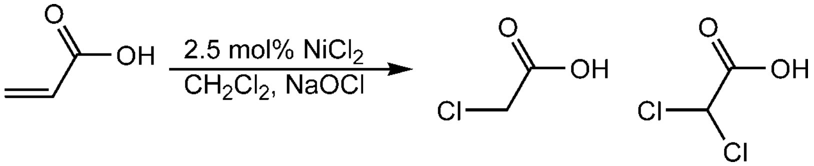
In the course of exploring the scope of this reaction, several unusual reactions were observed. Initially our group was interested in this chemistry for epoxidation. Nickel oxide hydroxide is inert toward most olefins, such as styrene and 1-hexene. However, as previously discussed α,β-unsaturated carboxylic acids are readily epoxidized. We reasoned that on the surface of the catalyst, the acid was becoming bound to the nickel thus positioning the olefin to accept an oxygen atom. In order to explore this, we attempted to epoxidize 3-butenoic acid (Scheme 4.1). Much to our surprise, we obtained fumaric acid in high yield (75%, >99% *trans* isomer by ^{1}H NMR). The fumaric acid was not further oxidized to the epoxide. This process formally involves isomerizaion of the double bond and an oxidation of carbon 4. In separate experiments, we attempted to epoxidize fumaric acid and maleic acid. Consistent with the results obtained from the oxidation of 3-butenoic acid, these attempts fail to yield epoxide and give only starting material. It stands to reason that if the 3-butenoic acid were first isomerized by the catalyst to crotonic acid or its *cis* isomer, then it would have, in turn, been epoxidized. Since this product was not observed, we must conclude that the isomerization of the double bond happens after the oxidation of carbon 4. With this in mind, we propose the mechanism in scheme 4.1 for this oxidation.

Scheme 4.1. Oxidation of 3-butenoic acid to fumaric acid



It is curious that neither Payne nor Sharpless report the epoxidation of acrylic acid with their tungsten system.[3,4] This substrate is not even mentioned in either paper, leading us to believe that the tungsten system fails. We thought that our system may be able to epoxidize this simple α,β-unsaturated carboxylic acid. Our system did not yield the epoxide this acid, but instead led to the formation of monochloroacetic acid and dichloroacetic acid most probably via a radical mechanism as nickel oxide hydroxide is known to oxidize via a free radical mechanism.[70,71,72,73] A mixture of chloroacetic acid and dichloroacetic acid (ranging from 1:1 to 5:1) was obtained from this reaction, demonstrating the cleavage of carbon-carbon bonds and chloriniation (Scheme 4.2). We were unable to determine the fate of the C_1 fragment that should have been generated. It is possible that it was lost in the workup due to volatility or high water solubility. A methyl group, particularly one in the α position, seems to increase the efficiency of the epoxidation. The stabilizing effect of a methyl group can be evidenced in the epoxidation of crotonic acid. The epoxidation of crotonic acid proceeds with fairly low conversion to the epoxide (45%) giving the balance of the material as chloroacetic acid and dichloroacetic acid plus a host of unidentified products in small concentrations.

Scheme 4.2. Oxidation of acrylic acid



CONCLUSIONS

We have demonstrated a very effective, inexpensive method of oxidizing alcohols, and aldehydes selectively and in high yields using heterogeneous nickel oxide hydroxide. The reaction seems to be general for a variety of different aromatic and aliphatic alcohols giving the desired products in high yields in most cases. This reaction can often be run in the absence of organic solvents, thus decreasing the environmental impact of this process. However, nickel oxide hydroxide is a very reactive catalyst and can react in unexpected ways with certain organic substrates.

EXPERIMENTAL

General considerations and instrumentation

Solvents were used as received. Commercial bleach (*ca.* 5-6% aqueous NaOCl) was sparged with nitrogen for 5 minutes immediately before use. All NMR chemical shifts are given in ppm and were recorded on a Mercury-300BB or an Inova-300 spectrometer (^{1}H, 299.91 MHz; ^{13}C{^{1}H} 75.41 MHz) using the solvent as an internal standard (residual proton in $CDCl_3$: ^{1}H 7.26 ppm; ^{13}C 77.0 ppm; or residual proton in DMSO-d_6: ^{1}H 2.49 ppm; ^{13}C 39.51 ppm). GC data were obtained with an Agilent 6850 gas chromatograph with helium carrier gas and an FID detector. The column employed was a J&W Scientific column, model 19091Z-413E with a 30 m length, an inner diameter of 0.32 mm, and a film thickness of 0.25 μm.

Procedure A: Standard procedure for the oxidation of primary alcohols and aldehydes

A 500 mL flask was charged with $NiCl_2$ hexahydrate (0.27 g, 1.14 mmol) and water (5 mL). A primary alcohol or an aldehyde (45 mmol) was added followed by dichloromethane (15 mL). The reaction was cooled in an ice bath and cold bleach (300 mL) was added in a steady stream over 5 minutes. A fine black precipitate formed immediately. The resulting slurry was stirred for 2 hours at 0˚C and 2 hours at room temperature. The slurry was then acidified with 2 M hydrochloric acid until the aqueous layer was strongly acidic by pH paper. The aqueous layer was extracted with diethyl ether (3 x 100 mL). The combined organic extracts were dried over anhydrous $MgSO_4$ and filtered. Removal of the solvent by rotary evaporation and brief high vacuum gave the crude product. The purities could generally be improved to > 98% by distillation of the crude product or by recrystallization in the case of solids.

Procedure B

This procedure was identical to Procedure A except that the dichloromethane was omitted.

Procedure C: Standard procedure for the oxidation of secondary alcohols

A 500 mL flask was charged with $NiCl_2$ hexahydrate (0.27 g, 1.14 mmol) and water (5 mL). A secondary alcohol (45 mmol) was added followed by dichloromethane (15 mL). The reaction was cooled in an ice bath and cold bleach (300 mL) was added in a steady stream over 5 minutes. A fine black precipitate formed immediately. The resulting slurry was stirred for 2 hours at 0˚C and 2 hours at room temperature. The aqueous layer was extracted with diethyl ether (3 x 100 mL). The combined organic extracts were dried over anhydrous $MgSO_4$ and filtered. Removal of the solvent by rotary evaporation and brief high vacuum gave the crude product. The purities could generally be improved to > 98% by distillation of the crude product or by crystallization in the case of solids.

Procedure D

This procedure was identical to Procedure C except that the dichloromethane was omitted.

Procedure E: Standard procedure for the epoxidation of α,β-unsaturated carboxylic acids

In a 500 mL round bottom flask, sodium hydroxide (1.8 g, 45 mmol) was dissolved in water (10 mL) and an α,β-unsaturated carboxylic acid (45 mmol) was added. The resulting solution was cooled in an ice bath and a solution of nickel(acetate)$_2$ tetrahydrate (0.28 g, 1.14 mmol) in water (5 mL) was added. Cold bleach (300 mL) was added in a steady stream over 5 minutes. A fine black precipitate formed immediately. The resulting slurry was stirred for 2 hours at 0˚C and 2 hours at room temperature. The slurry was then acidified with 2 M hydrochloric acid until the aqueous layer was strongly acidic by pH paper. The aqueous layer was extracted with diethyl ether (3 x

100 mL). The combined organic extracts were dried over anhydrous $MgSO_4$ and filtered. Each product was then analyzed by GC.

Oxidation of primary alcohols. Heptanoic acid ($C_7H_{14}O_2$) (Table 4.1, entry 1). Procedure A

The crude product was obtained with 91% purity by GC analysis, 5.44 g (93%). Distillation gave the product with 98% purity. Yield: 5.10 g (87%). ^1H NMR ($CDCl_3$): δ 0.80-0.96 (m, 3H), 1.19-1.34 (m, 6H), 1.54-1.68 (m, 2H), 2.34 (t, $^3J_{HH}$ = 7.7 Hz, 2H), 10.54 (broad, 1H). ^{13}C NMR ($CDCl_3$): δ 14.3, 22.7, 24.9, 28.9, 31.6, 34.3, 180.7. MS (ESI) *m/z* = 129 $[M-H]^-$. CAS# [111-14-8].

Procedure B

The crude product was obtained with 92% purity by GC analysis, 5.32 g (91%). Distillation gave the product with 98% purity. Yield: 5.04 g (86%). The characterization data were identical to those obtained above using Procedure A.

Isobutyric acid ($C_4H_8O_2$) (Table 4.1, entry 2). Procedure A

The crude product was obtained with 95% purity by GC analysis, 3.76 g (95%). Distillation gave the product with 97% purity. Yield: 3.52 g (89%). ^1H NMR ($CDCl_3$): δ 1.19 (d, $^3J_{HH}$ = 7.0 Hz, 6H), 2.58 (sept, $^3J_{HH}$ = 7.0 Hz, 1H), 11.40 (broad, 1H). ^{13}C NMR ($CDCl_3$): δ 19.0, 34.1, 184.1. MS (ESI) *m/z* = 101 $[M-H]^-$. CAS# [503-74-2].

Procedure B

The crude product was obtained with 95% purity by GC analysis, 3.81 g (96%). Distillation gave the product with 97% purity. Yield: 3.53 g (89%). The characterization data were identical to those obtained above using Procedure A.

Benzoic acid ($C_7H_6O_2$) (Table 4.1, entry 3). Procedure A

The crude product was obtained with 93% purity by GC analysis, 4.77 g (87%). The product was recrystallized from ethanol. Yield: 4.12 g (75%). ^{1}H NMR ($CDCl_3$): δ 7.49 (t, $^3J_{HH}$ = 7.4 Hz, 2H), 7.63 (t, $^3J_{HH}$ = 7.4 Hz, 1H), 8.14 (d, $^3J_{HH}$ = 7.4 Hz, 2H), 11.59 (broad, 1H). ^{13}C NMR ($CDCl_3$): δ 128.8, 129.5, 130.5, 134.1, 172.9. MS (ESI) *m/z* = 121 $[M-H]^-$. CAS# [65-85-0].

Procedure B

The crude product was obtained with 95% purity by GC analysis, 4.77g (87%). The product was recrystallized from ethanol. Yield: 4.10 g (75%). The characterization data were identical to those obtained above using Procedure A.

Adipic acid ($C_6H_{10}O_4$) (Table 4.1, entry 4). Procedure A

Note: Only 22.5 mmol of diol were used. The product was recrystallized from water (5 mL). Yield: 2.24 g (68%). ^{1}H NMR (DMSO-d_6): 1.47 (m, $^3J_{HH}$ = 3.0 Hz, 4H), 2.17 (t, $^3J_{HH}$ = 3.0 Hz, 4H), 11.97 (broad, 1H). ^{13}C NMR (DMSO-d_6): 24.7, 34.0, 175.0. MS (EI) *m/z* = 145 $[M-H]^-$. CAS# [124-04-9].

Procedure B

Note: Only 22.5 mmol of diol were used. The product was recrystallized from water. Yield: 2.37 g (72%). The characterization data were identical to those obtained above using Procedure A.

Trimethyl acetic acid ($C_5H_{10}O_2$) (Table 4.1, entry 5). Procedure A

The product was obtained with 98% purity by GC analysis; thus, no further purification was necessary. Yield: 4.04 g (88%). ^{1}H NMR ($CDCl_3$): δ 1.25 (s, 9H), 11.09 (broad, 1H). ^{13}C NMR ($CDCl_3$): δ 27.2, 38.8, 185.9. MS (ESI) *m/z* = 101 [M-H]$^-$. CAS# [75-98-9].

Procedure B

The crude product was obtained with 97% purity by GC analysis so no further purification was required. Yield 3.72 g (81%). The characterization data were identical to those obtained above using Procedure A.

Oxidation of secondary alcohols. 2-Octanone ($C_8H_{16}O$) (Table 4.2, entry 1). Procedure C

The product was obtained with >99% purity by GC analysis; thus, no further purification was required. Yield: 4.09 g (71%). ^{1}H NMR ($CDCl_3$): δ 0.75 (t, $^3J_{HH}$ = 6.9 Hz, 3H), 1.15 (m, 6H), 1.43 (m, 2H), 2.00 (s, 3H), 2.29 (t, $^3J_{HH}$ = 7.4 Hz, 2H). ^{13}C NMR

($CDCl_3$): δ 14.1, 22.6, 23.9, 28.9, 29.8, 31.7, 43.8, 209.2. MS (EI) *m/z* = 128 [M+·]. CAS# [111-13-7].

Procedure D

The product was obtained in >99% purity by GC analysis; thus, no further purification was required. Yield: 4.04 g, (70%). The characterization data were identical to those obtained above using Procedure C.

Cyclopentanone (C_5H_8O) (Table 4.2, entry 2). Procedure C

The product was obtained with 94% purity by GC analysis, 2.46 g (65%). Distillation gave > 99% purity. Yield: 2.25 g (59%). ^1H NMR ($CDCl_3$): δ 1.71-1.82 (m, 4H), 1.91-2.00 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 23.3, 38.3, 220.4. MS (EI) *m/z* = 84 [M+·]. CAS# [120-92-3].

Procedure D

The product was obtained in 97% purity by GC analysis; thus, no further purification was required. Yield: 2.50 g (66%). The characterization data were identical to those obtained above using Procedure C.

Cyclohexanone ($C_6H_{10}O$) (Table 4.2, entry 3). Procedure C

The product was obtained with 90% purity by GC analysis, 3.84 g (87%). Distillation gave the product with 98% purity. Yield: 3.71 g (84%). ^1H NMR ($CDCl_3$):

δ 1.63-1.73 (m, 2H), 1.77-1.87 (m, 4H), 2.30 (t, $^3J_{HH}$ = 6.9 Hz, 4H). ^{13}C NMR ($CDCl_3$): δ 25.2, 27.2, 42.2, 212.5. MS (EI) *m/z* = 98 [M+·]. CAS# [108-94-1].

Procedure D

The product was obtained in 92% purity by GC analysis. Yield: 3.92 g (89%). Distillation gave the product with 98% purity. Yield: 3.31 g (75%). The characterization data were identical to those obtained above using Procedure C.

Acetophenone (C_8H_8O) (Table 4.2, entry 4). Procedure C

The product was obtained with 90% purity by GC analysis, 1.78 g (33%). Distillation gave the product with > 99% purity. Yield: 1.55 g (29%). ^{1}H NMR ($CDCl_3$): δ 2.60 (s, 3H), 7.45 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 7.56 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 7.93-7.98 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 28.9, 128.5, 128.8, 133.4, 137.3, 198.4. MS (EI) *m/z* = 120 [M+·]. CAS# [98-86-2].

Procedure D

Yield 2.94 g (55%). A mixture of starting material (67%) and product (33%) was obtained by GC analysis. This mixture was not characterized further.

Benzophenone ($C_{13}H_{10}O$) (Table 4.2, entry 5). Procedure C

The product was obtained with >99% purity; thus, no further purification was required. Yield: 7.37 g (90%). ^{1}H NMR ($CDCl_3$): δ 7.48 (t, $^3J_{HH}$ = 7.3 Hz, 4H), 7.59 (t,

$^3J_{HH}$ = 7.3 Hz, 2H), 7.79-7.83 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 128.5, 130.3, 132.7, 137.8, 197.0. MS (EI) *m/z* = 182 [M+·]. CAS# [119-61-9].

Procedure D

Only starting material was recovered from this reaction.

(+/-)-3-Methylcyclohexanone ($C_7H_{12}O$) (Table 4.2, entry 6). Procedure C

The product was obtained with >99% purity; thus, no further purification was required. Yield: 3.93 g (78%). ^{1}H NMR ($CDCl_3$): 0.97 (d, $^3J_{HH}$ = 6.3 Hz, 3H), 1.20-1.36 (m, 1H), 1.53-1.69 (m, 1H), 1.75-2.05 (m, 4H), 2.12-2.36 (m, 3H). ^{13}C NMR ($CDCl_3$): 22.3, 25.5, 33.5, 34.4, 41.3, 50.2, 212.2. MS (EI) *m/z* = 112 [M+·]. CAS# [591-24-2].

Procedure D

Only starting material was recovered from this reaction.

2-Adamantanone ($C_{10}H_{14}O$) (Table 4.2, entry 7). Procedure C

Diethyl ether was substituted for dichloromethane for this reaction because 2-adamantanol has low solubility in dichloromethane. The product was obtained with >99% purity; thus, no further purification was required. Yield: 6.62 g (98%). ^{1}H NMR ($CDCl_3$): δ 1.88-2.10 (m, 12H), 2.51 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 27.6, 36.5, 39.5, 47.2, 218.7. MS (EI) *m/z* = 150 [M+·]. CAS# [700-58-3].

Procedure D

Only starting material was recovered from this reaction.

(+/-)-2-*tert*-butylcyclohexanone ($C_{10}H_{18}O$) (Table 4.2, entry 8). Procedure C

This substrate was not oxidized by the catalyst even after 24 hours.

Adipic acid ($C_6H_{10}O_4$) (Table 4.2, entry 9). Procedure A

Adipic acid was recovered from the oxidation of cyclohexane-1,2-diol (mixture of diastereomers). Yield: 2.96 g (90%). Characterization data were identical to those obtained from the oxidation of 1,6-hexanediol.

Procedure B

Characterization data were identical to those obtained from the oxidation of 1,6-hexanediol. 2.84 g (88%).

Oxidation of aldehydes. Hexanoic acid ($C_6H_{12}O_2$) (Table 4.3, entry 1). Procedure A

Hexanal was oxidized according to Procedure A. The product was obtained with 92% purity by GC, 4.27 g (82%). Distillation gave the product with 94% purity by GC. Yield 3.64 g (70%). ^{1}H NMR ($CDCl_3$): δ 0.89-0.94 (m, 3H), 1.31-1.38 (m, 4H), 1.60-1.68 (m, 2H), 2.37 (t, $^3J_{HH}$ = 7.8 Hz, 2H), 10.82 (broad, 1H). ^{13}C NMR ($CDCl_3$): δ 14.1, 22.6, 24.6, 31.4, 34.3, 180.8. MS (ESI) *m/z* = 115 $[M-H]^-$. CAS# [142-62-1].

Procedure B

The product was obtained in 97% purity by GC analysis; thus, no further purification was necessary. Yield: 4.00 g (77%). The characterization data were identical to those obtained above using Procedure A.

Octanoic acid ($C_8H_{16}O_2$) (Table 4.3, entry 2). Procedure A

Octanal was oxidized according to Procedure A. The product was obtained with 94% purity by GC, 5.19 g (80%). ^{1}H NMR ($CDCl_3$): δ 0.84-0.92 (m, 3H), 1.20-1.39 (m, 8H), 1.54-1.68 (m, 2H), 2.34 (t, $^3J_{HH}$ = 7.7 Hz, 2H), 11.80 (broad, 1H). ^{13}C NMR ($CDCl_3$): δ 14.3, 22.8, 24.9, 29.1, 29.2, 31.9, 34.3, 180.4. MS (ESI) *m/z* = 143 $[M-H]^-$. CAS# [124-07-2].

Procedure B

The product was obtained in 98% purity by GC analysis; thus, no further purification was necessary. Yield: 5.13 g (79%). The characterization data were identical to those obtained above using Procedure A.

Benzoic acid ($C_7H_6O_2$) (Table 4.3, entry 3). Procedure A

Benzaldehyde was oxidized according to Procedure A. The product was obtained with >99% purity. Yield: 5.28 g (96%). The characterization data were identical to those obtained for the oxidation of benzylalcohol (Table 4.1, entry 3).

Procedure B

The product was obtained in >99% purity by GC analysis; thus, no further purification was necessary. Yield: 5.39 g (98%). The characterization data were identical to those obtained above using Procedure A.

Trimethyl acetic acid ($C_5H_{10}O_2$) (Table 4.3, entry 4). Procedure A

The product was obtained with 97% purity by GC analysis; thus, no further purification was necessary. Yield: 3.91 g (85%). The characterization data were identical to those obtained for the oxidation of neopentyl alcohol (Table 4.1, entry 5).

Procedure B

The product was obtained in 98% purity by GC analysis; thus, no further purification was necessary. Yield: 4.19 g (91%). The characterization data were identical to those obtained above using Procedure A.

Epoxidation of α,β-unsaturated carboxylic acids

All substrates in Table 4.4 were oxidized according to Procedure E. The product purity was assayed by GC using standards containing pure material synthesized by an independent route (*m*-chloroperbenzoic acid, *m*-CPBA). See chapter III for characterization data and details for preparation of the epoxide standards.

2-methyl-oxirane-2-carboxylic acid ($C_4H_6O_3$) (Table 4.4, entry 1)

95% purity by GC.

3-methyl-oxirane-2-carboxylic acid ($C_4H_6O_3$) (Table 4.4, entry 2)

42% purity by GC.

3,3-dimethyl-oxirane-2-carboxylic acid ($C_5H_8O_3$) (Table 4.4, entry 3)

71% purity by GC.

2,3-dimethyl-oxirane-2-carboxylic acid ($C_5H_8O_3$) (Table 4.4, entry 4)

85% purity by GC.

2-methyl-oxirane-2-carboxylic acid ($C_4H_6O_3$) (Table 4.4, entry 5)

89% purity by GC.

Oxidation of 3-butenoic acid. Procedure E

3-Butenoic acid (3.87 g, 45mmol) was oxidized according to Procedure E. Fumaric acid was recovered as the product. Yield 3.92 g (75%). ^{1}H NMR (DMSO-d_6): δ 6.58 (s, 2H), 13.08 (broad, 2H). ^{13}C NMR (DMSO-d_6): δ 134.60, 166.67. MS (ESI) *m/z* = 115 $[M-H]^-$. CAS# [110-17-8].

Oxidation of acrylic acid. Procedure E

The product was analyzed by ^{1}H NMR (4.15 ppm for monochloroacetic acid and 5.95 ppm for dichloroacetic acid) and GC. The product contained a mixture of monochloroacetic acid and dichloroacetic acid in ratios that varied from 1:1 to 5:1 under seemingly identical reaction conditions.

Kinetic data for the oxidation of benzyl alcohol

Benzyl alcohol (45 mmol) was oxidized according to procedure B, but the temperature was kept at 20 ± 1 ºC using a water bath. At 5 minute intervals, a 2-mL aliquot was removed from the reaction mixture and combined with 2-mL of aqueous saturated sodium thiosulfate in a scintillation vial. The black catalyst immediately bleached. Upon cooling, 2 drops of concentrated hydrochloric acid and 5 mL of diethyl ether were added to the vial. The vial was shaken, and allowed to settle. The ether extract was then assayed on the GC. The GC detector response was calibrated using a 1:1:1 molar mixture of commercial benzoic acid, benzaldehyde, and benzyl alcohol.

CHAPTER V

CONCLUSIONS

Several new salen-type ligands were synthesized based on biphenol and binaphthol. The synthesis of these ligands and their subsequent coordination to transition metals are described. The transition metal complexes were structurally characterized by X-ray diffraction of single crystals. These structures are unusual in that they have *trans* nitrogen atoms—this arrangement is not observed in any other salen complex due to geometric constraints. The manganese (III) complexes were evaluated for catalytic activity in epoxidation reactions. Despite the fact that these many of these complexes were optically active, little asymmetric induction was observed in any of the epoxidation reactions. This is likely due to the fact that the chiral centers are far from the metal atom.

The investigation of a soluble nickel salen complex for the epoxidation of olefins led to the discovery of a new heterogeneous catalyst for the epoxidation of α,β-unsaturated carboxylic acids. Nickel salen complexes, upon reaction with commercial bleach, yield a fine black powder, which we identified as nickel oxide hydroxide—a known but poorly characterized nickel peroxide containing species. The reaction of an aqueous nickel (II) source with commercial bleach also yields nickel oxide hydroxide. This material was characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). Extremely broad peaks in the X-ray diffraction pattern suggested that this material consisted of particles with a very small diameter and this was confirmed by TEM. This insoluble material was found to function as a heterogeneous catalyst for the epoxidation of α,β-unsaturated carboxylic acids in the presence of sodium hypochlorite. The high activity of this catalyst in the epoxidation of certain olefins is due in part to its small particle size, which increases the overall surface area of this heterogeneous catalyst. Large particles of nickel oxide hydroxide were prepared and the catalytic activity was comparatively less.

The oxidation of several other organic substrates was also explored using this catalyst. Both primary and secondary alcohols can be oxidized with our nickel-based system. Primary alcohols go through an aldehyde intermediate which is then in turn oxidized to the carboxylic acid.

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APPENDIX A

NEW SALEN LIGANDS BASED ON 2,2’-BIPHENOL AND BINAPHTHOL

X-Ray Structure Data for **3-4-Mn** (sm38)

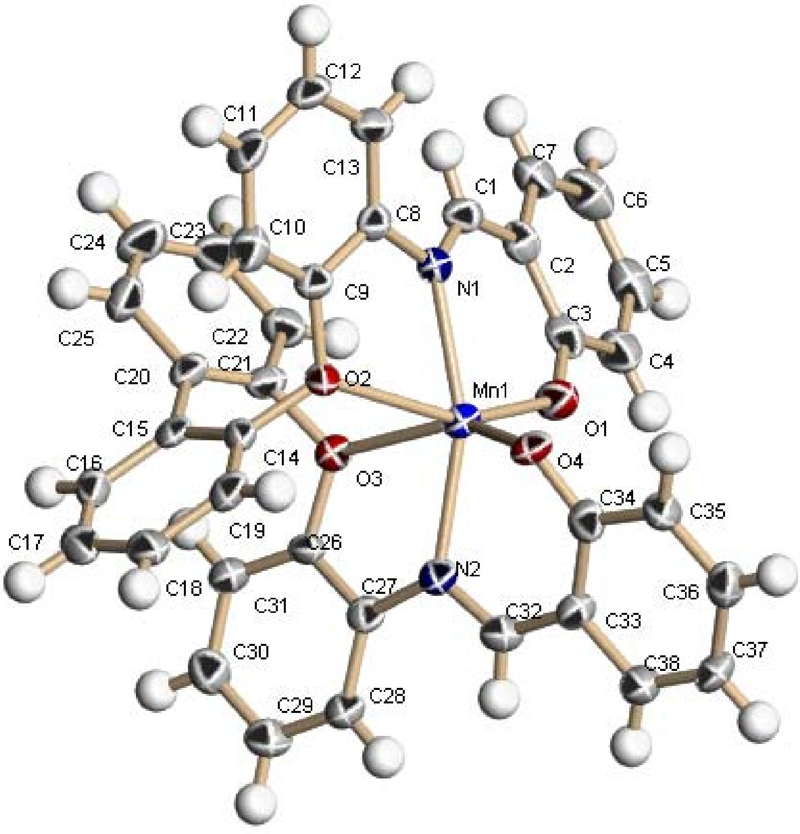


Table A.1. Crystal data and structure refinement for sm38.

Identification code	sm38	
CCDC number	265655	
Empirical formula	C38 H26 Mn N2 O4	
Formula weight	629.55	
Temperature	110(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.040(2) Å	α= 84.865(11)°.
	b = 10.464(2) Å	β= 79.931(11)°.
	c = 15.633(3) Å	γ = 66.126(11)°.
Volume	1478.4(5) Å^3	
Z	2	
Density (calculated)	1.414 Mg/m^3	
Absorption coefficient	4.004 mm^{-1}	
F(000)	650	
Crystal size	0.10 x 0.10 x 0.01 mm^3	
Theta range for data collection	2.87 to 58.75°.	
Index ranges	-11<=h<=11, -11<=k<=11, -17<=l<=17	
Reflections collected	13845	
Independent reflections	4035 [R(int) = 0.0966]	
Completeness to theta = 58.75°	95.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9611 and 0.6903	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4035 / 0 / 407	
Goodness-of-fit on F^2	1.068	
Final R indices [I>2sigma(I)]	R1 = 0.0475, wR2 = 0.0646	
R indices (all data)	R1 = 0.1017, wR2 = 0.0725	
Extinction coefficient	0.00083(9)	
Largest diff. peak and hole	0.339 and -0.428 e.Å^{-3}	

Table A.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for sm38. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Mn(1)	1775(1)	3818(1)	2323(1)	28(1)
O(1)	901(3)	2482(3)	2068(2)	33(1)
O(2)	3114(3)	4529(3)	3150(2)	25(1)
O(3)	4227(3)	2193(3)	2041(2)	28(1)
O(4)	282(3)	5800(3)	2250(2)	30(1)
N(1)	1585(3)	2982(4)	3675(2)	25(1)
N(2)	2791(4)	4223(4)	1006(2)	27(1)
C(1)	1336(4)	1874(4)	3888(3)	27(1)
C(2)	1038(4)	1013(4)	3356(3)	27(1)
C(3)	844(4)	1360(5)	2451(3)	30(1)
C(4)	574(4)	386(5)	2017(3)	35(1)
C(5)	490(4)	-801(5)	2401(3)	42(1)
C(6)	685(5)	-1128(5)	3276(3)	44(1)
C(7)	948(4)	-219(5)	3721(3)	38(1)
C(8)	1899(4)	3643(4)	4327(3)	22(1)
C(9)	2742(4)	4417(4)	4049(3)	27(1)
C(10)	3154(4)	5074(4)	4615(3)	33(1)
C(11)	2689(4)	4960(5)	5502(3)	38(1)
C(12)	1808(4)	4252(4)	5790(3)	34(1)
C(13)	1419(4)	3570(4)	5217(3)	30(1)
C(14)	4467(4)	4631(5)	2842(2)	24(1)
C(15)	5766(5)	3432(5)	2820(2)	27(1)
C(16)	7076(4)	3583(5)	2510(2)	31(1)
C(17)	7087(5)	4853(5)	2233(2)	34(1)
C(18)	5791(5)	6026(5)	2247(2)	34(1)
C(19)	4454(4)	5921(5)	2568(2)	31(1)
C(20)	5725(4)	2073(5)	3113(2)	29(1)
C(21)	5008(4)	1439(5)	2725(2)	27(1)

Table A.2 continued

	x	y	z	U(eq)
C(22)	4929(4)	193(5)	2974(3)	33(1)
C(23)	5647(5)	-545(5)	3664(3)	43(1)
C(24)	6387(5)	30(5)	4061(3)	47(1)
C(25)	6463(4)	1275(5)	3795(3)	40(1)
C(26)	5059(5)	2338(4)	1241(2)	24(1)
C(27)	4261(4)	3371(4)	681(2)	25(1)
C(28)	5022(4)	3498(5)	-138(2)	33(1)
C(29)	6488(5)	2655(5)	-363(3)	33(1)
C(30)	7254(5)	1673(5)	223(3)	36(1)
C(31)	6519(4)	1540(4)	1038(3)	30(1)
C(32)	1947(5)	5087(4)	479(3)	30(1)
C(33)	486(4)	6094(4)	691(3)	27(1)
C(34)	-282(5)	6434(4)	1556(3)	27(1)
C(35)	-1708(4)	7487(4)	1649(3)	29(1)
C(36)	-2387(4)	8153(4)	941(3)	31(1)
C(37)	-1634(5)	7808(4)	101(3)	31(1)
C(38)	-227(5)	6835(4)	-14(3)	32(1)

Table A.3. Bond lengths [Å] and angles [°] for sm38.

Mn(1)-O(4)	2.016(3)
Mn(1)-O(1)	2.024(3)
Mn(1)-N(2)	2.218(3)
Mn(1)-N(1)	2.220(3)
Mn(1)-O(3)	2.348(3)
Mn(1)-O(2)	2.370(2)
O(1)-C(3)	1.288(5)
O(2)-C(9)	1.398(4)
O(2)-C(14)	1.403(4)
O(3)-C(26)	1.410(4)
O(3)-C(21)	1.421(4)
O(4)-C(34)	1.311(4)
N(1)-C(1)	1.287(4)
N(1)-C(8)	1.426(4)
N(2)-C(32)	1.306(4)
N(2)-C(27)	1.409(5)
C(1)-C(2)	1.426(5)
C(2)-C(7)	1.392(5)
C(2)-C(3)	1.455(5)
C(3)-C(4)	1.408(5)
C(4)-C(5)	1.358(5)
C(5)-C(6)	1.408(5)
C(6)-C(7)	1.359(5)
C(8)-C(9)	1.387(5)
C(8)-C(13)	1.396(5)
C(9)-C(10)	1.376(5)
C(10)-C(11)	1.395(5)
C(11)-C(12)	1.366(5)
C(12)-C(13)	1.388(5)
C(14)-C(19)	1.375(5)
C(14)-C(15)	1.394(5)
C(15)-C(16)	1.386(5)

Table A.3 continued

C(15)-C(20)	1.469(5)
C(16)-C(17)	1.365(5)
C(17)-C(18)	1.380(5)
C(18)-C(19)	1.392(5)
C(20)-C(21)	1.392(5)
C(20)-C(25)	1.414(5)
C(21)-C(22)	1.356(5)
C(22)-C(23)	1.397(5)
C(23)-C(24)	1.374(6)
C(24)-C(25)	1.361(5)
C(26)-C(31)	1.357(5)
C(26)-C(27)	1.396(5)
C(27)-C(28)	1.397(5)
C(28)-C(29)	1.374(5)
C(29)-C(30)	1.388(5)
C(30)-C(31)	1.382(5)
C(32)-C(33)	1.419(5)
C(33)-C(38)	1.415(5)
C(33)-C(34)	1.431(5)
C(34)-C(35)	1.401(5)
C(35)-C(36)	1.385(5)
C(36)-C(37)	1.393(5)
C(37)-C(38)	1.358(5)
O(4)-Mn(1)-O(1)	109.52(11)
O(4)-Mn(1)-N(2)	85.90(12)
O(1)-Mn(1)-N(2)	101.65(11)
O(4)-Mn(1)-N(1)	110.26(11)
O(1)-Mn(1)-N(1)	84.64(12)
N(2)-Mn(1)-N(1)	159.85(12)
O(4)-Mn(1)-O(3)	149.22(10)
O(1)-Mn(1)-O(3)	94.64(10)
N(2)-Mn(1)-O(3)	70.35(11)

Table A.3 continued

O(4)-Mn(1)-O(2)	90.92(10)
O(1)-Mn(1)-O(2)	152.10(10)
N(2)-Mn(1)-O(2)	98.48(10)
N(1)-Mn(1)-O(2)	70.20(10)
O(3)-Mn(1)-O(2)	74.18(9)
C(3)-O(1)-Mn(1)	133.1(3)
C(9)-O(2)-C(14)	117.1(3)
C(9)-O(2)-Mn(1)	114.6(2)
C(14)-O(2)-Mn(1)	125.4(2)
C(26)-O(3)-C(21)	117.8(3)
C(26)-O(3)-Mn(1)	117.1(2)
C(21)-O(3)-Mn(1)	121.5(2)
C(34)-O(4)-Mn(1)	126.2(3)
C(1)-N(1)-C(8)	118.3(3)
C(1)-N(1)-Mn(1)	123.9(3)
C(8)-N(1)-Mn(1)	117.4(3)
C(32)-N(2)-C(27)	119.4(3)
C(32)-N(2)-Mn(1)	119.0(3)
C(27)-N(2)-Mn(1)	120.4(3)
N(1)-C(1)-C(2)	128.9(4)
C(7)-C(2)-C(1)	118.1(4)
C(7)-C(2)-C(3)	119.1(4)
C(1)-C(2)-C(3)	122.8(4)
O(1)-C(3)-C(4)	121.7(4)
O(1)-C(3)-C(2)	122.9(4)
C(4)-C(3)-C(2)	115.4(4)
C(5)-C(4)-C(3)	123.5(4)
C(4)-C(5)-C(6)	120.6(5)
C(7)-C(6)-C(5)	118.0(4)
C(6)-C(7)-C(2)	123.5(4)
C(9)-C(8)-C(13)	118.1(4)
C(9)-C(8)-N(1)	117.0(4)

Table A.3 continued

C(13)-C(8)-N(1)	124.9(4)
C(10)-C(9)-C(8)	122.7(4)
C(10)-C(9)-O(2)	121.5(4)
C(8)-C(9)-O(2)	115.7(4)
C(9)-C(10)-C(11)	118.2(4)
C(12)-C(11)-C(10)	120.3(4)
C(11)-C(12)-C(13)	121.2(4)
C(12)-C(13)-C(8)	119.6(4)
C(19)-C(14)-C(15)	122.5(4)
C(19)-C(14)-O(2)	118.2(4)
C(15)-C(14)-O(2)	119.3(4)
C(16)-C(15)-C(14)	117.2(4)
C(16)-C(15)-C(20)	122.2(4)
C(14)-C(15)-C(20)	120.6(4)
C(17)-C(16)-C(15)	121.2(4)
C(16)-C(17)-C(18)	120.9(4)
C(17)-C(18)-C(19)	119.6(4)
C(14)-C(19)-C(18)	118.5(4)
C(21)-C(20)-C(25)	114.4(4)
C(21)-C(20)-C(15)	123.1(4)
C(25)-C(20)-C(15)	122.4(4)
C(22)-C(21)-C(20)	125.3(4)
C(22)-C(21)-O(3)	117.2(4)
C(20)-C(21)-O(3)	117.3(4)
C(21)-C(22)-C(23)	118.3(4)
C(24)-C(23)-C(22)	118.5(5)
C(25)-C(24)-C(23)	122.3(4)
C(24)-C(25)-C(20)	121.1(4)
C(31)-C(26)-C(27)	123.0(4)
C(31)-C(26)-O(3)	122.3(4)
C(27)-C(26)-O(3)	114.6(4)
C(26)-C(27)-C(28)	116.5(4)

Table A.3 continued

C(26)-C(27)-N(2)	117.2(4)
C(28)-C(27)-N(2)	126.2(4)
C(29)-C(28)-C(27)	120.8(4)
C(28)-C(29)-C(30)	120.9(4)
C(31)-C(30)-C(29)	119.0(4)
C(26)-C(31)-C(30)	119.6(4)
N(2)-C(32)-C(33)	127.8(4)
C(38)-C(33)-C(32)	116.5(4)
C(38)-C(33)-C(34)	118.6(4)
C(32)-C(33)-C(34)	124.9(4)
O(4)-C(34)-C(35)	119.5(4)
O(4)-C(34)-C(33)	123.1(4)
C(35)-C(34)-C(33)	117.4(4)
C(36)-C(35)-C(34)	122.2(4)
C(35)-C(36)-C(37)	120.0(4)
C(38)-C(37)-C(36)	119.5(4)
C(37)-C(38)-C(33)	122.2(4)

Table A.4. Anisotropic displacement parameters ($Å^2$x 10^3) for sm38. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Mn(1)	28(1)	39(1)	18(1)	3(1)	-6(1)	-15(1)
O(1)	41(2)	38(2)	29(2)	7(2)	-10(1)	-25(2)
O(2)	21(2)	39(2)	16(2)	-2(1)	-1(1)	-14(2)
O(3)	26(2)	36(2)	23(2)	5(2)	-6(1)	-13(2)
O(4)	32(2)	41(2)	15(2)	3(1)	-6(1)	-14(2)
N(1)	21(2)	33(3)	23(2)	3(2)	-5(2)	-13(2)
N(2)	26(2)	36(3)	20(2)	-1(2)	-4(2)	-12(2)
C(1)	21(3)	30(3)	22(3)	3(2)	1(2)	-4(2)
C(2)	20(3)	25(3)	34(3)	-3(2)	-1(2)	-7(2)
C(3)	20(3)	33(3)	34(3)	-12(3)	5(2)	-9(2)
C(4)	36(3)	41(4)	31(3)	-8(3)	0(2)	-19(3)
C(5)	31(3)	43(4)	55(4)	-14(3)	4(3)	-20(3)
C(6)	37(3)	34(3)	59(4)	2(3)	4(3)	-17(3)
C(7)	30(3)	48(4)	36(3)	6(3)	-1(2)	-20(3)
C(8)	17(2)	23(3)	22(3)	2(2)	-5(2)	-3(2)
C(9)	23(3)	35(3)	19(3)	0(2)	-2(2)	-9(2)
C(10)	29(3)	36(3)	33(3)	-6(3)	-8(2)	-10(2)
C(11)	36(3)	61(4)	21(3)	-7(3)	-11(2)	-19(3)
C(12)	31(3)	49(4)	15(3)	-2(2)	-2(2)	-9(3)
C(13)	26(3)	36(3)	22(3)	6(2)	-2(2)	-8(2)
C(14)	20(3)	40(3)	14(2)	-1(2)	-3(2)	-15(3)
C(15)	28(3)	44(3)	11(2)	1(2)	-7(2)	-15(3)
C(16)	20(3)	49(4)	21(3)	-7(2)	-3(2)	-11(3)
C(17)	34(3)	56(4)	21(3)	-9(3)	-2(2)	-27(3)
C(18)	38(3)	52(4)	21(3)	1(2)	-5(2)	-26(3)
C(19)	33(3)	40(3)	22(3)	-1(2)	-12(2)	-15(3)
C(20)	25(3)	41(3)	17(3)	0(2)	-5(2)	-7(3)
C(21)	25(3)	31(3)	18(3)	4(2)	-2(2)	-5(2)
C(22)	32(3)	34(3)	32(3)	6(2)	-2(2)	-15(3)

Table A.4 continued

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(23)	38(3)	35(3)	41(3)	9(3)	3(3)	-6(3)
C(24)	45(3)	50(4)	36(3)	15(3)	-15(3)	-9(3)
C(25)	29(3)	56(4)	33(3)	0(3)	-14(2)	-12(3)
C(26)	27(3)	37(3)	15(3)	2(2)	-3(2)	-20(2)
C(27)	26(3)	30(3)	18(3)	-6(2)	-3(2)	-10(2)
C(28)	30(3)	49(3)	20(3)	3(2)	-6(2)	-17(3)
C(29)	37(3)	36(3)	24(3)	-3(2)	1(2)	-14(3)
C(30)	27(3)	41(3)	37(3)	-4(3)	-1(2)	-11(3)
C(31)	32(3)	39(3)	21(3)	6(2)	-7(2)	-16(3)
C(32)	33(3)	35(3)	23(3)	2(2)	-2(2)	-15(3)
C(33)	30(3)	30(3)	22(3)	4(2)	-8(2)	-12(2)
C(34)	27(3)	30(3)	29(3)	-6(2)	-5(2)	-15(2)
C(35)	24(3)	39(3)	24(3)	-2(2)	-1(2)	-13(3)
C(36)	29(3)	29(3)	38(3)	4(2)	-12(2)	-14(2)
C(37)	34(3)	40(3)	23(3)	2(2)	-14(2)	-15(3)
C(38)	32(3)	43(3)	25(3)	1(2)	-6(2)	-18(3)

Table A.5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for sm38.

	x	y	z	U(eq)
H(1)	1353	1590	4482	33
H(4)	444	569	1425	42
H(5)	297	-1416	2076	50
H(6)	633	-1960	3547	53
H(7)	1078	-434	4312	45
H(10)	3739	5591	4407	39
H(11)	2987	5376	5908	45
H(12)	1454	4226	6394	41
H(13)	831	3057	5429	36
H(16)	7982	2788	2491	37
H(17)	8000	4931	2028	40
H(18)	5809	6901	2039	41
H(19)	3553	6723	2598	37
H(22)	4400	-168	2688	40
H(23)	5625	-1426	3855	51
H(24)	6860	-459	4538	56
H(25)	7022	1615	4072	47
H(28)	4522	4175	-545	40
H(29)	6982	2747	-926	40
H(30)	8269	1100	67	43
H(31)	7033	894	1454	36
H(32)	2361	5035	-118	36
H(35)	-2226	7754	2217	35
H(36)	-3365	8844	1027	37
H(37)	-2101	8250	-387	37
H(38)	297	6645	-588	38

X-Ray Structure Data for **2-4-Co**

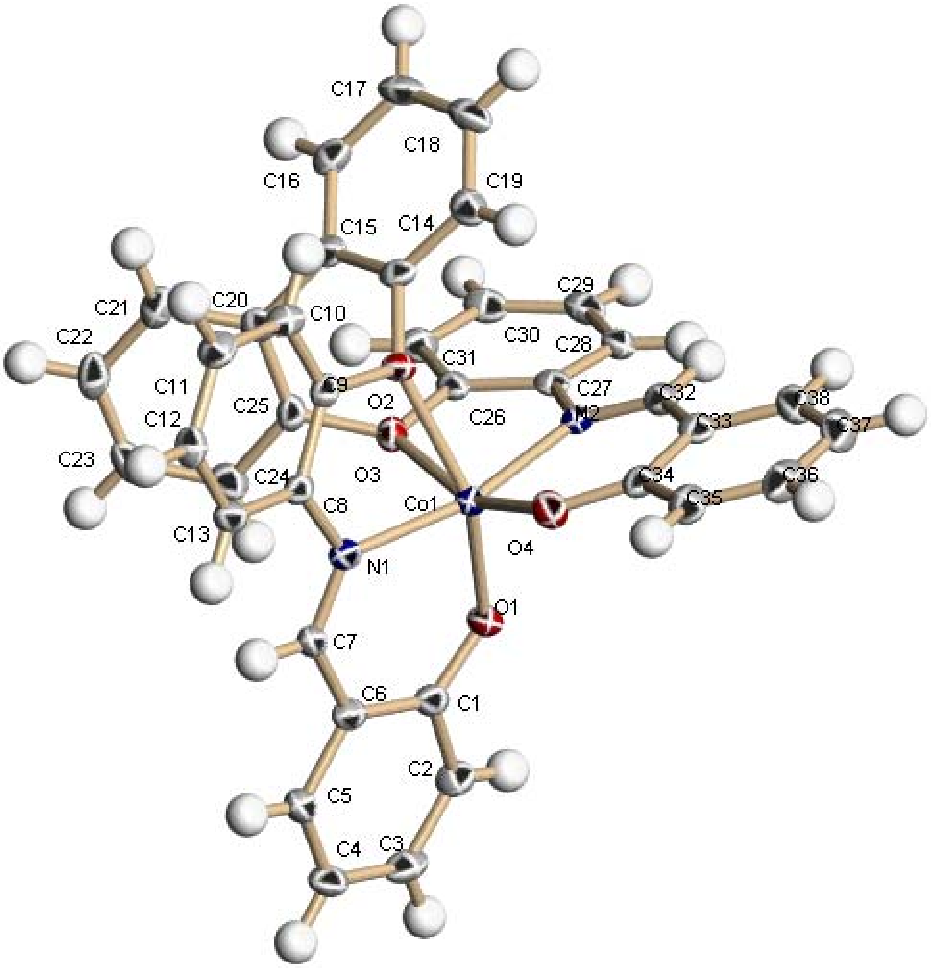


Table A.6. Crystal data and structure refinement for sm39.

Identification code	sm39	
CCDC number	264656	
Empirical formula	C40 H30 Cl4 Co N2 O4	
Formula weight	803.39	
Temperature	110(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.151(5) Å	α= 77.837(5)°.
	b = 12.226(5) Å	β= 88.328(5)°.
	c = 12.890(5) Å	γ = 73.528(5)°.
Volume	1794.1(13) Å^3	
Z	2	
Density (calculated)	1.487 Mg/m^3	
Absorption coefficient	6.860 mm^{-1}	
F(000)	822	
Crystal size	0.30 x 0.10 x 0.05 mm^3	
Theta range for data collection	3.51 to 58.91°.	
Index ranges	-13<=h<=13, -12<=k<=13, -14<=l<=14	
Reflections collected	10841	
Independent reflections	4868 [R(int) = 0.0318]	
Completeness to theta = 58.91°	94.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7254 and 0.2327	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4868 / 0 / 461	
Goodness-of-fit on F^2	1.059	
Final R indices [I>2sigma(I)]	R1 = 0.0427, wR2 = 0.0991	
R indices (all data)	R1 = 0.0556, wR2 = 0.1047	
Extinction coefficient	0.00008(11)	
Largest diff. peak and hole	0.811 and -0.586 e.Å^{-3}	

Table A.7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for sm39. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Co(1)	4288(1)	4576(1)	7557(1)	16(1)
Cl(1)	1484(1)	74(1)	7501(1)	36(1)
Cl(2)	173(1)	1270(1)	5542(1)	77(1)
Cl(3)	9359(1)	8400(1)	8136(1)	54(1)
Cl(4)	6905(1)	8910(2)	7694(1)	83(1)
O(1)	5866(2)	3633(2)	7392(2)	21(1)
O(2)	2467(2)	4972(2)	8072(2)	17(1)
O(3)	3678(2)	3098(2)	7290(2)	17(1)
O(4)	4261(2)	6189(2)	7592(2)	22(1)
N(1)	4431(2)	4029(2)	9201(2)	16(1)
N(2)	3800(2)	5035(2)	5962(2)	15(1)
C(1)	6628(3)	3002(3)	8139(3)	18(1)
C(2)	7723(3)	2395(3)	7843(3)	22(1)
C(3)	8587(3)	1759(3)	8579(3)	25(1)
C(4)	8417(3)	1676(3)	9661(3)	24(1)
C(5)	7353(3)	2219(3)	9989(3)	22(1)
C(6)	6442(3)	2873(3)	9256(3)	18(1)
C(7)	5370(3)	3384(3)	9707(3)	17(1)
C(8)	3425(3)	4450(3)	9759(2)	15(1)
C(9)	2390(3)	4916(3)	9172(2)	16(1)
C(10)	1359(3)	5351(3)	9618(3)	21(1)
C(11)	1352(3)	5342(3)	10698(3)	22(1)
C(12)	2366(3)	4904(3)	11300(3)	20(1)
C(13)	3396(3)	4456(3)	10849(2)	18(1)
C(14)	1518(3)	4905(3)	7523(2)	17(1)
C(15)	1295(3)	3826(3)	7619(2)	16(1)
C(16)	346(3)	3793(3)	7047(3)	22(1)
C(17)	-324(3)	4800(3)	6391(3)	26(1)

Table A.7 continued

	x	y	z	U(eq)
C(18)	-60(3)	5844(3)	6293(3)	26(1)
C(19)	860(3)	5915(3)	6862(3)	22(1)
C(20)	2057(3)	2731(3)	8269(2)	18(1)
C(21)	1635(3)	2001(3)	9065(3)	23(1)
C(22)	2357(3)	956(3)	9616(3)	26(1)
C(23)	3507(3)	623(3)	9388(3)	28(1)
C(24)	3949(3)	1336(3)	8611(3)	25(1)
C(25)	3219(3)	2374(3)	8065(2)	17(1)
C(26)	3437(3)	3162(3)	6222(2)	17(1)
C(27)	3560(3)	4154(3)	5515(2)	16(1)
C(28)	3452(3)	4201(3)	4425(3)	19(1)
C(29)	3199(3)	3293(3)	4087(3)	22(1)
C(30)	2999(3)	2359(3)	4809(3)	23(1)
C(31)	3127(3)	2283(3)	5891(3)	21(1)
C(32)	3664(3)	6069(3)	5387(3)	19(1)
C(33)	3829(3)	7065(3)	5721(3)	18(1)
C(34)	4115(3)	7076(3)	6795(3)	19(1)
C(35)	4254(3)	8135(3)	6972(3)	23(1)
C(36)	4174(3)	9088(3)	6164(3)	28(1)
C(37)	3908(3)	9068(3)	5123(3)	28(1)
C(38)	3732(3)	8077(3)	4919(3)	25(1)
C(39)	1042(4)	-78(4)	6262(3)	40(1)
C(40)	8191(4)	7841(4)	8128(4)	47(1)

Table A.8. Bond lengths [Å] and angles [°] for sm39.

Co(1)-O(1)	1.969(2)
Co(1)-O(4)	1.973(2)
Co(1)-N(2)	2.072(3)
Co(1)-N(1)	2.080(3)
Co(1)-O(3)	2.229(2)
Co(1)-O(2)	2.240(2)
Cl(1)-C(39)	1.762(4)
Cl(2)-C(39)	1.767(4)
Cl(3)-C(40)	1.743(5)
Cl(4)-C(40)	1.746(5)
O(1)-C(1)	1.309(4)
O(2)-C(14)	1.400(4)
O(2)-C(9)	1.407(4)
O(3)-C(26)	1.397(4)
O(3)-C(25)	1.403(4)
O(4)-C(34)	1.301(4)
N(1)-C(7)	1.290(4)
N(1)-C(8)	1.422(4)
N(2)-C(32)	1.292(4)
N(2)-C(27)	1.422(4)
C(1)-C(2)	1.413(5)
C(1)-C(6)	1.432(5)
C(2)-C(3)	1.375(5)
C(3)-C(4)	1.390(5)
C(4)-C(5)	1.374(5)
C(5)-C(6)	1.413(5)
C(6)-C(7)	1.440(5)
C(8)-C(9)	1.395(5)
C(8)-C(13)	1.405(5)
C(9)-C(10)	1.376(5)
C(10)-C(11)	1.390(5)
C(11)-C(12)	1.384(5)

Table A.8 continued

C(12)-C(13)	1.381(5)
C(14)-C(19)	1.388(5)
C(14)-C(15)	1.399(5)
C(15)-C(16)	1.402(5)
C(15)-C(20)	1.490(5)
C(16)-C(17)	1.387(5)
C(17)-C(18)	1.382(5)
C(18)-C(19)	1.387(5)
C(20)-C(25)	1.390(5)
C(20)-C(21)	1.398(5)
C(21)-C(22)	1.388(5)
C(22)-C(23)	1.382(5)
C(23)-C(24)	1.385(5)
C(24)-C(25)	1.384(5)
C(26)-C(31)	1.382(5)
C(26)-C(27)	1.398(5)
C(27)-C(28)	1.403(5)
C(28)-C(29)	1.385(5)
C(29)-C(30)	1.387(5)
C(30)-C(31)	1.389(5)
C(32)-C(33)	1.440(5)
C(33)-C(38)	1.414(5)
C(33)-C(34)	1.441(5)
C(34)-C(35)	1.417(5)
C(35)-C(36)	1.372(5)
C(36)-C(37)	1.395(5)
C(37)-C(38)	1.367(5)
O(1)-Co(1)-O(4)	110.48(10)
O(1)-Co(1)-N(2)	96.86(9)
O(4)-Co(1)-N(2)	92.10(10)
O(1)-Co(1)-N(1)	91.89(9)
O(4)-Co(1)-N(1)	93.57(10)

Table A.8 continued

N(2)-Co(1)-N(1)	167.20(10)
O(1)-Co(1)-O(3)	88.14(9)
O(4)-Co(1)-O(3)	159.21(9)
N(2)-Co(1)-O(3)	76.04(9)
N(1)-Co(1)-O(3)	95.00(10)
O(1)-Co(1)-O(2)	158.02(9)
O(4)-Co(1)-O(2)	88.80(9)
N(2)-Co(1)-O(2)	92.72(9)
N(1)-Co(1)-O(2)	75.95(9)
O(3)-Co(1)-O(2)	75.01(8)
C(1)-O(1)-Co(1)	128.0(2)
C(14)-O(2)-C(9)	118.0(2)
C(14)-O(2)-Co(1)	126.76(18)
C(9)-O(2)-Co(1)	112.06(17)
C(26)-O(3)-C(25)	118.4(2)
C(26)-O(3)-Co(1)	113.38(18)
C(25)-O(3)-Co(1)	125.35(18)
C(34)-O(4)-Co(1)	127.8(2)
C(7)-N(1)-C(8)	120.8(3)
C(7)-N(1)-Co(1)	123.5(2)
C(8)-N(1)-Co(1)	115.68(19)
C(32)-N(2)-C(27)	119.9(3)
C(32)-N(2)-Co(1)	123.6(2)
C(27)-N(2)-Co(1)	116.4(2)
O(1)-C(1)-C(2)	118.7(3)
O(1)-C(1)-C(6)	124.9(3)
C(2)-C(1)-C(6)	116.4(3)
C(3)-C(2)-C(1)	122.2(3)
C(2)-C(3)-C(4)	121.1(3)
C(5)-C(4)-C(3)	118.7(3)
C(4)-C(5)-C(6)	121.7(3)
C(5)-C(6)-C(1)	119.7(3)

Table A.8 continued

C(5)-C(6)-C(7)	116.0(3)
C(1)-C(6)-C(7)	124.3(3)
N(1)-C(7)-C(6)	127.2(3)
C(9)-C(8)-C(13)	117.5(3)
C(9)-C(8)-N(1)	117.3(3)
C(13)-C(8)-N(1)	125.2(3)
C(10)-C(9)-C(8)	122.9(3)
C(10)-C(9)-O(2)	121.2(3)
C(8)-C(9)-O(2)	115.9(3)
C(9)-C(10)-C(11)	118.5(3)
C(12)-C(11)-C(10)	120.1(3)
C(13)-C(12)-C(11)	121.0(3)
C(12)-C(13)-C(8)	120.0(3)
C(19)-C(14)-O(2)	118.0(3)
C(19)-C(14)-C(15)	122.4(3)
O(2)-C(14)-C(15)	119.5(3)
C(16)-C(15)-C(14)	117.8(3)
C(16)-C(15)-C(20)	120.2(3)
C(14)-C(15)-C(20)	122.0(3)
C(17)-C(16)-C(15)	120.3(3)
C(18)-C(17)-C(16)	120.4(3)
C(17)-C(18)-C(19)	120.9(3)
C(18)-C(19)-C(14)	118.2(3)
C(25)-C(20)-C(21)	117.5(3)
C(25)-C(20)-C(15)	120.3(3)
C(21)-C(20)-C(15)	122.2(3)
C(22)-C(21)-C(20)	120.7(3)
C(23)-C(22)-C(21)	120.4(3)
C(22)-C(23)-C(24)	120.2(3)
C(25)-C(24)-C(23)	118.9(3)
C(24)-C(25)-C(20)	122.5(3)
C(24)-C(25)-O(3)	118.5(3)

Table A.8 continued

C(20)-C(25)-O(3)	119.0(3)
C(31)-C(26)-O(3)	121.8(3)
C(31)-C(26)-C(27)	122.6(3)
O(3)-C(26)-C(27)	115.5(3)
C(28)-C(27)-C(26)	117.8(3)
C(28)-C(27)-N(2)	125.1(3)
C(26)-C(27)-N(2)	117.1(3)
C(29)-C(28)-C(27)	119.7(3)
C(30)-C(29)-C(28)	121.2(3)
C(29)-C(30)-C(31)	120.0(3)
C(26)-C(31)-C(30)	118.5(3)
N(2)-C(32)-C(33)	127.0(3)
C(38)-C(33)-C(34)	119.1(3)
C(38)-C(33)-C(32)	116.4(3)
C(34)-C(33)-C(32)	124.4(3)
O(4)-C(34)-C(35)	119.0(3)
O(4)-C(34)-C(33)	124.6(3)
C(35)-C(34)-C(33)	116.4(3)
C(36)-C(35)-C(34)	122.4(3)
C(35)-C(36)-C(37)	120.9(3)
C(38)-C(37)-C(36)	118.8(3)
C(37)-C(38)-C(33)	122.4(3)
Cl(1)-C(39)-Cl(2)	110.6(2)
Cl(3)-C(40)-Cl(4)	113.4(3)

Table A.9. Anisotropic displacement parameters ($Å^2 x 10^3$) for sm39. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Co(1)	13(1)	16(1)	16(1)	-1(1)	-1(1)	-3(1)
Cl(1)	28(1)	47(1)	34(1)	-16(1)	2(1)	-6(1)
Cl(2)	126(1)	48(1)	58(1)	3(1)	-44(1)	-30(1)
Cl(3)	51(1)	64(1)	61(1)	-30(1)	17(1)	-29(1)
Cl(4)	58(1)	123(1)	57(1)	-38(1)	-25(1)	8(1)
O(1)	16(1)	25(1)	19(1)	0(1)	-2(1)	-4(1)
O(2)	12(1)	22(1)	17(1)	-4(1)	-2(1)	-5(1)
O(3)	17(1)	16(1)	16(1)	-1(1)	2(1)	-5(1)
O(4)	25(1)	19(1)	20(1)	-2(1)	-3(1)	-7(1)
N(1)	14(1)	16(1)	18(1)	-2(1)	0(1)	-5(1)
N(2)	11(1)	17(2)	17(1)	-3(1)	1(1)	-5(1)
C(1)	15(2)	16(2)	24(2)	-1(1)	-2(2)	-6(1)
C(2)	18(2)	24(2)	23(2)	-8(2)	4(2)	-5(2)
C(3)	13(2)	20(2)	40(2)	-8(2)	3(2)	-3(2)
C(4)	16(2)	19(2)	33(2)	1(2)	-6(2)	-3(2)
C(5)	20(2)	22(2)	21(2)	3(2)	-3(2)	-6(2)
C(6)	14(2)	15(2)	25(2)	-1(1)	-2(1)	-5(1)
C(7)	16(2)	18(2)	17(2)	2(1)	-2(1)	-7(2)
C(8)	13(2)	12(2)	20(2)	-2(1)	1(1)	-5(1)
C(9)	18(2)	14(2)	16(2)	-3(1)	2(1)	-8(1)
C(10)	16(2)	22(2)	25(2)	-6(2)	0(2)	-5(2)
C(11)	19(2)	23(2)	23(2)	-8(2)	6(2)	-5(2)
C(12)	27(2)	20(2)	15(2)	-4(1)	4(2)	-8(2)
C(13)	16(2)	17(2)	20(2)	-2(1)	-2(1)	-6(1)
C(14)	11(2)	24(2)	17(2)	-8(1)	2(1)	-4(1)
C(15)	13(2)	23(2)	13(2)	-5(1)	4(1)	-5(1)
C(16)	19(2)	28(2)	22(2)	-10(2)	6(2)	-11(2)
C(17)	14(2)	43(2)	21(2)	-11(2)	-5(2)	-3(2)
C(18)	19(2)	34(2)	20(2)	-4(2)	-4(2)	2(2)

Table A.9 continued

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(19)	19(2)	22(2)	20(2)	-4(2)	1(2)	-1(2)
C(20)	19(2)	22(2)	15(2)	-6(1)	-2(1)	-6(2)
C(21)	26(2)	27(2)	21(2)	-5(2)	5(2)	-13(2)
C(22)	40(2)	22(2)	22(2)	-1(2)	1(2)	-21(2)
C(23)	36(2)	19(2)	24(2)	5(2)	-8(2)	-6(2)
C(24)	21(2)	23(2)	26(2)	-3(2)	-1(2)	-1(2)
C(25)	22(2)	15(2)	16(2)	0(1)	1(1)	-10(2)
C(26)	12(2)	22(2)	14(2)	-3(1)	1(1)	-2(1)
C(27)	9(2)	17(2)	20(2)	-3(1)	-1(1)	1(1)
C(28)	15(2)	24(2)	17(2)	-1(1)	-1(1)	-3(1)
C(29)	17(2)	26(2)	19(2)	-6(2)	-3(1)	1(2)
C(30)	19(2)	24(2)	25(2)	-9(2)	-2(2)	-1(2)
C(31)	18(2)	16(2)	26(2)	-4(2)	-1(2)	-2(1)
C(32)	14(2)	24(2)	17(2)	-3(2)	1(1)	-5(1)
C(33)	11(2)	17(2)	24(2)	-3(1)	2(1)	0(1)
C(34)	12(2)	16(2)	26(2)	-2(2)	4(1)	-3(1)
C(35)	22(2)	21(2)	25(2)	-7(2)	5(2)	-6(2)
C(36)	25(2)	18(2)	41(2)	-8(2)	7(2)	-7(2)
C(37)	28(2)	16(2)	34(2)	4(2)	3(2)	-1(2)
C(38)	22(2)	23(2)	26(2)	1(2)	0(2)	-3(2)
C(39)	41(2)	47(3)	38(2)	-16(2)	1(2)	-16(2)
C(40)	58(3)	41(3)	49(3)	-15(2)	-6(2)	-22(2)

Table A.10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10 ^{3}) for sm39.

	x	y	z	U(eq)
H(2)	7868	2428	7110	26
H(3)	9312	1369	8345	30
H(4)	9024	1253	10164	29
H(5)	7227	2152	10727	27
H(7)	5352	3229	10460	21
H(10)	668	5649	9198	25
H(11)	650	5639	11023	26
H(12)	2354	4910	12036	24
H(13)	4084	4153	11274	21
H(16)	161	3078	7107	26
H(17)	-968	4772	6008	32
H(18)	-515	6523	5829	32
H(19)	1036	6635	6800	26
H(21)	846	2223	9230	28
H(22)	2059	466	10153	31
H(23)	3995	-96	9765	34
H(24)	4741	1115	8455	29
H(28)	3551	4851	3921	23
H(29)	3162	3311	3349	26
H(30)	2775	1772	4562	27
H(31)	3003	1642	6392	25
H(32)	3430	6185	4666	23
H(35)	4409	8187	7675	27
H(36)	4301	9771	6314	33
H(37)	3851	9731	4567	34
H(38)	3536	8068	4214	30
H(39A)	604	-662	6374	48
H(39B)	1725	-362	5850	48

Table A.10 continuted

	x	y	z	U(eq)
H(40A)	8098	7419	8855	56
H(40B)	8353	7270	7661	56

X-Ray Structure Data for **2-4-Ni** (sm43)

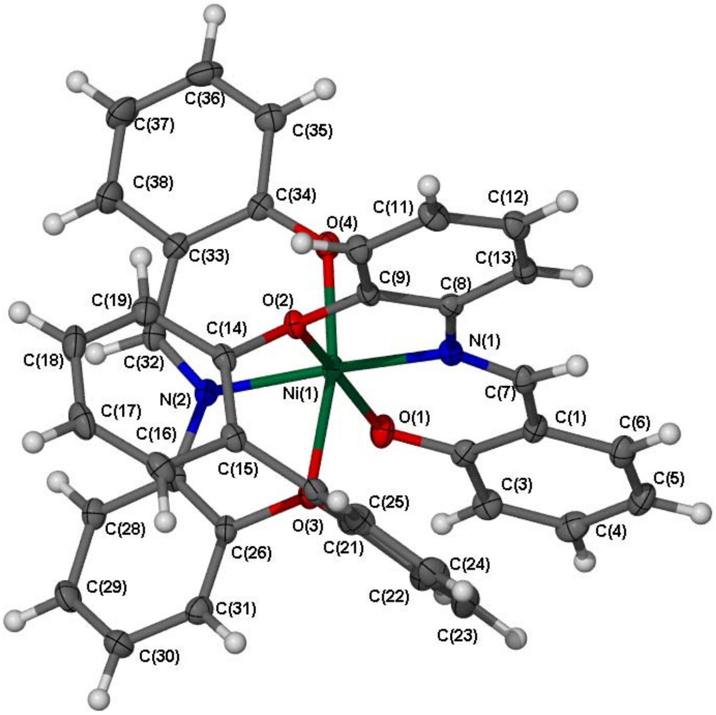


Table A.11. Crystal data and structure refinement for sm43.

Identification code	sm43	
CCDC number	264658	
Empirical formula	C40 H30 Cl4 N2 Ni O4	
Formula weight	803.17	
Temperature	110(2) K	
Wavelength	0.71069 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.062(5) Å	α= 78.888(5)°.
	b = 12.119(5) Å	β= 88.475(5)°.
	c = 12.858(5) Å	γ = 74.846(5)°.
Volume	1779.6(12) $Å^3$	
Z	2	
Density (calculated)	1.499 Mg/m^3	
Absorption coefficient	0.891 mm^{-1}	
F(000)	824	
Crystal size	0.30 x 0.30 x 0.10 mm^3	
Theta range for data collection	1.61 to 28.29°.	
Index ranges	-15<=h<=15, -16<=k<=16, -17<=l<=16	
Reflections collected	19921	
Independent reflections	7993 [R(int) = 0.0302]	
Completeness to theta = 28.29°	90.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9162 and 0.7759	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7993 / 4 / 476	
Goodness-of-fit on F^2	1.079	
Final R indices [I>2sigma(I)]	R1 = 0.0452, wR2 = 0.1179	
R indices (all data)	R1 = 0.0574, wR2 = 0.1323	
Largest diff. peak and hole	1.114 and -0.530 $e.Å^{-3}$	

Table A.12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for sm43. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ni(1)	4277(1)	4593(1)	7566(1)	14(1)
Cl(1)	1505(1)	59(1)	7535(1)	39(1)
Cl(2)	196(1)	1240(1)	5596(1)	67(1)
O(1)	5870(1)	3769(2)	7341(1)	20(1)
O(2)	2473(1)	5070(2)	8034(1)	16(1)
O(3)	3722(1)	3082(1)	7326(1)	16(1)
O(4)	4374(2)	6164(2)	7640(1)	19(1)
N(1)	4414(2)	4058(2)	9148(2)	16(1)
N(2)	3816(2)	5030(2)	6020(2)	15(1)
C(1)	6406(2)	2911(2)	9178(2)	18(1)
C(2)	6609(2)	3093(2)	8062(2)	18(1)
C(3)	7700(2)	2496(2)	7743(2)	22(1)
C(4)	8538(2)	1813(2)	8460(2)	24(1)
C(5)	8356(2)	1676(2)	9549(2)	24(1)
C(6)	7304(2)	2211(2)	9894(2)	22(1)
C(7)	5348(2)	3404(2)	9648(2)	18(1)
C(8)	3417(2)	4465(2)	9727(2)	15(1)
C(9)	2387(2)	4966(2)	9137(2)	15(1)
C(10)	1358(2)	5388(2)	9595(2)	20(1)
C(11)	1342(2)	5321(2)	10688(2)	22(1)
C(12)	2348(2)	4849(2)	11289(2)	21(1)
C(13)	3380(2)	4420(2)	10820(2)	18(1)
C(14)	1533(2)	4949(2)	7483(2)	17(1)
C(15)	1305(2)	3862(2)	7605(2)	17(1)
C(16)	359(2)	3795(2)	7039(2)	22(1)
C(17)	-306(2)	4765(3)	6371(2)	25(1)
C(18)	-32(2)	5820(3)	6245(2)	26(1)
C(19)	892(2)	5920(2)	6808(2)	21(1)

Table A.12 continued

	x	y	z	U(eq)
C(20)	2039(2)	2796(2)	8276(2)	18(1)
C(21)	3206(2)	2411(2)	8101(2)	18(1)
C(22)	3904(2)	1393(2)	8671(2)	23(1)
C(23)	3416(3)	718(2)	9453(2)	28(1)
C(24)	2260(3)	1072(2)	9649(2)	27(1)
C(25)	1572(2)	2095(2)	9066(2)	23(1)
C(26)	3449(2)	3143(2)	6260(2)	16(1)
C(27)	3563(2)	4140(2)	5561(2)	16(1)
C(28)	3420(2)	4182(2)	4477(2)	19(1)
C(29)	3133(2)	3279(2)	4136(2)	24(1)
C(30)	2957(2)	2333(2)	4852(2)	24(1)
C(31)	3124(2)	2261(2)	5928(2)	21(1)
C(32)	3700(2)	6061(2)	5449(2)	19(1)
C(33)	3883(2)	7050(2)	5804(2)	19(1)
C(34)	4203(2)	7058(2)	6865(2)	17(1)
C(35)	4359(2)	8117(2)	7066(2)	23(1)
C(36)	4253(3)	9081(2)	6279(2)	28(1)
C(37)	3952(3)	9069(2)	5238(2)	31(1)
C(38)	3769(2)	8073(2)	5016(2)	26(1)
C(39)	1047(3)	-97(3)	6293(3)	46(1)
C(40)	1781(2)	2015(2)	1962(4)	52(2)
Cl(3)	505(1)	1660(1)	1838(1)	47(1)
Cl(4)	2913(2)	850(2)	2464(1)	92(1)
C(40')	2786(5)	1535(4)	2089(13)	45(1)
Cl(3')	1359(4)	2142(4)	2289(3)	45(1)
Cl(4')	3149(3)	37(4)	2335(3)	45(1)

Table A.13. Bond lengths [Å] and angles [°] for sm43.

Ni(1)-O(4)	1.9577(19)
Ni(1)-O(1)	1.9630(18)
Ni(1)-N(2)	2.009(2)
Ni(1)-N(1)	2.010(2)
Ni(1)-O(3)	2.1835(18)
Ni(1)-O(2)	2.1997(18)
Cl(1)-C(39)	1.762(3)
Cl(2)-C(39)	1.761(4)
O(1)-C(2)	1.302(3)
O(2)-C(9)	1.403(3)
O(2)-C(14)	1.406(3)
O(3)-C(21)	1.401(3)
O(3)-C(26)	1.402(3)
O(4)-C(34)	1.298(3)
N(1)-C(7)	1.299(3)
N(1)-C(8)	1.423(3)
N(2)-C(32)	1.297(3)
N(2)-C(27)	1.426(3)
C(1)-C(6)	1.418(3)
C(1)-C(7)	1.431(3)
C(1)-C(2)	1.434(4)
C(2)-C(3)	1.418(4)
C(3)-C(4)	1.370(4)
C(4)-C(5)	1.397(4)
C(5)-C(6)	1.370(4)
C(8)-C(13)	1.397(3)
C(8)-C(9)	1.402(3)
C(9)-C(10)	1.376(3)
C(10)-C(11)	1.393(4)
C(11)-C(12)	1.383(4)
C(12)-C(13)	1.387(4)
C(14)-C(19)	1.379(4)

Table A.13 continued

C(14)-C(15)	1.395(4)
C(15)-C(16)	1.398(3)
C(15)-C(20)	1.486(3)
C(16)-C(17)	1.384(4)
C(17)-C(18)	1.382(4)
C(18)-C(19)	1.388(4)
C(20)-C(21)	1.389(4)
C(20)-C(25)	1.399(3)
C(21)-C(22)	1.381(4)
C(22)-C(23)	1.389(4)
C(23)-C(24)	1.379(4)
C(24)-C(25)	1.387(4)
C(26)-C(31)	1.371(4)
C(26)-C(27)	1.396(3)
C(27)-C(28)	1.398(3)
C(28)-C(29)	1.380(4)
C(29)-C(30)	1.384(4)
C(30)-C(31)	1.386(4)
C(32)-C(33)	1.431(4)
C(33)-C(38)	1.420(4)
C(33)-C(34)	1.430(3)
C(34)-C(35)	1.416(4)
C(35)-C(36)	1.371(4)
C(36)-C(37)	1.400(4)
C(37)-C(38)	1.364(4)
C(40)-Cl(4)	1.7214(11)
C(40)-Cl(3)	1.7217(12)
C(40')-Cl(4')	1.7200(13)
C(40')-Cl(3')	1.7200(12)
O(4)-Ni(1)-O(1)	103.52(8)
O(4)-Ni(1)-N(2)	93.40(8)
O(1)-Ni(1)-N(2)	95.17(8)

Table A.13 continued

O(4)-Ni(1)-N(1)	93.17(8)
O(1)-Ni(1)-N(1)	93.52(8)
N(2)-Ni(1)-N(1)	167.58(8)
O(4)-Ni(1)-O(3)	165.21(7)
O(1)-Ni(1)-O(3)	89.47(7)
N(2)-Ni(1)-O(3)	78.20(7)
N(1)-Ni(1)-O(3)	93.05(7)
O(4)-Ni(1)-O(2)	89.15(7)
O(1)-Ni(1)-O(2)	165.22(7)
N(2)-Ni(1)-O(2)	91.57(7)
N(1)-Ni(1)-O(2)	78.00(7)
O(3)-Ni(1)-O(2)	79.04(6)
C(2)-O(1)-Ni(1)	126.71(16)
C(9)-O(2)-C(14)	116.86(17)
C(9)-O(2)-Ni(1)	111.31(13)
C(14)-O(2)-Ni(1)	125.44(14)
C(21)-O(3)-C(26)	117.98(18)
C(21)-O(3)-Ni(1)	124.28(14)
C(26)-O(3)-Ni(1)	112.23(14)
C(34)-O(4)-Ni(1)	126.85(16)
C(7)-N(1)-C(8)	120.0(2)
C(7)-N(1)-Ni(1)	123.91(17)
C(8)-N(1)-Ni(1)	116.09(15)
C(32)-N(2)-C(27)	119.6(2)
C(32)-N(2)-Ni(1)	124.17(17)
C(27)-N(2)-Ni(1)	116.19(15)
C(6)-C(1)-C(7)	115.9(2)
C(6)-C(1)-C(2)	119.3(2)
C(7)-C(1)-C(2)	124.7(2)
O(1)-C(2)-C(3)	118.9(2)
O(1)-C(2)-C(1)	124.5(2)
C(3)-C(2)-C(1)	116.6(2)

Table A.13 continued

C(4)-C(3)-C(2)	122.2(2)
C(3)-C(4)-C(5)	121.1(2)
C(6)-C(5)-C(4)	118.8(2)
C(5)-C(6)-C(1)	121.9(2)
N(1)-C(7)-C(1)	126.4(2)
C(13)-C(8)-C(9)	117.5(2)
C(13)-C(8)-N(1)	125.9(2)
C(9)-C(8)-N(1)	116.6(2)
C(10)-C(9)-C(8)	122.7(2)
C(10)-C(9)-O(2)	121.3(2)
C(8)-C(9)-O(2)	115.9(2)
C(9)-C(10)-C(11)	118.5(2)
C(12)-C(11)-C(10)	120.0(2)
C(11)-C(12)-C(13)	121.0(2)
C(12)-C(13)-C(8)	120.2(2)
C(19)-C(14)-C(15)	122.5(2)
C(19)-C(14)-O(2)	117.8(2)
C(15)-C(14)-O(2)	119.7(2)
C(14)-C(15)-C(16)	117.1(2)
C(14)-C(15)-C(20)	122.8(2)
C(16)-C(15)-C(20)	120.1(2)
C(17)-C(16)-C(15)	121.2(2)
C(18)-C(17)-C(16)	120.1(2)
C(17)-C(18)-C(19)	120.2(2)
C(14)-C(19)-C(18)	118.9(2)
C(21)-C(20)-C(25)	117.0(2)
C(21)-C(20)-C(15)	121.5(2)
C(25)-C(20)-C(15)	121.4(2)
C(22)-C(21)-C(20)	123.2(2)
C(22)-C(21)-O(3)	117.4(2)
C(20)-C(21)-O(3)	119.4(2)
C(21)-C(22)-C(23)	118.5(3)

Table A.13 continued

C(24)-C(23)-C(22)	120.0(3)
C(23)-C(24)-C(25)	120.7(2)
C(24)-C(25)-C(20)	120.7(3)
C(31)-C(26)-C(27)	122.6(2)
C(31)-C(26)-O(3)	121.8(2)
C(27)-C(26)-O(3)	115.6(2)
C(26)-C(27)-C(28)	117.6(2)
C(26)-C(27)-N(2)	116.7(2)
C(28)-C(27)-N(2)	125.7(2)
C(29)-C(28)-C(27)	120.0(2)
C(28)-C(29)-C(30)	121.1(2)
C(29)-C(30)-C(31)	119.7(2)
C(26)-C(31)-C(30)	118.9(2)
N(2)-C(32)-C(33)	126.1(2)
C(38)-C(33)-C(34)	119.2(2)
C(38)-C(33)-C(32)	115.9(2)
C(34)-C(33)-C(32)	124.8(2)
O(4)-C(34)-C(35)	118.6(2)
O(4)-C(34)-C(33)	124.6(2)
C(35)-C(34)-C(33)	116.8(2)
C(36)-C(35)-C(34)	122.1(3)
C(35)-C(36)-C(37)	121.0(3)
C(38)-C(37)-C(36)	118.7(3)
C(37)-C(38)-C(33)	122.1(3)
Cl(2)-C(39)-Cl(1)	110.8(2)
Cl(4)-C(40)-Cl(3)	114.43(14)
Cl(4')-C(40')-Cl(3')	113.1(4)

Table A.14. Anisotropic displacement parameters ($Å^2$x 10^3) for sm43. The anisotropic displacement factor exponent takes the form: $-2\pi^2$[h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ni(1)	14(1)	17(1)	12(1)	0(1)	0(1)	-5(1)
Cl(1)	33(1)	50(1)	37(1)	-18(1)	1(1)	-8(1)
Cl(2)	103(1)	48(1)	53(1)	-5(1)	-28(1)	-26(1)
O(1)	15(1)	25(1)	17(1)	0(1)	0(1)	-3(1)
O(2)	15(1)	21(1)	11(1)	-2(1)	0(1)	-5(1)
O(3)	17(1)	19(1)	11(1)	-1(1)	1(1)	-5(1)
O(4)	23(1)	19(1)	17(1)	0(1)	-2(1)	-8(1)
N(1)	16(1)	18(1)	15(1)	-2(1)	1(1)	-7(1)
N(2)	12(1)	18(1)	14(1)	-2(1)	1(1)	-3(1)
C(1)	16(1)	17(1)	19(1)	1(1)	-2(1)	-4(1)
C(2)	15(1)	17(1)	22(1)	-2(1)	0(1)	-6(1)
C(3)	17(1)	25(1)	23(1)	-5(1)	2(1)	-6(1)
C(4)	16(1)	22(1)	34(2)	-5(1)	2(1)	-3(1)
C(5)	20(1)	20(1)	29(1)	2(1)	-6(1)	-3(1)
C(6)	23(1)	22(1)	20(1)	2(1)	-2(1)	-8(1)
C(7)	20(1)	20(1)	14(1)	0(1)	-1(1)	-8(1)
C(8)	17(1)	14(1)	15(1)	-2(1)	1(1)	-6(1)
C(9)	18(1)	17(1)	11(1)	-3(1)	0(1)	-7(1)
C(10)	18(1)	23(1)	19(1)	-4(1)	0(1)	-6(1)
C(11)	22(1)	27(1)	19(1)	-8(1)	6(1)	-9(1)
C(12)	26(1)	22(1)	15(1)	-3(1)	2(1)	-9(1)
C(13)	20(1)	19(1)	15(1)	-1(1)	-2(1)	-9(1)
C(14)	13(1)	24(1)	14(1)	-7(1)	1(1)	-4(1)
C(15)	15(1)	23(1)	14(1)	-5(1)	3(1)	-6(1)
C(16)	19(1)	31(2)	18(1)	-10(1)	3(1)	-10(1)
C(17)	16(1)	40(2)	20(1)	-10(1)	-3(1)	-5(1)
C(18)	23(1)	32(2)	18(1)	-2(1)	-5(1)	1(1)
C(19)	20(1)	23(1)	20(1)	-5(1)	1(1)	-3(1)

Table A.14 continued

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(20)	22(1)	20(1)	14(1)	-3(1)	0(1)	-10(1)
C(21)	23(1)	19(1)	13(1)	-1(1)	1(1)	-9(1)
C(22)	25(1)	22(1)	20(1)	-1(1)	-2(1)	-4(1)
C(23)	40(2)	22(1)	21(1)	4(1)	-5(1)	-9(1)
C(24)	43(2)	25(1)	18(1)	0(1)	3(1)	-19(1)
C(25)	28(1)	28(1)	17(1)	-5(1)	6(1)	-15(1)
C(26)	13(1)	20(1)	12(1)	-2(1)	1(1)	-1(1)
C(27)	12(1)	19(1)	15(1)	-3(1)	1(1)	-4(1)
C(28)	18(1)	23(1)	15(1)	0(1)	0(1)	-5(1)
C(29)	27(1)	29(2)	15(1)	-6(1)	-1(1)	-6(1)
C(30)	30(1)	22(1)	23(1)	-7(1)	-2(1)	-7(1)
C(31)	25(1)	18(1)	18(1)	-1(1)	2(1)	-5(1)
C(32)	17(1)	23(1)	14(1)	1(1)	0(1)	-4(1)
C(33)	18(1)	17(1)	20(1)	-1(1)	1(1)	-2(1)
C(34)	15(1)	18(1)	18(1)	-1(1)	2(1)	-3(1)
C(35)	22(1)	23(1)	24(1)	-5(1)	3(1)	-6(1)
C(36)	36(2)	15(1)	33(2)	-5(1)	4(1)	-6(1)
C(37)	43(2)	18(1)	27(2)	4(1)	0(1)	-6(1)
C(38)	34(2)	22(1)	20(1)	2(1)	-3(1)	-5(1)
C(39)	53(2)	48(2)	41(2)	-18(2)	-6(2)	-10(2)
C(40)	73(4)	68(4)	33(3)	-32(3)	18(3)	-35(3)
Cl(3)	45(1)	58(1)	48(1)	-24(1)	14(1)	-22(1)
Cl(4)	68(1)	141(2)	55(1)	-43(1)	-31(1)	16(1)
C(40')	52(2)	45(2)	34(1)	-11(1)	5(1)	0(1)
Cl(3')	52(2)	45(2)	34(1)	-11(1)	5(1)	0(1)
Cl(4')	52(2)	45(2)	34(1)	-11(1)	5(1)	0(1)

Table A.15. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($\AA^2$x 10^3) for sm43.

	x	y	z	U(eq)
H(3)	7854	2573	7008	26
H(4)	9256	1424	8212	29
H(5)	8950	1221	10042	29
H(6)	7172	2111	10633	27
H(7)	5328	3235	10400	21
H(10)	673	5718	9174	24
H(11)	640	5599	11022	26
H(12)	2333	4817	12033	25
H(13)	4063	4096	11244	21
H(16)	169	3071	7113	26
H(17)	-952	4705	6000	30
H(18)	-478	6479	5772	32
H(19)	1079	6645	6729	26
H(22)	4700	1159	8531	28
H(23)	3879	13	9853	34
H(24)	1931	610	10188	32
H(25)	775	2322	9205	27
H(28)	3521	4833	3976	23
H(29)	3055	3306	3398	28
H(30)	2722	1736	4607	29
H(31)	3017	1612	6427	25
H(32)	3473	6171	4727	23
H(35)	4544	8160	7769	27
H(36)	4386	9768	6443	34
H(37)	3877	9741	4697	37
H(38)	3559	8064	4312	32
H(39A)	1725	-378	5872	56
H(39B)	597	-684	6399	56

Table A.15 continued

	x	y	z	U(eq)
H(42A)	1986	2391	1256	62
H(42B)	1666	2593	2430	62
H(40A)	2967	1821	1347	54
H(40B)	3261	1798	2558	54

X-Ray Structure Data for **2-4-Cu** (sm42)

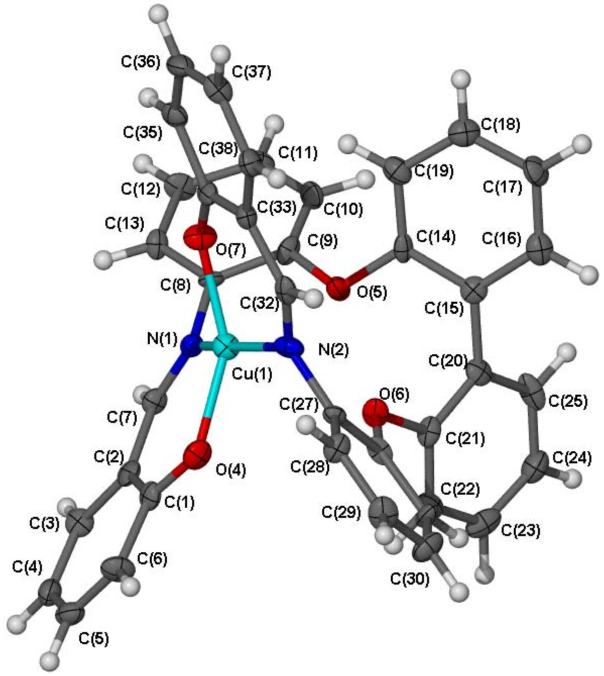


Table A.16. Crystal data and structure refinement for sm42.

Identification code	sm42	
CCDC number	264657	
Empirical formula	C39 H28 Cl2 Cu N2 O4	
Formula weight	723.07	
Temperature	110(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.1638(14) Å	α= 86.426(8)°.
	b = 10.7654(15) Å	β= 79.784(8)°.
	c = 14.831(2) Å	γ = 80.540(8)°.
Volume	1574.4(4) $Å^3$	
Z	2	
Density (calculated)	1.525 Mg/m^3	
Absorption coefficient	2.926 mm^{-1}	
F(000)	742	
Crystal size	0.10 x 0.10 x 0.03 mm^3	
Theta range for data collection	4.17 to 59.00°.	
Index ranges	-11<=h<=10, -11<=k<=9, -16<=l<=16	
Reflections collected	8824	
Independent reflections	4175 [R(int) = 0.0849]	
Completeness to theta = 59.00°	92.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9173 and 0.7585	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4175 / 0 / 433	
Goodness-of-fit on F^2	1.006	
Final R indices [I>2sigma(I)]	R1 = 0.0521, wR2 = 0.1068	
R indices (all data)	R1 = 0.1074, wR2 = 0.1240	
Largest diff. peak and hole	0.527 and -0.449 e.$Å^{-3}$	

Table A.17. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for sm42. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu(1)	820(1)	2549(1)	2518(1)	21(1)
N(1)	1510(5)	2553(5)	1188(3)	17(1)
N(2)	625(5)	2626(5)	3868(3)	20(1)
O(4)	831(4)	766(4)	2607(3)	24(1)
O(5)	3065(4)	3785(4)	1969(3)	22(1)
O(6)	3233(4)	1854(4)	3198(3)	22(1)
O(7)	-145(4)	4211(4)	2388(3)	24(1)
Cl(1)	5594(2)	7512(2)	1510(1)	33(1)
Cl(2)	4883(2)	8374(2)	-277(1)	30(1)
C(1)	891(6)	33(6)	1924(4)	20(2)
C(2)	1300(6)	385(6)	985(4)	22(2)
C(3)	1372(6)	-484(6)	295(4)	22(2)
C(4)	1036(6)	-1669(6)	492(4)	24(2)
C(5)	621(6)	-2003(6)	1409(5)	26(2)
C(6)	554(7)	-1211(6)	2096(5)	26(2)
C(7)	1647(6)	1603(6)	689(4)	19(2)
C(8)	1924(6)	3671(5)	745(4)	16(2)
C(9)	2766(6)	4306(6)	1135(4)	19(2)
C(10)	3350(6)	5270(6)	656(4)	21(2)
C(11)	3020(7)	5695(6)	-189(4)	25(2)
C(12)	2106(6)	5132(6)	-553(4)	24(2)
C(13)	1557(6)	4134(6)	-89(4)	19(2)
C(14)	3406(6)	4561(6)	2581(4)	18(2)
C(15)	4477(6)	4057(6)	3034(4)	19(2)
C(16)	4835(6)	4841(6)	3633(4)	25(2)
C(17)	4162(7)	6044(6)	3793(4)	26(2)
C(18)	3072(7)	6488(6)	3363(4)	26(2)
C(19)	2676(6)	5752(6)	2757(4)	24(2)

Table A.17 continued

	x	y	z	U(eq)
C(20)	5249(6)	2786(6)	2822(4)	20(2)
C(21)	4627(6)	1715(6)	2881(4)	20(2)
C(22)	5349(6)	564(6)	2595(4)	23(2)
C(23)	6730(7)	446(7)	2288(4)	28(2)
C(24)	7390(7)	1472(6)	2244(4)	28(2)
C(25)	6634(7)	2631(6)	2506(4)	26(2)
C(26)	2735(6)	1221(6)	3997(4)	17(2)
C(27)	1362(6)	1645(5)	4350(4)	14(1)
C(28)	788(6)	1092(6)	5160(4)	22(2)
C(29)	1526(6)	154(6)	5638(4)	28(2)
C(30)	2878(6)	-235(6)	5277(4)	27(2)
C(31)	3486(6)	303(6)	4471(4)	21(2)
C(32)	-207(6)	3485(6)	4324(4)	19(2)
C(33)	-1008(6)	4561(6)	3988(4)	19(2)
C(34)	-912(6)	4884(6)	3044(4)	20(2)
C(35)	-1707(6)	6040(6)	2796(4)	22(2)
C(36)	-2517(6)	6789(6)	3436(5)	26(2)
C(37)	-2629(6)	6461(6)	4374(4)	23(2)
C(38)	-1867(6)	5375(6)	4621(4)	21(2)
C(39)	4381(6)	8430(6)	930(4)	29(2)

Table A.18. Bond lengths [Å] and angles [°] for sm42.

Cu(1)-O(7)	1.910(4)
Cu(1)-O(4)	1.915(4)
Cu(1)-N(1)	1.973(5)
Cu(1)-N(2)	1.982(5)
N(1)-C(7)	1.275(7)
N(1)-C(8)	1.423(7)
N(2)-C(32)	1.283(7)
N(2)-C(27)	1.423(7)
O(4)-C(1)	1.310(7)
O(5)-C(9)	1.389(7)
O(5)-C(14)	1.393(7)
O(6)-C(26)	1.387(7)
O(6)-C(21)	1.398(7)
O(7)-C(34)	1.308(7)
Cl(1)-C(39)	1.763(6)
Cl(2)-C(39)	1.773(6)
C(1)-C(2)	1.427(8)
C(1)-C(6)	1.433(8)
C(2)-C(3)	1.415(8)
C(2)-C(7)	1.435(8)
C(3)-C(4)	1.375(8)
C(4)-C(5)	1.393(8)
C(5)-C(6)	1.355(9)
C(8)-C(13)	1.395(8)
C(8)-C(9)	1.397(8)
C(9)-C(10)	1.377(8)
C(10)-C(11)	1.384(8)
C(11)-C(12)	1.388(8)
C(12)-C(13)	1.381(8)
C(14)-C(19)	1.387(8)
C(14)-C(15)	1.396(8)
C(15)-C(16)	1.395(8)

Table A.18 continued

C(15)-C(20)	1.483(8)
C(16)-C(17)	1.375(9)
C(17)-C(18)	1.379(8)
C(18)-C(19)	1.385(9)
C(20)-C(25)	1.388(8)
C(20)-C(21)	1.394(8)
C(21)-C(22)	1.382(8)
C(22)-C(23)	1.384(8)
C(23)-C(24)	1.376(9)
C(24)-C(25)	1.393(9)
C(26)-C(31)	1.382(8)
C(26)-C(27)	1.411(8)
C(27)-C(28)	1.384(8)
C(28)-C(29)	1.391(8)
C(29)-C(30)	1.389(8)
C(30)-C(31)	1.384(8)
C(32)-C(33)	1.419(8)
C(33)-C(38)	1.404(8)
C(33)-C(34)	1.411(8)
C(34)-C(35)	1.434(8)
C(35)-C(36)	1.352(8)
C(36)-C(37)	1.403(8)
C(37)-C(38)	1.361(8)
O(7)-Cu(1)-O(4)	149.30(18)
O(7)-Cu(1)-N(1)	89.91(19)
O(4)-Cu(1)-N(1)	93.57(19)
O(7)-Cu(1)-N(2)	93.56(19)
O(4)-Cu(1)-N(2)	91.09(19)
N(1)-Cu(1)-N(2)	164.6(2)
C(7)-N(1)-C(8)	116.7(5)
C(7)-N(1)-Cu(1)	124.4(4)
C(8)-N(1)-Cu(1)	118.9(4)

Table A.18 continued

C(32)-N(2)-C(27)	119.0(6)
C(32)-N(2)-Cu(1)	122.1(4)
C(27)-N(2)-Cu(1)	118.7(4)
C(1)-O(4)-Cu(1)	126.0(4)
C(9)-O(5)-C(14)	118.6(5)
C(26)-O(6)-C(21)	120.0(5)
C(34)-O(7)-Cu(1)	126.4(4)
O(4)-C(1)-C(2)	123.9(6)
O(4)-C(1)-C(6)	120.2(6)
C(2)-C(1)-C(6)	115.9(6)
C(3)-C(2)-C(1)	119.9(6)
C(3)-C(2)-C(7)	116.8(6)
C(1)-C(2)-C(7)	123.3(6)
C(4)-C(3)-C(2)	122.2(6)
C(3)-C(4)-C(5)	117.7(6)
C(6)-C(5)-C(4)	122.3(7)
C(5)-C(6)-C(1)	122.0(6)
N(1)-C(7)-C(2)	126.4(6)
C(13)-C(8)-C(9)	118.4(6)
C(13)-C(8)-N(1)	122.0(6)
C(9)-C(8)-N(1)	119.5(5)
C(10)-C(9)-O(5)	124.7(6)
C(10)-C(9)-C(8)	120.6(6)
O(5)-C(9)-C(8)	114.3(5)
C(9)-C(10)-C(11)	120.3(6)
C(10)-C(11)-C(12)	119.5(6)
C(13)-C(12)-C(11)	120.3(6)
C(12)-C(13)-C(8)	120.5(6)
C(19)-C(14)-O(5)	121.3(6)
C(19)-C(14)-C(15)	122.0(6)
O(5)-C(14)-C(15)	116.6(6)
C(16)-C(15)-C(14)	116.7(6)

Table A.18 continued

C(16)-C(15)-C(20)	122.5(6)
C(14)-C(15)-C(20)	120.7(6)
C(17)-C(16)-C(15)	122.5(6)
C(16)-C(17)-C(18)	119.1(6)
C(17)-C(18)-C(19)	120.9(6)
C(18)-C(19)-C(14)	118.8(6)
C(25)-C(20)-C(21)	117.1(6)
C(25)-C(20)-C(15)	120.4(6)
C(21)-C(20)-C(15)	122.5(6)
C(22)-C(21)-C(20)	121.3(6)
C(22)-C(21)-O(6)	120.8(6)
C(20)-C(21)-O(6)	117.8(5)
C(21)-C(22)-C(23)	119.9(6)
C(24)-C(23)-C(22)	120.6(6)
C(23)-C(24)-C(25)	118.4(6)
C(20)-C(25)-C(24)	122.6(6)
C(31)-C(26)-O(6)	125.4(5)
C(31)-C(26)-C(27)	120.1(6)
O(6)-C(26)-C(27)	114.4(5)
C(28)-C(27)-C(26)	118.4(5)
C(28)-C(27)-N(2)	122.5(5)
C(26)-C(27)-N(2)	119.0(5)
C(27)-C(28)-C(29)	122.1(6)
C(30)-C(29)-C(28)	118.1(6)
C(31)-C(30)-C(29)	121.3(6)
C(26)-C(31)-C(30)	119.9(6)
N(2)-C(32)-C(33)	128.6(6)
C(38)-C(33)-C(34)	118.7(6)
C(38)-C(33)-C(32)	118.7(6)
C(34)-C(33)-C(32)	122.5(6)
O(7)-C(34)-C(33)	124.7(6)
O(7)-C(34)-C(35)	118.2(6)

C(33)-C(34)-C(35)	117.1(5)
C(36)-C(35)-C(34)	121.7(6)
C(35)-C(36)-C(37)	121.4(6)
C(38)-C(37)-C(36)	117.6(6)
C(37)-C(38)-C(33)	123.5(6)
Cl(1)-C(39)-Cl(2)	111.6(4)

Table A.19. Anisotropic displacement parameters ($Å^2$x 10^3) for sm42. The anisotropic displacement factor exponent takes the form: $-2\pi^2$[h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cu(1)	22(1)	23(1)	18(1)	-1(1)	-1(1)	-5(1)
N(1)	16(3)	17(3)	17(3)	2(2)	-2(2)	-3(2)
N(2)	20(3)	14(3)	23(3)	-1(2)	5(3)	-4(2)
O(4)	26(3)	29(3)	15(3)	6(2)	-4(2)	-3(2)
O(5)	32(3)	18(3)	21(3)	5(2)	-13(2)	-8(2)
O(6)	23(3)	26(3)	18(3)	9(2)	-2(2)	-12(2)
O(7)	28(3)	23(3)	17(3)	-2(2)	4(2)	0(2)
Cl(1)	31(1)	35(1)	34(1)	2(1)	-7(1)	-2(1)
Cl(2)	30(1)	34(1)	28(1)	-3(1)	-1(1)	-9(1)
C(1)	11(4)	27(4)	21(4)	2(3)	-2(3)	-6(3)
C(2)	10(4)	23(4)	30(4)	-1(3)	-5(3)	2(3)
C(3)	18(4)	27(4)	18(4)	-1(3)	3(3)	-2(3)
C(4)	21(4)	25(4)	26(4)	-4(3)	-10(3)	0(3)
C(5)	22(4)	18(4)	37(5)	5(3)	-6(3)	-3(3)
C(6)	36(4)	20(4)	20(4)	6(3)	0(3)	-7(3)
C(7)	20(4)	23(4)	12(4)	4(3)	-2(3)	-4(3)
C(8)	21(4)	10(4)	17(4)	3(3)	-3(3)	1(3)
C(9)	17(4)	29(4)	10(4)	2(3)	-3(3)	0(3)
C(10)	16(4)	23(4)	26(4)	-3(3)	-3(3)	-7(3)
C(11)	36(4)	17(4)	20(4)	2(3)	-1(3)	-6(3)
C(12)	35(4)	23(4)	12(4)	7(3)	1(3)	-9(3)
C(13)	16(4)	30(4)	12(4)	-1(3)	-1(3)	-6(3)
C(14)	19(4)	27(4)	10(4)	6(3)	-5(3)	-11(3)
C(15)	17(4)	24(4)	14(4)	0(3)	4(3)	-4(3)
C(16)	25(4)	34(5)	17(4)	0(3)	-1(3)	-10(3)
C(17)	34(4)	27(5)	20(4)	-4(3)	-9(3)	-9(3)
C(18)	29(4)	26(4)	21(4)	0(3)	0(3)	-2(3)
C(19)	25(4)	23(4)	23(4)	-3(3)	1(3)	-9(3)

Table A.19 continued

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(20)	26(4)	23(4)	11(4)	-3(3)	-2(3)	-5(3)
C(21)	13(4)	31(4)	13(4)	0(3)	1(3)	-4(3)
C(22)	26(4)	21(4)	23(4)	1(3)	-3(3)	-8(3)
C(23)	30(4)	32(5)	16(4)	4(3)	0(3)	8(3)
C(24)	21(4)	37(5)	27(4)	3(3)	-6(3)	-1(3)
C(25)	33(5)	38(5)	12(4)	2(3)	1(3)	-25(3)
C(26)	23(4)	23(4)	5(4)	0(3)	5(3)	-13(3)
C(27)	19(4)	11(4)	13(4)	2(3)	-2(3)	-5(3)
C(28)	19(4)	29(4)	16(4)	4(3)	0(3)	-4(3)
C(29)	29(4)	36(5)	17(4)	6(3)	-1(3)	-13(3)
C(30)	26(4)	32(5)	19(4)	4(3)	-5(3)	4(3)
C(31)	16(4)	19(4)	28(4)	10(3)	-10(3)	-4(3)
C(32)	18(4)	24(4)	16(4)	4(3)	-2(3)	-13(3)
C(33)	17(4)	21(4)	19(4)	-2(3)	-4(3)	-6(3)
C(34)	9(4)	19(4)	31(4)	-7(3)	-3(3)	-1(3)
C(35)	22(4)	19(4)	26(4)	0(3)	-3(3)	-9(3)
C(36)	22(4)	16(4)	40(5)	-5(3)	-7(3)	-1(3)
C(37)	28(4)	27(4)	14(4)	-1(3)	3(3)	-11(3)
C(38)	23(4)	25(4)	18(4)	-3(3)	-5(3)	-6(3)
C(39)	24(4)	31(5)	34(5)	-1(3)	-6(3)	-9(3)

Table A.20. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for sm42.

	x	y	z	U(eq)
H(3)	1663	-241	-326	26
H(4)	1085	-2240	20	28
H(5)	377	-2815	1557	31
H(6)	274	-1488	2710	31
H(7)	2014	1711	59	22
H(10)	3982	5646	906	26
H(11)	3416	6366	-516	30
H(12)	1856	5434	-1124	28
H(13)	924	3760	-340	23
H(16)	5573	4533	3942	30
H(17)	4443	6562	4196	31
H(18)	2587	7310	3483	31
H(19)	1917	6058	2468	28
H(22)	4897	-145	2609	27
H(23)	7227	-351	2105	34
H(24)	8340	1391	2040	34
H(25)	7084	3344	2468	32
H(28)	-139	1362	5398	26
H(29)	1116	-211	6196	33
H(30)	3395	-883	5589	32
H(31)	4419	41	4244	25
H(32)	-299	3388	4972	22
H(35)	-1664	6286	2166	26
H(36)	-3021	7554	3246	31
H(37)	-3216	6979	4820	27
H(38)	-1919	5155	5255	25
H(39A)	4250	9315	1117	35
H(39B)	3504	8118	1107	35

X-Ray Structure Data for **2-8-Co** (sm51)

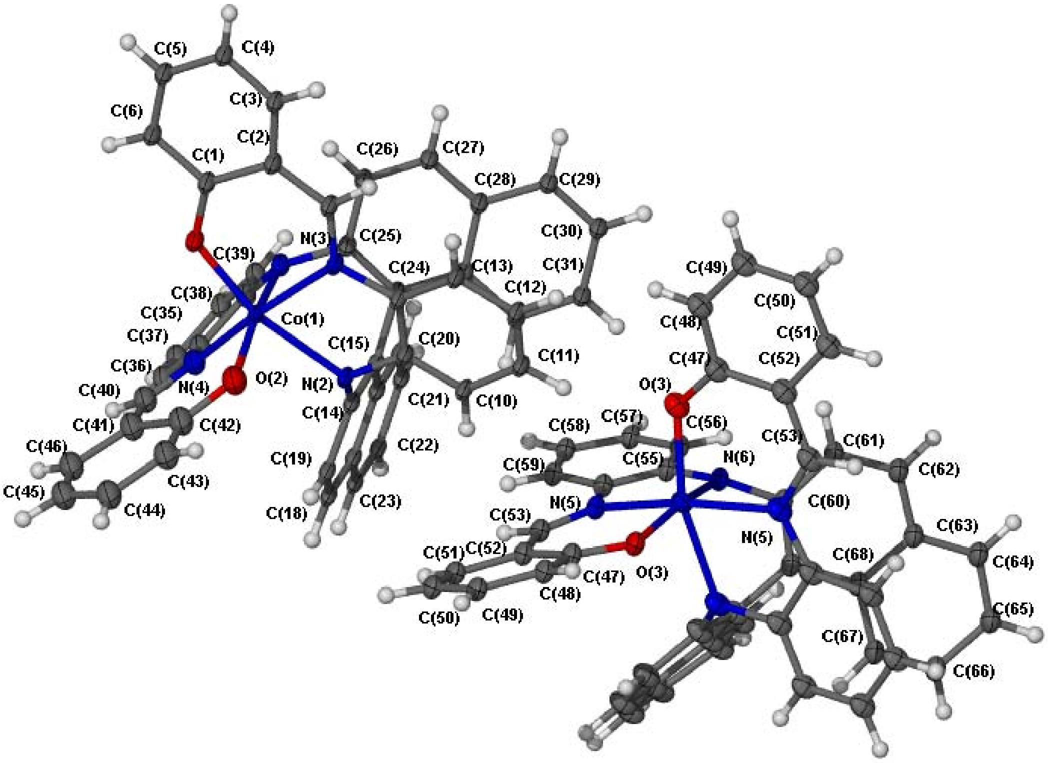


Table A.21. Crystal data and structure refinement for sm51.

Identification code	sm51	
CCDC number	264660	
Empirical formula	C48.67 H35.33 Co N2 O5.33	
Formula weight	792.39	
Temperature	110(2) K	
Wavelength	1.54178 Å	
Crystal system	Tetragonal	
Space group	P4(1)2(1)2	
Unit cell dimensions	a = 15.439(2) Å	α= 90°.
	b = 15.439(2) Å	β= 90°.
	c = 56.434(12) Å	γ = 90°.
Volume	13452(4) $Å^3$	
Z	12	
Density (calculated)	1.174 Mg/m^3	
Absorption coefficient	3.369 mm^{-1}	
F(000)	4932	
Crystal size	0.20 x 0.10 x 0.10 mm^3	
Theta range for data collection	4.24 to 58.95°.	
Index ranges	-17<=h<=17, -17<=k<=16, -62<=l<=59	
Reflections collected	107481	
Independent reflections	9364 [R(int) = 0.3251]	
Completeness to theta = 58.95°	97.0 %	
Absorption correction	None	
Max. and min. transmission	0.7293 and 0.5522	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9364 / 604 / 766	
Goodness-of-fit on F^2	1.003	
Final R indices [I>2sigma(I)]	R1 = 0.1038, wR2 = 0.2095	
R indices (all data)	R1 = 0.1783, wR2 = 0.2477	
Absolute structure parameter	-0.011(9)	
Largest diff. peak and hole	0.455 and -0.365 e.$Å^{-3}$	

Table A.22. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for sm51. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Co(1)	5157(1)	8808(1)	1562(1)	34(1)
Co(2)	6107(1)	3893(1)	2500	30(1)
O(1)	5095(5)	10053(4)	1506(1)	44(2)
O(2)	4081(5)	8321(5)	1435(1)	53(2)
O(3)	5441(4)	7486(4)	1713(1)	36(1)
O(4)	6614(4)	9009(4)	1645(1)	34(1)
O(5)	6108(4)	5035(4)	2658(1)	37(2)
O(6)	6290(4)	2490(4)	2421(1)	33(1)
N(1)	4825(5)	8940(5)	1915(1)	34(2)
N(4)	5803(6)	8552(5)	1242(1)	39(2)
N(5)	5736(5)	3256(5)	2812(1)	27(2)
C(1)	4866(7)	10666(6)	1660(2)	37(2)
C(2)	4662(6)	10518(6)	1906(2)	32(2)
C(3)	4446(6)	11212(6)	2043(2)	33(2)
C(4)	4436(7)	12046(7)	1967(2)	38(2)
C(5)	4659(7)	12194(7)	1727(2)	39(2)
C(6)	4874(7)	11540(6)	1584(2)	36(2)
C(7)	4665(6)	9661(6)	2009(2)	32(2)
C(8)	4824(7)	8161(6)	2051(2)	37(2)
C(9)	5159(7)	7423(6)	1953(2)	36(2)
C(10)	5226(7)	6646(6)	2068(2)	39(2)
C(11)	4951(7)	6600(7)	2303(2)	42(2)
C(12)	4563(7)	7303(7)	2409(2)	45(2)
C(13)	4491(7)	8084(7)	2287(2)	44(2)
C(14)	6192(7)	7040(6)	1643(2)	33(2)
C(15)	6971(7)	7236(6)	1743(2)	31(2)
C(16)	7739(7)	6798(6)	1656(2)	35(2)
C(17)	7644(7)	6194(6)	1468(2)	36(2)

Table A.22 continued

	x	y	z	U(eq)
C(18)	6833(7)	6047(6)	1369(2)	36(2)
C(19)	6087(7)	6438(6)	1450(2)	35(2)
C(20)	8567(7)	6958(6)	1753(2)	37(2)
C(21)	9286(8)	6544(7)	1663(2)	43(2)
C(22)	9179(8)	5915(6)	1478(2)	44(2)
C(23)	8421(8)	5785(6)	1381(2)	40(2)
C(24)	7030(7)	7908(6)	1929(2)	30(2)
C(25)	6854(6)	8775(6)	1874(2)	32(2)
C(26)	6890(6)	9434(7)	2040(2)	35(2)
C(27)	7083(6)	9219(7)	2269(2)	35(2)
C(28)	7250(6)	8376(6)	2339(2)	33(2)
C(29)	7454(7)	8157(7)	2581(2)	38(2)
C(30)	7581(7)	7317(7)	2642(2)	39(2)
C(31)	7546(7)	6655(7)	2474(2)	37(2)
C(32)	7379(6)	6834(6)	2245(2)	34(2)
C(33)	7233(7)	7702(6)	2171(2)	32(2)
C(34)	7135(7)	8802(6)	1451(2)	37(2)
C(35)	6715(7)	8577(6)	1248(2)	38(2)
C(36)	7257(7)	8343(6)	1045(2)	41(2)
C(37)	8128(8)	8384(7)	1066(2)	45(2)
C(38)	8540(8)	8618(7)	1275(2)	47(2)
C(39)	8017(7)	8849(6)	1468(2)	39(2)
C(40)	5394(8)	8492(7)	1050(2)	47(2)
C(41)	4457(8)	8387(8)	1020(2)	56(2)
C(42)	3854(8)	8258(8)	1215(2)	55(2)
C(43)	3009(8)	8087(8)	1157(2)	60(2)
C(44)	2738(9)	8039(9)	917(2)	66(2)
C(45)	3303(9)	8189(9)	745(2)	68(2)
C(46)	4152(9)	8353(8)	786(2)	63(2)
C(47)	5819(6)	5219(7)	2868(2)	35(2)

Table A.22 continued

	x	y	z	U(eq)
C(48)	5729(6)	6079(7)	2931(2)	39(2)
C(49)	5459(7)	6337(8)	3152(2)	44(2)
C(50)	5268(7)	5744(7)	3330(2)	43(2)
C(51)	5363(6)	4883(7)	3271(2)	37(2)
C(52)	5608(6)	4579(7)	3043(2)	32(2)
C(53)	5585(6)	3672(6)	3004(2)	29(2)
C(54)	5684(6)	2343(6)	2801(2)	29(2)
C(55)	5957(6)	1928(6)	2601(2)	31(2)
C(56)	5892(6)	1062(7)	2564(2)	35(2)
C(57)	5552(7)	550(7)	2734(2)	41(2)
C(58)	5249(7)	922(7)	2940(2)	42(2)
C(59)	5309(6)	1800(7)	2976(2)	37(2)
C(60)	6978(7)	2159(7)	2275(2)	33(2)
C(61)	6762(7)	2020(6)	2041(2)	35(2)
C(62)	7408(7)	1741(7)	1887(2)	41(2)
C(63)	8256(8)	1636(7)	1964(2)	47(2)
C(64)	8907(8)	1393(7)	1807(2)	57(2)
C(65)	9745(8)	1305(8)	1894(2)	65(2)
C(66)	9942(8)	1442(8)	2130(2)	64(2)
C(67)	9332(8)	1666(8)	2287(2)	56(2)
C(68)	8469(7)	1784(7)	2209(2)	47(2)
C(69)	7778(7)	2052(7)	2373(2)	36(2)
C(1E)	5520(20)	4130(20)	358(7)	123(2)
C(2E)	4903(19)	4092(13)	521(6)	123(2)
O(1E)	4945(16)	3923(19)	749(5)	123(2)
O(3E)	4113(14)	4243(13)	458(5)	123(2)
C(4E)	3407(19)	4193(19)	659(6)	123(2)
C(5E)	2630(20)	4400(20)	521(8)	123(2)
C(1F)	3459(15)	1374(16)	694(5)	116(2)
C(2F)	2671(15)	1463(10)	790(5)	116(2)

Table A.22 continued

	x	y	z	U(eq)
O(1F)	2026(10)	1873(10)	690(3)	116(2)
O(3F)	2544(10)	1122(8)	993(3)	116(2)
C(4F)	3264(16)	619(12)	1129(5)	116(2)
C(5F)	2793(16)	373(14)	1344(5)	116(2)

Table A.23. Bond lengths [Å] and angles [°] for sm51.

Co(1)-O(1)	1.950(7)
Co(1)-O(2)	1.957(8)
Co(1)-N(1)	2.070(7)
Co(1)-N(4)	2.099(8)
Co(1)-O(3)	2.254(6)
Co(1)-O(4)	2.319(7)
Co(2)-O(5)	1.975(7)
Co(2)-O(5)#1	1.975(7)
Co(2)-N(5)#1	2.096(7)
Co(2)-N(5)	2.096(7)
Co(2)-O(6)#1	2.230(6)
Co(2)-O(6)	2.230(6)
O(1)-C(1)	1.333(11)
O(2)-C(42)	1.295(12)
O(3)-C(14)	1.406(12)
O(3)-C(9)	1.426(11)
O(4)-C(34)	1.392(11)
O(4)-C(25)	1.394(10)
O(5)-C(47)	1.300(10)
O(6)-C(55)	1.433(10)
O(6)-C(60)	1.437(11)
N(1)-C(7)	1.258(11)
N(1)-C(8)	1.426(12)
N(4)-C(40)	1.259(12)
N(4)-C(35)	1.409(13)
N(5)-C(53)	1.281(11)
N(5)-C(54)	1.413(12)
C(1)-C(6)	1.416(13)
C(1)-C(2)	1.444(12)
C(2)-C(3)	1.363(13)
C(2)-C(7)	1.442(13)
C(3)-C(4)	1.358(13)

Table A.23 continued.

C(4)-C(5)	1.412(13)
C(5)-C(6)	1.335(13)
C(8)-C(9)	1.368(13)
C(8)-C(13)	1.431(13)
C(9)-C(10)	1.369(13)
C(10)-C(11)	1.395(13)
C(11)-C(12)	1.377(14)
C(12)-C(13)	1.394(14)
C(14)-C(15)	1.362(14)
C(14)-C(19)	1.438(12)
C(15)-C(16)	1.452(14)
C(15)-C(24)	1.479(13)
C(16)-C(20)	1.412(14)
C(16)-C(17)	1.419(13)
C(17)-C(18)	1.392(14)
C(17)-C(23)	1.443(14)
C(18)-C(19)	1.379(14)
C(20)-C(21)	1.379(14)
C(21)-C(22)	1.435(14)
C(22)-C(23)	1.309(14)
C(24)-C(25)	1.399(13)
C(24)-C(33)	1.435(12)
C(25)-C(26)	1.385(12)
C(26)-C(27)	1.364(13)
C(27)-C(28)	1.385(13)
C(28)-C(33)	1.407(12)
C(28)-C(29)	1.444(13)
C(29)-C(30)	1.357(14)
C(30)-C(31)	1.398(13)
C(31)-C(32)	1.342(12)
C(32)-C(33)	1.424(13)
C(34)-C(35)	1.364(14)

Table A.23 continued.

C(34)-C(39)	1.367(14)
C(35)-C(36)	1.462(14)
C(36)-C(37)	1.353(15)
C(37)-C(38)	1.389(15)
C(38)-C(39)	1.402(13)
C(40)-C(41)	1.464(16)
C(41)-C(46)	1.403(15)
C(41)-C(42)	1.456(16)
C(42)-C(43)	1.372(17)
C(43)-C(44)	1.416(16)
C(44)-C(45)	1.327(17)
C(45)-C(46)	1.356(17)
C(47)-C(48)	1.382(14)
C(47)-C(52)	1.436(13)
C(48)-C(49)	1.374(13)
C(49)-C(50)	1.388(14)
C(50)-C(51)	1.377(14)
C(51)-C(52)	1.418(12)
C(52)-C(53)	1.418(14)
C(54)-C(55)	1.366(12)
C(54)-C(59)	1.418(13)
C(55)-C(56)	1.356(13)
C(56)-C(57)	1.350(13)
C(57)-C(58)	1.376(13)
C(58)-C(59)	1.373(13)
C(60)-C(69)	1.365(14)
C(60)-C(61)	1.377(13)
C(61)-C(62)	1.389(13)
C(62)-C(63)	1.387(15)
C(63)-C(64)	1.389(15)
C(63)-C(68)	1.443(14)
C(64)-C(65)	1.389(16)

Table A.23 continued.

C(65)-C(66)	1.384(16)
C(66)-C(67)	1.337(15)
C(67)-C(68)	1.414(16)
C(68)-C(69)	1.472(14)
C(69)-C(69)#1	1.478(18)
C(1E)-C(2E)	1.33(3)
C(2E)-O(3E)	1.29(3)
C(2E)-O(1E)	1.31(3)
O(3E)-C(4E)	1.57(3)
C(4E)-C(5E)	1.47(3)
C(1F)-C(2F)	1.34(3)
C(2F)-O(3F)	1.28(3)
C(2F)-O(1F)	1.31(2)
O(3F)-C(4F)	1.56(2)
C(4F)-C(5F)	1.47(3)
O(1)-Co(1)-O(2)	106.2(3)
O(1)-Co(1)-N(1)	92.6(3)
O(2)-Co(1)-N(1)	100.2(3)
O(1)-Co(1)-N(4)	94.1(3)
O(2)-Co(1)-N(4)	91.1(3)
N(1)-Co(1)-N(4)	164.7(3)
O(1)-Co(1)-O(3)	164.3(3)
O(2)-Co(1)-O(3)	87.4(3)
N(1)-Co(1)-O(3)	76.8(3)
N(4)-Co(1)-O(3)	93.6(3)
O(1)-Co(1)-O(4)	87.0(3)
O(2)-Co(1)-O(4)	161.5(3)
N(1)-Co(1)-O(4)	91.8(3)
N(4)-Co(1)-O(4)	74.8(3)
O(3)-Co(1)-O(4)	81.7(2)
O(5)-Co(2)-O(5)#1	101.8(4)
O(5)-Co(2)-N(5)#1	97.7(3)

Table A.23 continued.

(5)#1-Co(2)-N(5)#1	92.3(3)
O(5)-Co(2)-N(5)	92.3(3)
O(5)#1-Co(2)-N(5)	97.7(3)
N(5)#1-Co(2)-N(5)	164.1(4)
O(5)-Co(2)-O(6)#1	91.3(2)
O(5)#1-Co(2)-O(6)#1	163.3(2)
N(5)#1-Co(2)-O(6)#1	75.4(3)
N(5)-Co(2)-O(6)#1	92.2(3)
O(5)-Co(2)-O(6)	163.3(2)
O(5)#1-Co(2)-O(6)	91.3(2)
N(5)#1-Co(2)-O(6)	92.2(3)
N(5)-Co(2)-O(6)	75.4(3)
O(6)#1-Co(2)-O(6)	78.1(3)
C(1)-O(1)-Co(1)	127.4(6)
C(42)-O(2)-Co(1)	127.4(7)
C(14)-O(3)-C(9)	118.9(7)
C(14)-O(3)-Co(1)	119.9(5)
C(9)-O(3)-Co(1)	111.2(5)
C(34)-O(4)-C(25)	121.0(7)
C(34)-O(4)-Co(1)	111.8(6)
C(25)-O(4)-Co(1)	114.3(5)
C(47)-O(5)-Co(2)	127.4(6)
C(55)-O(6)-C(60)	117.2(7)
C(55)-O(6)-Co(2)	113.6(5)
C(60)-O(6)-Co(2)	123.6(5)
C(7)-N(1)-C(8)	121.4(8)
C(7)-N(1)-Co(1)	122.7(6)
C(8)-N(1)-Co(1)	115.8(6)
C(40)-N(4)-C(35)	121.7(9)
C(40)-N(4)-Co(1)	121.0(8)
C(35)-N(4)-Co(1)	116.7(6)
C(53)-N(5)-C(54)	121.8(8)

Table A.23 continued.

C(53)-N(5)-Co(2)	121.6(7)
C(54)-N(5)-Co(2)	116.6(6)
O(1)-C(1)-C(6)	118.5(8)
O(1)-C(1)-C(2)	125.0(9)
C(6)-C(1)-C(2)	116.4(9)
C(3)-C(2)-C(7)	119.7(8)
C(3)-C(2)-C(1)	118.3(9)
C(7)-C(2)-C(1)	122.0(9)
C(4)-C(3)-C(2)	124.5(9)
C(3)-C(4)-C(5)	117.2(9)
C(6)-C(5)-C(4)	121.1(10)
C(5)-C(6)-C(1)	122.4(9)
N(1)-C(7)-C(2)	130.2(9)
C(9)-C(8)-N(1)	118.9(8)
C(9)-C(8)-C(13)	116.3(9)
N(1)-C(8)-C(13)	124.8(9)
C(8)-C(9)-C(10)	124.4(9)
C(8)-C(9)-O(3)	116.3(8)
C(10)-C(9)-O(3)	119.3(8)
C(9)-C(10)-C(11)	118.4(10)
C(12)-C(11)-C(10)	120.3(9)
C(11)-C(12)-C(13)	120.1(10)
C(12)-C(13)-C(8)	120.3(10)
C(15)-C(14)-O(3)	120.2(8)
C(15)-C(14)-C(19)	123.8(10)
O(3)-C(14)-C(19)	115.8(9)
C(14)-C(15)-C(16)	118.5(9)
C(14)-C(15)-C(24)	120.4(9)
C(16)-C(15)-C(24)	121.1(9)
C(20)-C(16)-C(17)	119.9(9)
C(20)-C(16)-C(15)	121.8(9)
C(17)-C(16)-C(15)	118.3(10)

Table A.23 continued.

C(18)-C(17)-C(16)	120.1(9)
C(18)-C(17)-C(23)	122.6(9)
C(16)-C(17)-C(23)	117.2(10)
C(19)-C(18)-C(17)	123.0(9)
C(18)-C(19)-C(14)	116.2(10)
C(21)-C(20)-C(16)	120.2(10)
C(20)-C(21)-C(22)	119.3(11)
C(23)-C(22)-C(21)	120.9(10)
C(22)-C(23)-C(17)	122.1(10)
C(25)-C(24)-C(33)	117.7(8)
C(25)-C(24)-C(15)	120.1(8)
C(33)-C(24)-C(15)	122.2(8)
C(26)-C(25)-O(4)	116.7(8)
C(26)-C(25)-C(24)	123.0(9)
O(4)-C(25)-C(24)	120.3(8)
C(27)-C(26)-C(25)	118.0(9)
C(26)-C(27)-C(28)	122.6(9)
C(27)-C(28)-C(33)	120.0(9)
C(27)-C(28)-C(29)	122.1(9)
C(33)-C(28)-C(29)	118.0(9)
C(30)-C(29)-C(28)	119.9(9)
C(29)-C(30)-C(31)	121.2(9)
C(32)-C(31)-C(30)	120.7(10)
C(31)-C(32)-C(33)	120.5(9)
C(28)-C(33)-C(32)	119.6(8)
C(28)-C(33)-C(24)	118.7(9)
C(32)-C(33)-C(24)	121.7(8)
C(35)-C(34)-C(39)	123.0(9)
C(35)-C(34)-O(4)	116.4(9)
C(39)-C(34)-O(4)	120.6(9)
C(34)-C(35)-N(4)	120.1(9)
C(34)-C(35)-C(36)	116.8(10)

Table A.23 continued.

N(4)-C(35)-C(36)	123.0(9)
C(37)-C(36)-C(35)	119.3(10)
C(36)-C(37)-C(38)	122.7(10)
C(37)-C(38)-C(39)	117.6(11)
C(34)-C(39)-C(38)	120.4(10)
N(4)-C(40)-C(41)	127.0(10)
C(46)-C(41)-C(42)	119.4(11)
C(46)-C(41)-C(40)	116.3(11)
C(42)-C(41)-C(40)	124.1(10)
O(2)-C(42)-C(43)	120.2(11)
O(2)-C(42)-C(41)	122.8(11)
C(43)-C(42)-C(41)	116.9(11)
C(42)-C(43)-C(44)	121.4(13)
C(45)-C(44)-C(43)	119.7(13)
C(44)-C(45)-C(46)	122.9(13)
C(45)-C(46)-C(41)	119.6(12)
O(5)-C(47)-C(48)	118.8(9)
O(5)-C(47)-C(52)	123.8(9)
C(48)-C(47)-C(52)	117.4(9)
C(49)-C(48)-C(47)	122.9(10)
C(48)-C(49)-C(50)	121.9(11)
C(51)-C(50)-C(49)	116.1(10)
C(50)-C(51)-C(52)	124.5(10)
C(53)-C(52)-C(51)	117.6(9)
C(53)-C(52)-C(47)	125.2(8)
C(51)-C(52)-C(47)	117.1(9)
N(5)-C(53)-C(52)	128.6(9)
C(55)-C(54)-N(5)	119.1(8)
C(55)-C(54)-C(59)	115.1(9)
N(5)-C(54)-C(59)	125.7(8)
C(56)-C(55)-C(54)	124.5(9)
C(56)-C(55)-O(6)	121.0(8)

Table A.23 continued.

C(54)-C(55)-O(6)	114.5(8)
C(57)-C(56)-C(55)	119.9(9)
C(56)-C(57)-C(58)	119.0(10)
C(59)-C(58)-C(57)	121.0(10)
C(58)-C(59)-C(54)	120.5(9)
C(69)-C(60)-C(61)	126.1(9)
C(69)-C(60)-O(6)	118.6(8)
C(61)-C(60)-O(6)	115.2(9)
C(60)-C(61)-C(62)	118.2(10)
C(63)-C(62)-C(61)	121.3(9)
C(62)-C(63)-C(64)	121.1(10)
C(62)-C(63)-C(68)	119.7(10)
C(64)-C(63)-C(68)	119.2(11)
C(63)-C(64)-C(65)	118.6(11)
C(66)-C(65)-C(64)	121.8(12)
C(67)-C(66)-C(65)	121.5(13)
C(66)-C(67)-C(68)	119.5(11)
C(67)-C(68)-C(63)	119.5(10)
C(67)-C(68)-C(69)	121.7(10)
C(63)-C(68)-C(69)	118.9(10)
C(60)-C(69)-C(68)	115.7(8)
C(60)-C(69)-C(69)#1	122.3(7)
C(68)-C(69)-C(69)#1	122.0(8)
O(3E)-C(2E)-O(1E)	111(2)
O(3E)-C(2E)-C(1E)	119(3)
O(1E)-C(2E)-C(1E)	131(3)
C(2E)-O(3E)-C(4E)	117(2)
C(5E)-C(4E)-O(3E)	100(2)
O(3F)-C(2F)-O(1F)	118(2)
O(3F)-C(2F)-C(1F)	117(2)
O(1F)-C(2F)-C(1F)	125(3)
C(2F)-O(3F)-C(4F)	122.6(19)

Table A.23 continued.

C(5F)-C(4F)-O(3F)	100.7(19)

Symmetry transformations used to generate equivalent atoms: #1 -y+1,-x+1,-z+1/2

Table A.24. Anisotropic displacement parameters (Å^{2}x 10^3) for sm51. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Co(1)	59(1)	24(1)	20(1)	2(1)	1(1)	2(1)
Co(2)	34(1)	34(1)	22(1)	1(1)	1(1)	-4(1)
O(1)	69(4)	37(4)	27(3)	4(3)	1(3)	4(3)
O(2)	58(4)	67(4)	34(3)	11(3)	-4(3)	0(3)
O(3)	58(3)	24(3)	26(3)	4(2)	4(3)	1(3)
O(4)	51(3)	23(3)	27(3)	3(2)	6(3)	5(3)
O(5)	37(3)	47(4)	26(3)	1(3)	5(3)	1(3)
O(6)	42(3)	33(3)	24(3)	-3(2)	5(2)	-6(3)
N(1)	48(4)	29(3)	25(3)	3(3)	3(3)	0(3)
N(4)	57(4)	32(3)	27(3)	-1(3)	-1(3)	9(3)
N(5)	22(3)	40(3)	19(3)	-4(3)	-1(3)	2(3)
C(1)	53(3)	31(3)	26(3)	4(3)	1(3)	2(3)
C(2)	45(3)	32(3)	21(3)	-1(3)	3(3)	-1(3)
C(3)	42(4)	35(4)	21(3)	-3(3)	5(3)	1(4)
C(4)	45(4)	39(4)	30(4)	-4(3)	4(3)	8(4)
C(5)	47(4)	37(4)	32(4)	1(3)	0(3)	8(4)
C(6)	49(4)	32(4)	29(4)	4(3)	1(3)	7(4)
C(7)	44(4)	32(4)	20(3)	1(3)	3(3)	-2(3)
C(8)	53(3)	29(3)	29(3)	2(3)	7(3)	-1(3)
C(9)	56(3)	25(3)	28(3)	5(3)	6(3)	-2(3)
C(10)	58(4)	28(4)	32(4)	7(3)	9(3)	-4(4)
C(11)	61(4)	32(4)	32(4)	13(3)	9(4)	-4(4)
C(12)	64(4)	36(4)	35(4)	9(3)	10(4)	-3(4)
C(13)	59(4)	36(4)	37(4)	4(3)	11(4)	0(4)
C(14)	56(3)	18(3)	25(3)	3(3)	5(3)	3(3)
C(15)	53(3)	17(3)	22(3)	2(3)	4(3)	2(3)
C(16)	61(4)	17(3)	26(3)	3(3)	10(3)	4(3)
C(17)	66(4)	18(3)	26(3)	1(3)	13(3)	6(3)

Table A.24. continued

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(18)	66(4)	18(4)	24(3)	0(3)	9(3)	1(4)
C(19)	61(4)	18(4)	26(3)	5(3)	6(3)	-3(3)
C(20)	62(4)	22(4)	26(4)	4(3)	9(3)	10(3)
C(21)	68(4)	31(4)	31(4)	6(3)	10(4)	13(4)
C(22)	70(5)	28(4)	34(4)	4(3)	11(4)	16(4)
C(23)	72(4)	22(4)	27(4)	0(3)	11(4)	11(4)
C(24)	44(3)	23(3)	22(3)	-2(3)	3(3)	5(3)
C(25)	44(3)	26(3)	24(3)	-2(3)	2(3)	4(3)
C(26)	42(4)	32(4)	31(3)	-5(3)	1(3)	-3(3)
C(27)	40(4)	34(4)	31(3)	-10(3)	-6(3)	0(3)
C(28)	40(3)	34(3)	25(3)	-9(3)	-3(3)	0(3)
C(29)	45(4)	41(4)	27(3)	-9(3)	-6(3)	1(4)
C(30)	46(4)	44(4)	27(4)	-3(3)	-7(3)	3(4)
C(31)	45(4)	40(4)	26(3)	-5(3)	-9(3)	4(4)
C(32)	43(4)	33(4)	25(3)	-8(3)	-2(3)	2(3)
C(33)	40(3)	31(3)	24(3)	-6(3)	1(3)	3(3)
C(34)	56(3)	24(3)	30(3)	2(3)	12(3)	9(3)
C(35)	57(3)	27(3)	30(3)	5(3)	6(3)	10(3)
C(36)	58(4)	31(4)	33(4)	4(3)	12(4)	7(4)
C(37)	62(4)	36(4)	38(4)	5(3)	19(4)	6(4)
C(38)	61(4)	36(4)	43(4)	3(4)	16(4)	3(4)
C(39)	58(4)	24(4)	36(4)	4(3)	13(4)	5(4)
C(40)	59(4)	50(4)	32(4)	-2(3)	-3(4)	8(4)
C(41)	62(4)	66(4)	39(3)	-4(3)	-6(3)	7(4)
C(42)	57(4)	68(4)	39(3)	4(3)	-7(3)	2(4)
C(43)	60(4)	76(5)	45(4)	0(4)	-12(4)	3(4)
C(44)	64(5)	84(5)	49(4)	-4(4)	-15(4)	7(4)
C(45)	69(5)	87(5)	48(4)	-8(4)	-14(4)	9(5)
C(46)	66(5)	79(5)	44(4)	-6(4)	-9(4)	8(4)
C(47)	32(3)	45(3)	27(3)	-3(3)	2(3)	0(3)

Table A.24 continued

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(48)	36(4)	46(4)	35(4)	-5(3)	4(3)	3(4)
C(49)	40(4)	51(4)	42(4)	-11(4)	2(4)	2(4)
C(50)	37(4)	56(4)	35(4)	-9(4)	2(3)	2(4)
C(51)	31(4)	52(4)	29(3)	1(3)	2(3)	0(4)
C(52)	26(3)	46(3)	23(3)	1(3)	2(3)	2(3)
C(53)	21(3)	45(4)	21(3)	-2(3)	2(3)	4(3)
C(54)	29(3)	34(3)	24(3)	0(3)	2(3)	-2(3)
C(55)	36(3)	32(3)	24(3)	4(3)	6(3)	-7(3)
C(56)	42(4)	34(4)	29(3)	4(3)	5(3)	-6(3)
C(57)	49(4)	37(4)	37(4)	5(3)	2(3)	-10(4)
C(58)	47(4)	39(4)	38(4)	12(3)	7(4)	-7(4)
C(59)	40(4)	41(4)	30(3)	4(3)	6(3)	-2(3)
C(60)	39(3)	38(3)	22(3)	-2(3)	6(3)	-11(3)
C(61)	41(4)	38(4)	26(3)	-5(3)	-1(3)	-15(3)
C(62)	49(4)	44(4)	31(4)	-8(3)	0(3)	-13(4)
C(63)	49(4)	51(4)	42(3)	-12(3)	7(3)	-13(3)
C(64)	54(4)	63(4)	55(4)	-18(4)	9(4)	-13(4)
C(65)	57(4)	69(5)	69(4)	-24(4)	12(4)	-8(4)
C(66)	56(4)	68(5)	67(4)	-22(4)	6(4)	-9(4)
C(67)	52(4)	60(4)	56(4)	-20(4)	2(4)	-11(4)
C(68)	47(4)	49(4)	43(3)	-12(3)	4(3)	-11(3)
C(69)	41(4)	42(4)	26(3)	-9(3)	4(3)	-14(3)
C(1E)	51(3)	122(3)	197(3)	56(3)	-40(3)	22(3)
C(2E)	51(3)	122(3)	197(3)	56(3)	-40(3)	22(3)
O(1E)	51(3)	122(3)	197(3)	56(3)	-40(3)	22(3)
O(3E)	51(3)	122(3)	197(3)	56(3)	-40(3)	22(3)
C(4E)	51(3)	122(3)	197(3)	56(3)	-40(3)	22(3)
C(5E)	51(3)	122(3)	197(3)	56(3)	-40(3)	22(3)
C(1F)	78(3)	97(3)	172(3)	-21(3)	-61(3)	22(3)
C(2F)	78(3)	97(3)	172(3)	-21(3)	-61(3)	22(3)

Table A.24 continued

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1F)	78(3)	97(3)	172(3)	-21(3)	-61(3)	22(3)
O(3F)	78(3)	97(3)	172(3)	-21(3)	-61(3)	22(3)
C(4F)	78(3)	97(3)	172(3)	-21(3)	-61(3)	22(3)
C(5F)	78(3)	97(3)	172(3)	-21(3)	-61(3)	22(3)

Table A.25. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for sm51.

	x	y	z	U(eq)
H(3A)	4292	11106	2204	39
H(4A)	4285	12509	2069	46
H(5A)	4656	12769	1667	46
H(6A)	5038	11666	1426	43
H(7A)	4522	9639	2172	39
H(10A)	5454	6151	1990	47
H(11A)	5033	6080	2391	50
H(12A)	4343	7257	2566	54
H(13A)	4220	8567	2360	52
H(18A)	6790	5659	1239	44
H(19A)	5536	6317	1383	42
H(20A)	8628	7352	1882	44
H(21A)	9847	6673	1723	52
H(22A)	9665	5589	1426	53
H(23A)	8381	5409	1248	49
H(26A)	6782	10018	1996	42
H(27A)	7105	9666	2384	42
H(29A)	7499	8600	2697	45
H(30A)	7696	7176	2803	47
H(31A)	7642	6072	2521	44
H(32A)	7359	6377	2133	40
H(36A)	6999	8165	900	49
H(37A)	8474	8246	932	54
H(38A)	9153	8621	1287	56
H(39A)	8277	9039	1612	47
H(40A)	5728	8517	908	57
H(43A)	2597	7999	1279	72
H(44A)	2154	7900	880	79
H(45A)	3104	8182	586	81

Table A.25 continued

	x	y	z	U(eq)
H(46A)	4539	8443	657	76
H(48A)	5860	6511	2817	47
H(49A)	5400	6938	3185	53
H(50A)	5083	5921	3483	52
H(51A)	5257	4465	3391	45
H(53A)	5438	3328	3137	35
H(56A)	6085	817	2419	42
H(57A)	5521	-60	2712	49
H(58A)	4995	567	3058	50
H(59A)	5098	2044	3119	44
H(61A)	6188	2112	1986	42
H(62A)	7267	1620	1727	50
H(64A)	8781	1288	1645	69
H(65A)	10195	1147	1788	78
H(66A)	10523	1375	2182	76
H(67A)	9478	1746	2449	67
H(1EA)	6031	3808	413	185
H(1EB)	5680	4733	329	185
H(1EC)	5310	3868	210	185
H(4EA)	3376	3607	730	148
H(4EB)	3512	4626	785	148
H(5EA)	2112	4263	616	185
H(5EB)	2621	4048	376	185
H(5EC)	2627	5012	480	185
H(1FA)	3468	1647	537	173
H(1FB)	3596	757	678	173
H(1FC)	3889	1653	796	173
H(4FA)	3462	105	1039	139
H(4FB)	3766	995	1165	139
H(5FA)	3182	54	1450	173

Table A.25 continued

	x	y	z	U(eq)
H(5FB)	2300	5	1302	173
H(5FC)	2584	895	1425	173

X-Ray Structure Data for **2-8-Cu** (sm47)

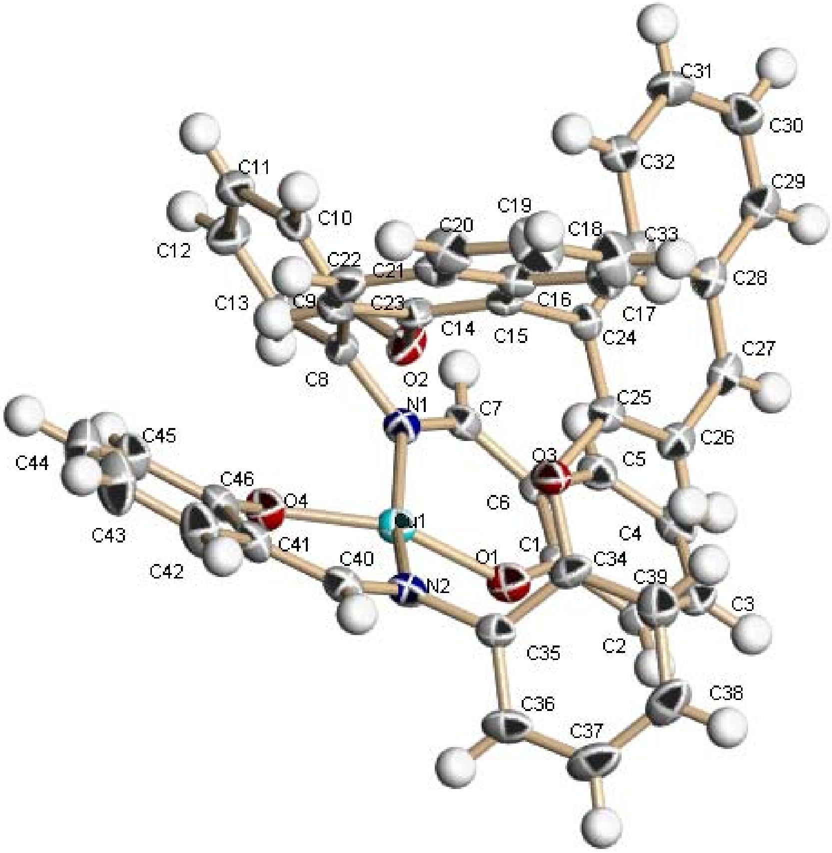


Table A.26. Crystal data and structure refinement for sm47.

Identification code	sm47	
CCDC number	264659	
Empirical formula	C50 H38 Cu N2 O6	
Formula weight	826.36	
Temperature	110(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 9.6049(2) Å	α= 90°.
	b = 20.1868(4) Å	β= 95.9610(10)°.
	c = 10.4445(2) Å	γ = 90°.
Volume	2014.16(7) $Å^3$	
Z	2	
Density (calculated)	1.363 Mg/m^3	
Absorption coefficient	1.207 mm^{-1}	
F(000)	858	
Crystal size	0.10 x 0.10 x 0.05 mm^3	
Theta range for data collection	4.26 to 59.36°.	
Index ranges	-10<=h<=10, -22<=k<=21, -11<=l<=11	
Reflections collected	10807	
Independent reflections	4955 [R(int) = 0.0290]	
Completeness to theta = 59.36°	98.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9421 and 0.8888	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4955 / 1 / 534	
Goodness-of-fit on F^2	1.009	
Final R indices [I>2sigma(I)]	R1 = 0.0315, wR2 = 0.0798	
R indices (all data)	R1 = 0.0347, wR2 = 0.0816	
Absolute structure parameter	-0.01(2)	
Largest diff. peak and hole	0.355 and -0.297 $e.Å^{-3}$	

Table A.27. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for sm47. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu(1)	8667(1)	-30(1)	6250(1)	22(1)
O(1)	7953(2)	-671(1)	5034(2)	27(1)
O(2)	7515(2)	1225(1)	6055(2)	26(1)
O(3)	8447(2)	705(1)	3500(2)	30(1)
O(4)	9636(2)	295(1)	7799(2)	28(1)
O(5)	6168(3)	3712(2)	-760(2)	53(1)
O(6)	5013(3)	3969(2)	910(3)	66(1)
N(1)	6843(3)	80(1)	6953(2)	22(1)
N(2)	10278(3)	144(1)	5249(2)	23(1)
C(1)	6721(3)	-953(2)	4919(3)	21(1)
C(2)	6446(4)	-1433(2)	3933(3)	25(1)
C(3)	5161(4)	-1734(2)	3729(3)	26(1)
C(4)	4090(4)	-1589(2)	4494(3)	27(1)
C(5)	4339(3)	-1129(2)	5466(3)	24(1)
C(6)	5628(3)	-803(2)	5691(3)	21(1)
C(7)	5753(3)	-266(2)	6614(3)	22(1)
C(8)	6708(3)	646(2)	7747(3)	20(1)
C(9)	7047(3)	1257(2)	7268(3)	21(1)
C(10)	6858(3)	1835(2)	7926(3)	23(1)
C(11)	6354(4)	1793(2)	9138(3)	27(1)
C(12)	6069(4)	1188(2)	9650(3)	32(1)
C(13)	6239(3)	612(2)	8968(3)	25(1)
C(14)	7994(3)	1780(2)	5447(3)	21(1)
C(15)	7490(3)	1865(2)	4178(3)	18(1)
C(16)	8085(3)	2384(2)	3479(3)	23(1)
C(17)	7730(4)	2471(2)	2146(3)	31(1)
C(18)	8356(4)	2955(2)	1488(3)	41(1)
C(19)	9329(4)	3386(2)	2130(4)	45(1)

Table A.27 continued

	x	y	z	U(eq)
C(20)	9714(4)	3315(2)	3416(3)	34(1)
C(21)	9125(3)	2804(2)	4117(3)	24(1)
C(22)	9593(4)	2686(2)	5431(3)	27(1)
C(23)	9069(4)	2178(2)	6082(3)	25(1)
C(24)	6492(3)	1365(2)	3543(3)	19(1)
C(25)	7020(3)	769(2)	3217(3)	22(1)
C(26)	6154(3)	237(2)	2726(3)	24(1)
C(27)	4745(4)	330(2)	2540(3)	23(1)
C(28)	4129(4)	941(2)	2812(3)	23(1)
C(29)	2662(4)	1052(2)	2607(3)	27(1)
C(30)	2082(4)	1637(2)	2917(3)	31(1)
C(31)	2947(4)	2146(2)	3447(3)	30(1)
C(32)	4365(3)	2072(2)	3652(3)	24(1)
C(33)	5012(4)	1468(2)	3340(3)	22(1)
C(34)	9218(3)	196(2)	3046(3)	25(1)
C(35)	10206(3)	-84(2)	3938(3)	21(1)
C(36)	11101(4)	-564(2)	3552(3)	31(1)
C(37)	11002(4)	-759(2)	2273(4)	38(1)
C(38)	10022(4)	-475(2)	1382(3)	37(1)
C(39)	9118(3)	11(2)	1755(3)	33(1)
C(40)	11287(3)	533(2)	5654(3)	26(1)
C(41)	11505(4)	858(2)	6871(3)	26(1)
C(42)	12542(4)	1349(2)	7048(3)	38(1)
C(43)	12755(4)	1719(2)	8152(3)	45(1)
C(44)	11921(4)	1589(2)	9138(4)	41(1)
C(45)	10900(4)	1115(2)	9020(3)	32(1)
C(46)	10629(3)	733(2)	7873(3)	25(1)
C(47)	6945(4)	4620(2)	614(4)	41(1)
C(48)	6025(4)	4056(2)	158(4)	36(1)
C(49)	4033(7)	3431(3)	554(8)	113(3)

Table A.27 continued

	x	y	z	U(eq)
C(50)	2733(6)	3554(3)	773(10)	130(3)

Table A.28. Bond lengths [Å] and angles [°] for sm47.

Cu(1)-O(1)	1.892(2)
Cu(1)-O(4)	1.897(2)
Cu(1)-N(1)	1.981(2)
Cu(1)-N(2)	1.987(2)
O(1)-C(1)	1.307(4)
O(2)-C(9)	1.389(4)
O(2)-C(14)	1.391(4)
O(3)-C(25)	1.377(4)
O(3)-C(34)	1.379(4)
O(4)-C(46)	1.298(4)
O(5)-C(48)	1.203(4)
O(6)-C(48)	1.323(4)
O(6)-C(49)	1.460(6)
N(1)-C(7)	1.278(4)
N(1)-C(8)	1.425(4)
N(2)-C(40)	1.284(4)
N(2)-C(35)	1.440(4)
C(1)-C(2)	1.419(5)
C(1)-C(6)	1.421(4)
C(2)-C(3)	1.373(5)
C(3)-C(4)	1.397(5)
C(4)-C(5)	1.378(5)
C(5)-C(6)	1.400(5)
C(6)-C(7)	1.447(4)
C(8)-C(9)	1.383(5)
C(8)-C(13)	1.397(4)
C(9)-C(10)	1.376(4)
C(10)-C(11)	1.405(4)
C(11)-C(12)	1.373(5)
C(12)-C(13)	1.383(5)
C(14)-C(15)	1.374(4)
C(14)-C(23)	1.417(5)

Table A.28 continued

C(15)-C(16)	1.428(4)
C(15)-C(24)	1.499(5)
C(16)-C(17)	1.410(4)
C(16)-C(21)	1.423(5)
C(17)-C(18)	1.368(5)
C(18)-C(19)	1.398(6)
C(19)-C(20)	1.363(5)
C(20)-C(21)	1.417(5)
C(21)-C(22)	1.419(5)
C(22)-C(23)	1.357(5)
C(24)-C(25)	1.363(5)
C(24)-C(33)	1.431(5)
C(25)-C(26)	1.421(5)
C(26)-C(27)	1.360(5)
C(27)-C(28)	1.410(5)
C(28)-C(29)	1.420(5)
C(28)-C(33)	1.434(5)
C(29)-C(30)	1.360(5)
C(30)-C(31)	1.400(5)
C(31)-C(32)	1.365(5)
C(32)-C(33)	1.422(5)
C(34)-C(35)	1.380(5)
C(34)-C(39)	1.393(4)
C(35)-C(36)	1.383(5)
C(36)-C(37)	1.387(5)
C(37)-C(38)	1.378(6)
C(38)-C(39)	1.393(5)
C(40)-C(41)	1.427(5)
C(41)-C(42)	1.404(5)
C(41)-C(46)	1.431(5)
C(42)-C(43)	1.372(5)
C(43)-C(44)	1.394(6)

Table A.28 continued

C(44)-C(45)	1.366(5)
C(45)-C(46)	1.426(5)
C(47)-C(48)	1.489(6)
C(49)-C(50)	1.316(8)
O(1)-Cu(1)-O(4)	156.93(10)
O(1)-Cu(1)-N(1)	93.01(10)
O(4)-Cu(1)-N(1)	91.13(10)
O(1)-Cu(1)-N(2)	90.88(10)
O(4)-Cu(1)-N(2)	92.75(10)
N(1)-Cu(1)-N(2)	160.49(10)
C(1)-O(1)-Cu(1)	128.4(2)
C(9)-O(2)-C(14)	122.1(2)
C(25)-O(3)-C(34)	123.6(2)
C(46)-O(4)-Cu(1)	125.35(19)
C(48)-O(6)-C(49)	116.2(4)
C(7)-N(1)-C(8)	118.5(3)
C(7)-N(1)-Cu(1)	124.5(2)
C(8)-N(1)-Cu(1)	116.3(2)
C(40)-N(2)-C(35)	118.0(3)
C(40)-N(2)-Cu(1)	122.5(2)
C(35)-N(2)-Cu(1)	118.75(19)
O(1)-C(1)-C(2)	117.5(3)
O(1)-C(1)-C(6)	124.7(3)
C(2)-C(1)-C(6)	117.7(3)
C(3)-C(2)-C(1)	120.8(3)
C(2)-C(3)-C(4)	121.4(3)
C(5)-C(4)-C(3)	118.8(3)
C(4)-C(5)-C(6)	121.5(3)
C(5)-C(6)-C(1)	119.8(3)
C(5)-C(6)-C(7)	118.4(3)
C(1)-C(6)-C(7)	121.5(3)
N(1)-C(7)-C(6)	127.1(3)

Table A.28 continued

C(9)-C(8)-C(13)	119.0(3)
C(9)-C(8)-N(1)	117.7(2)
C(13)-C(8)-N(1)	123.3(3)
C(10)-C(9)-C(8)	121.9(3)
C(10)-C(9)-O(2)	124.6(3)
C(8)-C(9)-O(2)	113.5(3)
C(9)-C(10)-C(11)	118.3(3)
C(12)-C(11)-C(10)	120.4(3)
C(11)-C(12)-C(13)	120.6(3)
C(12)-C(13)-C(8)	119.7(3)
C(15)-C(14)-O(2)	116.2(3)
C(15)-C(14)-C(23)	123.2(3)
O(2)-C(14)-C(23)	120.1(3)
C(14)-C(15)-C(16)	117.7(3)
C(14)-C(15)-C(24)	119.2(3)
C(16)-C(15)-C(24)	122.6(3)
C(17)-C(16)-C(21)	118.3(3)
C(17)-C(16)-C(15)	121.9(3)
C(21)-C(16)-C(15)	119.8(3)
C(18)-C(17)-C(16)	120.8(3)
C(17)-C(18)-C(19)	120.7(3)
C(20)-C(19)-C(18)	120.4(3)
C(19)-C(20)-C(21)	120.3(3)
C(20)-C(21)-C(22)	121.3(3)
C(20)-C(21)-C(16)	119.4(3)
C(22)-C(21)-C(16)	119.3(3)
C(23)-C(22)-C(21)	121.0(3)
C(22)-C(23)-C(14)	118.9(3)
C(25)-C(24)-C(33)	118.8(3)
C(25)-C(24)-C(15)	117.9(3)
C(33)-C(24)-C(15)	123.2(3)
C(24)-C(25)-O(3)	114.6(3)

Table A.28 continued

C(24)-C(25)-C(26)	122.5(3)
O(3)-C(25)-C(26)	122.6(3)
C(27)-C(26)-C(25)	119.0(3)
C(26)-C(27)-C(28)	121.6(3)
C(27)-C(28)-C(29)	122.5(3)
C(27)-C(28)-C(33)	118.9(3)
C(29)-C(28)-C(33)	118.6(3)
C(30)-C(29)-C(28)	121.7(3)
C(29)-C(30)-C(31)	119.4(3)
C(32)-C(31)-C(30)	121.5(3)
C(31)-C(32)-C(33)	120.7(3)
C(32)-C(33)-C(24)	122.8(3)
C(32)-C(33)-C(28)	118.0(3)
C(24)-C(33)-C(28)	119.2(3)
O(3)-C(34)-C(35)	115.4(3)
O(3)-C(34)-C(39)	123.2(3)
C(35)-C(34)-C(39)	121.1(3)
C(34)-C(35)-C(36)	119.7(3)
C(34)-C(35)-N(2)	118.2(3)
C(36)-C(35)-N(2)	122.1(3)
C(35)-C(36)-C(37)	119.8(3)
C(38)-C(37)-C(36)	120.4(3)
C(37)-C(38)-C(39)	120.4(3)
C(34)-C(39)-C(38)	118.5(3)
N(2)-C(40)-C(41)	127.6(3)
C(42)-C(41)-C(40)	118.6(3)
C(42)-C(41)-C(46)	119.4(3)
C(40)-C(41)-C(46)	121.8(3)
C(43)-C(42)-C(41)	122.5(3)
C(42)-C(43)-C(44)	118.1(4)
C(45)-C(44)-C(43)	121.8(3)

Table A.28 continued

C(44)-C(45)-C(46)	121.4(3)
O(4)-C(46)-C(45)	119.1(3)
O(4)-C(46)-C(41)	124.1(3)
C(45)-C(46)-C(41)	116.7(3)
O(5)-C(48)-O(6)	123.2(4)
O(5)-C(48)-C(47)	125.7(3)
O(6)-C(48)-C(47)	111.1(3)
C(50)-C(49)-O(6)	114.4(5)

Table A.29. Anisotropic displacement parameters ($Å^2$x 10^3) for sm47. The anisotropic displacement factor exponent takes the form: $-2\pi^2$[h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cu(1)	19(1)	23(1)	26(1)	1(1)	5(1)	-2(1)
O(1)	19(1)	29(1)	35(1)	0(1)	8(1)	-4(1)
O(2)	40(2)	21(1)	19(1)	1(1)	8(1)	-4(1)
O(3)	25(1)	24(1)	40(1)	-8(1)	-5(1)	4(1)
O(4)	22(1)	32(1)	30(1)	2(1)	4(1)	-5(1)
O(5)	53(2)	70(2)	37(1)	-10(2)	11(1)	-12(2)
O(6)	67(2)	35(2)	109(3)	-20(2)	64(2)	-12(2)
N(1)	23(1)	18(2)	24(1)	2(1)	1(1)	-1(1)
N(2)	18(1)	22(2)	28(1)	3(1)	3(1)	2(1)
C(1)	19(2)	17(2)	26(2)	6(1)	-1(1)	0(2)
C(2)	26(2)	21(2)	28(2)	-1(1)	7(2)	-1(2)
C(3)	31(2)	17(2)	29(2)	-4(1)	0(2)	0(2)
C(4)	21(2)	23(2)	36(2)	5(2)	1(1)	-6(2)
C(5)	24(2)	19(2)	29(2)	4(1)	2(1)	0(2)
C(6)	21(2)	19(2)	23(2)	4(1)	2(1)	1(2)
C(7)	19(2)	24(2)	22(2)	5(1)	2(1)	1(2)
C(8)	19(2)	21(2)	19(2)	-2(1)	2(1)	0(2)
C(9)	20(2)	24(2)	18(2)	1(1)	0(1)	1(2)
C(10)	24(2)	21(2)	21(2)	5(1)	-1(1)	3(2)
C(11)	29(2)	29(2)	24(2)	-2(2)	3(1)	5(2)
C(12)	43(2)	31(2)	22(2)	2(2)	12(2)	5(2)
C(13)	25(2)	25(2)	26(2)	3(1)	6(2)	-2(2)
C(14)	25(2)	13(2)	26(2)	0(1)	5(1)	1(2)
C(15)	19(2)	14(2)	23(2)	1(1)	6(1)	3(2)
C(16)	21(2)	20(2)	29(2)	1(1)	4(1)	3(2)
C(17)	33(2)	27(2)	30(2)	6(2)	-3(2)	-6(2)
C(18)	45(3)	48(3)	31(2)	16(2)	5(2)	-8(2)
C(19)	41(2)	39(2)	55(2)	21(2)	7(2)	-14(2)

Table A.29 continued

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(20)	25(2)	28(2)	48(2)	7(2)	4(2)	-9(2)
C(21)	20(2)	20(2)	35(2)	3(1)	8(1)	3(2)
C(22)	22(2)	23(2)	36(2)	-6(2)	3(2)	-1(2)
C(23)	27(2)	22(2)	24(2)	1(1)	-2(1)	5(2)
C(24)	19(2)	22(2)	17(1)	2(1)	1(1)	-2(2)
C(25)	23(2)	22(2)	20(2)	3(1)	5(1)	-1(2)
C(26)	30(2)	20(2)	22(2)	1(1)	5(1)	-1(2)
C(27)	29(2)	21(2)	19(2)	-1(1)	6(1)	-9(2)
C(28)	26(2)	24(2)	18(1)	1(1)	5(1)	-6(2)
C(29)	26(2)	32(2)	25(2)	-4(2)	10(1)	-9(2)
C(30)	21(2)	42(2)	32(2)	2(2)	6(1)	0(2)
C(31)	26(2)	30(2)	36(2)	-1(2)	11(2)	6(2)
C(32)	24(2)	22(2)	27(2)	-1(1)	6(1)	-1(2)
C(33)	26(2)	24(2)	17(2)	3(1)	7(1)	-5(2)
C(34)	22(2)	19(2)	33(2)	-7(1)	9(1)	-2(2)
C(35)	17(2)	20(2)	27(1)	2(2)	6(1)	-1(2)
C(36)	19(2)	28(2)	47(2)	-1(2)	12(2)	4(2)
C(37)	28(2)	36(2)	53(2)	-14(2)	18(2)	0(2)
C(38)	30(2)	45(2)	37(2)	-17(2)	15(2)	-8(2)
C(39)	28(2)	41(2)	30(2)	0(2)	4(1)	-3(2)
C(40)	17(2)	29(2)	31(2)	5(2)	2(1)	1(2)
C(41)	18(2)	32(2)	27(2)	4(1)	-2(1)	-1(2)
C(42)	28(2)	50(3)	34(2)	5(2)	-3(2)	-13(2)
C(43)	42(2)	52(3)	38(2)	5(2)	-10(2)	-25(2)
C(44)	46(2)	45(3)	29(2)	-5(2)	-7(2)	-13(2)
C(45)	32(2)	39(2)	24(2)	3(2)	-2(2)	-4(2)
C(46)	18(2)	26(2)	29(2)	7(2)	-4(1)	2(2)
C(47)	31(2)	47(3)	46(2)	-5(2)	11(2)	0(2)
C(48)	32(2)	37(2)	40(2)	5(2)	11(2)	5(2)
C(49)	96(5)	45(3)	216(8)	-57(4)	108(5)	-39(4)

Table A.29 continued

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(50)	53(4)	59(4)	265(10)	-34(5)	-48(5)	-8(4)

Table A.30. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for sm47.

	x	y	z	U(eq)
H(2)	7160	-1547	3408	30
H(3)	4995	-2049	3053	31
H(4)	3207	-1803	4346	32
H(5)	3619	-1031	5996	29
H(7)	4935	-159	7010	26
H(10)	7064	2253	7569	27
H(11)	6209	2186	9607	33
H(12)	5751	1165	10481	38
H(13)	6039	194	9328	30
H(17)	7048	2191	1699	37
H(18)	8127	2997	585	50
H(19)	9725	3732	1668	54
H(20)	10380	3609	3844	40
H(22)	10284	2967	5862	32
H(23)	9417	2089	6950	29
H(26)	6553	-177	2531	29
H(27)	4162	-26	2218	27
H(29)	2072	708	2243	32
H(30)	1097	1699	2775	37
H(31)	2537	2553	3669	36
H(32)	4926	2428	4008	29
H(36)	11782	-760	4161	37
H(37)	11613	-1091	2009	46
H(38)	9963	-612	508	44
H(39)	8449	213	1142	39
H(40)	11969	613	5075	31
H(42)	13118	1428	6377	45
H(43)	13452	2055	8242	54
H(44)	12066	1837	9914	49

Table A.30 continued

	x	y	z	U(eq)
H(45)	10359	1038	9717	38
H(47A)	7710	4660	68	62
H(47B)	7332	4541	1506	62
H(47C)	6396	5030	568	62
H(49A)	4050	3334	-374	135
H(49B)	4357	3028	1039	135
H(50A)	2505	4016	554	195
H(50B)	2630	3478	1685	195
H(50C)	2098	3260	243	195

X-Ray Structure Data for **2-11-Co** (sm67)

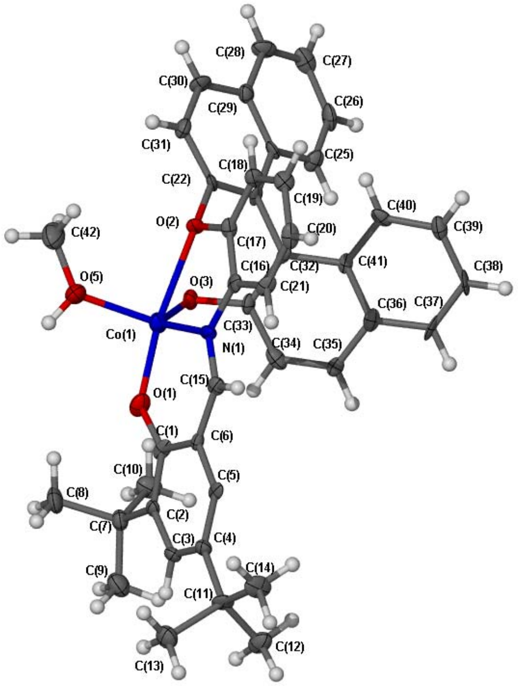


Table A.31. Crystal data and structure refinement for sm67a.

Identification code	sm67a	
Empirical formula	$C_{43} H_{44}CoNO5$	
Formula weight	713.72	
Temperature	293(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 15.1115(18) Å	α= 90°.
	b = 12.3348(15) Å	β= 103.912(7)°.
	c = 20.062(3) Å	γ = 90°.
Volume	3629.8(9) Å^3	
Z	4	
Density (calculated)	1.306 Mg/m^3	
Absorption coefficient	4.076 mm^{-1}	
F(000)	1504	
Crystal size	0.20 x 0.20 x 0.10 mm^3	
Theta range for data collection	3.01 to 58.95°.	
Index ranges	-14<=h<=16, -13<=k<=13, -20<=l<=22	
Reflections collected	16603	
Independent reflections	4825 [R(int) = 0.1004]	
Completeness to theta = 58.95°	92.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6860 and 0.4961	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4825 / 0 / 460	
Goodness-of-fit on F^2	1.024	
Final R indices [I>2sigma(I)]	R1 = 0.0766, wR2 = 0.1667	
R indices (all data)	R1 = 0.1191, wR2 = 0.1898	
Largest diff. peak and hole	0.716 and -0.517 e.Å^{-3}	

Table A.32. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for sm67a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Co(1)	1823(1)	69(1)	4736(1)	23(1)
O(1)	1379(3)	-871(3)	3967(2)	27(1)
O(2)	2647(2)	1172(3)	5666(2)	17(1)
O(3)	1465(2)	1529(3)	4366(2)	21(1)
O(4)	56(3)	2138(3)	4855(3)	52(2)
O(5)	1075(3)	-528(3)	5355(2)	34(1)
N(1)	3118(3)	-467(3)	4949(2)	18(1)
C(1)	1858(4)	-1509(4)	3667(3)	20(1)
C(2)	1447(4)	-1991(4)	3022(3)	17(1)
C(3)	1945(4)	-2732(4)	2747(3)	20(1)
C(4)	2852(4)	-3030(4)	3059(3)	18(1)
C(5)	3265(4)	-2514(4)	3656(3)	17(1)
C(6)	2804(4)	-1739(4)	3965(3)	14(1)
C(7)	457(4)	-1713(4)	2641(3)	23(2)
C(8)	-207(4)	-2129(5)	3062(3)	34(2)
C(9)	163(4)	-2229(5)	1935(3)	33(2)
C(10)	341(4)	-486(5)	2539(3)	31(2)
C(11)	3337(4)	-3870(4)	2714(3)	23(2)
C(12)	3313(4)	-3521(5)	1979(3)	32(2)
C(13)	2830(4)	-4974(4)	2689(3)	31(2)
C(14)	4320(4)	-4051(5)	3101(3)	32(2)
C(15)	3329(4)	-1230(4)	4561(3)	18(1)
C(16)	3798(4)	-50(4)	5509(3)	19(1)
C(17)	3551(4)	829(4)	5867(3)	18(1)
C(18)	4172(4)	1301(4)	6415(3)	20(1)
C(19)	5035(4)	900(4)	6618(3)	22(2)

Table A.32 continued

	x	y	z	U(eq)
C(20)	5293(4)	28(4)	6267(3)	23(2)
C(21)	4693(4)	-434(4)	5726(3)	20(1)
C(22)	2503(4)	2281(4)	5764(3)	17(1)
C(23)	2602(3)	2992(4)	5257(3)	15(1)
C(24)	2462(4)	4125(4)	5377(3)	16(1)
C(25)	2470(4)	4916(4)	4867(3)	22(2)
C(26)	2338(4)	5991(5)	4985(3)	28(2)
C(27)	2207(4)	6327(5)	5622(3)	28(2)
C(28)	2171(4)	5588(5)	6123(3)	28(2)
C(29)	2282(4)	4471(4)	6006(3)	20(1)
C(30)	2182(4)	3678(4)	6498(3)	23(2)
C(31)	2283(4)	2595(4)	6372(3)	20(1)
C(32)	2805(4)	2618(4)	4611(3)	16(1)
C(33)	2173(4)	1939(4)	4173(3)	18(1)
C(34)	2308(4)	1707(4)	3518(3)	24(2)
C(35)	3060(4)	2036(4)	3310(3)	19(1)
C(36)	3754(4)	2629(4)	3761(3)	19(1)
C(37)	4572(4)	2922(5)	3588(3)	25(2)
C(38)	5249(4)	3444(4)	4040(3)	22(2)
C(39)	5142(4)	3691(4)	4691(3)	23(2)
C(40)	4350(4)	3465(4)	4879(3)	20(2)
C(41)	3631(4)	2915(4)	4421(3)	16(1)
C(42)	873(5)	-43(5)	5941(3)	40(2)
C(43)	69(4)	3196(5)	5105(4)	44(2)

Table A.33. Bond lengths [Å] and angles [°] for sm67a.

Co(1)-O(1)	1.917(4)
Co(1)-O(3)	1.974(4)
Co(1)-O(5)	2.010(4)
Co(1)-N(1)	2.012(5)
Co(1)-O(2)	2.402(3)
O(1)-C(1)	1.309(6)
O(2)-C(17)	1.394(6)
O(2)-C(22)	1.406(6)
O(3)-C(33)	1.322(6)
O(4)-C(43)	1.397(7)
O(4)-H(4)	0.8200
O(5)-C(42)	1.415(7)
O(5)-H(5)	0.9300
N(1)-C(15)	1.309(7)
N(1)-C(16)	1.424(7)
C(1)-C(2)	1.424(7)
C(1)-C(6)	1.439(8)
C(2)-C(3)	1.380(7)
C(2)-C(7)	1.546(8)
C(3)-C(4)	1.411(8)
C(3)-H(3)	0.9300
C(4)-C(5)	1.366(7)
C(4)-C(11)	1.528(8)
C(5)-C(6)	1.411(7)
C(6)-C(15)	1.413(7)
C(7)-C(9)	1.518(8)
C(7)-C(10)	1.532(8)
C(7)-C(8)	1.547(8)
C(8)-H(8A)	0.9600
C(8)-H(8B)	0.9600
C(8)-H(8C)	0.9600
C(9)-H(9A)	0.9600

Table A.33 continued

C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600
C(10)-H(10A)	0.9600
C(10)-H(10B)	0.9600
C(10)-H(10C)	0.9600
C(11)-C(14)	1.518(8)
C(11)-C(12)	1.527(8)
C(11)-C(13)	1.558(7)
C(12)-H(12A)	0.9600
C(12)-H(12B)	0.9600
C(12)-H(12C)	0.9600
C(13)-H(13A)	0.9600
C(13)-H(13B)	0.9600
C(13)-H(13C)	0.9600
C(14)-H(14A)	0.9600
C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600
C(15)-H(15)	0.9300
C(16)-C(21)	1.400(8)
C(16)-C(17)	1.400(8)
C(17)-C(18)	1.389(7)
C(18)-C(19)	1.363(8)
C(18)-H(18)	0.9300
C(19)-C(20)	1.391(8)
C(19)-H(19)	0.9300
C(20)-C(21)	1.362(8)
C(20)-H(20)	0.9300
C(21)-H(21)	0.9300
C(22)-C(23)	1.378(8)
C(22)-C(31)	1.396(8)
C(23)-C(24)	1.442(7)
C(23)-C(32)	1.476(8)

Table A.33 continued

C(24)-C(25)	1.416(8)
C(24)-C(29)	1.418(8)
C(25)-C(26)	1.370(7)
C(25)-H(25)	0.9300
C(26)-C(27)	1.402(9)
C(26)-H(26)	0.9300
C(27)-C(28)	1.367(8)
C(27)-H(27)	0.9300
C(28)-C(29)	1.415(8)
C(28)-H(28)	0.9300
C(29)-C(30)	1.423(8)
C(30)-C(31)	1.374(7)
C(30)-H(30)	0.9300
C(31)-H(31)	0.9300
C(32)-C(33)	1.407(7)
C(32)-C(41)	1.437(7)
C(33)-C(34)	1.407(8)
C(34)-C(35)	1.363(8)
C(34)-H(34)	0.9300
C(35)-C(36)	1.413(7)
C(35)-H(35)	0.9300
C(36)-C(37)	1.408(8)
C(36)-C(41)	1.427(8)
C(37)-C(38)	1.356(8)
C(37)-H(37)	0.9300
C(38)-C(39)	1.388(8)
C(38)-H(38)	0.9300
C(39)-C(40)	1.368(8)
C(39)-H(39)	0.9300
C(40)-C(41)	1.417(7)
C(40)-H(40)	0.9300
C(42)-H(42A)	0.9600

Table A.33 continued

C(42)-H(42B)	0.9600
C(42)-H(42C)	0.9600
C(43)-H(43A)	0.9600
C(43)-H(43B)	0.9600
C(43)-H(43C)	0.9600
O(1)-Co(1)-O(3)	103.80(16)
O(1)-Co(1)-O(5)	97.85(17)
O(3)-Co(1)-O(5)	114.98(17)
O(1)-Co(1)-N(1)	96.12(17)
O(3)-Co(1)-N(1)	122.99(17)
O(5)-Co(1)-N(1)	114.28(18)
O(1)-Co(1)-O(2)	169.59(15)
O(3)-Co(1)-O(2)	79.55(13)
O(5)-Co(1)-O(2)	89.44(15)
N(1)-Co(1)-O(2)	74.03(15)
C(1)-O(1)-Co(1)	127.4(4)
C(17)-O(2)-C(22)	115.3(4)
C(17)-O(2)-Co(1)	110.0(3)
C(22)-O(2)-Co(1)	126.2(3)
C(33)-O(3)-Co(1)	106.9(3)
C(43)-O(4)-H(4)	109.5
C(42)-O(5)-Co(1)	128.6(4)
C(42)-O(5)-H(5)	115.7
Co(1)-O(5)-H(5)	115.7
C(15)-N(1)-C(16)	119.8(5)
C(15)-N(1)-Co(1)	118.2(4)
C(16)-N(1)-Co(1)	122.0(4)
O(1)-C(1)-C(2)	120.0(5)
O(1)-C(1)-C(6)	122.1(5)
C(2)-C(1)-C(6)	117.9(5)
C(3)-C(2)-C(1)	118.6(5)
C(3)-C(2)-C(7)	120.4(5)

Table A.33 continued

C(1)-C(2)-C(7)	121.0(5)
C(2)-C(3)-C(4)	124.0(5)
C(2)-C(3)-H(3)	118.0
C(4)-C(3)-H(3)	118.0
C(5)-C(4)-C(3)	117.2(5)
C(5)-C(4)-C(11)	123.0(5)
C(3)-C(4)-C(11)	119.7(5)
C(4)-C(5)-C(6)	122.0(5)
C(5)-C(6)-C(15)	115.9(5)
C(5)-C(6)-C(1)	119.8(5)
C(15)-C(6)-C(1)	124.3(5)
C(9)-C(7)-C(10)	106.9(5)
C(9)-C(7)-C(2)	113.6(5)
C(10)-C(7)-C(2)	110.6(4)
C(9)-C(7)-C(8)	106.7(5)
C(10)-C(7)-C(8)	109.4(5)
C(2)-C(7)-C(8)	109.5(5)
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(7)-C(9)-H(9A)	109.5
C(7)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(7)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(7)-C(10)-H(10A)	109.5
C(7)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5

Table A.33 continued

C(7)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(14)-C(11)-C(12)	109.2(5)
C(14)-C(11)-C(4)	112.6(5)
C(12)-C(11)-C(4)	110.1(5)
C(14)-C(11)-C(13)	107.5(5)
C(12)-C(11)-C(13)	108.5(5)
C(4)-C(11)-C(13)	108.8(5)
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(11)-C(13)-H(13A)	109.5
C(11)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(11)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(11)-C(14)-H(14A)	109.5
C(11)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(11)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
N(1)-C(15)-C(6)	131.0(5)
N(1)-C(15)-H(15)	114.5
C(6)-C(15)-H(15)	114.5
C(21)-C(16)-C(17)	117.3(5)
C(21)-C(16)-N(1)	125.6(5)

Table A.33 continued

C(17)-C(16)-N(1)	117.0(5)
C(18)-C(17)-O(2)	122.1(5)
C(18)-C(17)-C(16)	121.2(5)
O(2)-C(17)-C(16)	116.7(5)
C(19)-C(18)-C(17)	120.0(5)
C(19)-C(18)-H(18)	120.0
C(17)-C(18)-H(18)	120.0
C(18)-C(19)-C(20)	119.6(5)
C(18)-C(19)-H(19)	120.2
C(20)-C(19)-H(19)	120.2
C(21)-C(20)-C(19)	120.8(5)
C(21)-C(20)-H(20)	119.6
C(19)-C(20)-H(20)	119.6
C(20)-C(21)-C(16)	121.0(5)
C(20)-C(21)-H(21)	119.5
C(16)-C(21)-H(21)	119.5
C(23)-C(22)-C(31)	124.0(5)
C(23)-C(22)-O(2)	118.0(5)
C(31)-C(22)-O(2)	118.0(5)
C(22)-C(23)-C(24)	116.6(5)
C(22)-C(23)-C(32)	122.0(5)
C(24)-C(23)-C(32)	121.3(5)
C(25)-C(24)-C(29)	118.2(5)
C(25)-C(24)-C(23)	121.3(5)
C(29)-C(24)-C(23)	120.5(5)
C(26)-C(25)-C(24)	121.0(6)
C(26)-C(25)-H(25)	119.5
C(24)-C(25)-H(25)	119.5
C(25)-C(26)-C(27)	120.2(6)
C(25)-C(26)-H(26)	119.9
C(27)-C(26)-H(26)	119.9
C(28)-C(27)-C(26)	120.8(6)

Table A.33 continued

C(28)-C(27)-H(27)	119.6
C(26)-C(27)-H(27)	119.6
C(27)-C(28)-C(29)	120.0(6)
C(27)-C(28)-H(28)	120.0
C(29)-C(28)-H(28)	120.0
C(28)-C(29)-C(24)	119.8(5)
C(28)-C(29)-C(30)	121.2(6)
C(24)-C(29)-C(30)	119.0(5)
C(31)-C(30)-C(29)	120.5(6)
C(31)-C(30)-H(30)	119.8
C(29)-C(30)-H(30)	119.8
C(30)-C(31)-C(22)	119.3(5)
C(30)-C(31)-H(31)	120.3
C(22)-C(31)-H(31)	120.3
C(33)-C(32)-C(41)	119.2(5)
C(33)-C(32)-C(23)	118.8(5)
C(41)-C(32)-C(23)	122.0(5)
O(3)-C(33)-C(34)	120.3(5)
O(3)-C(33)-C(32)	121.3(5)
C(34)-C(33)-C(32)	118.4(5)
C(35)-C(34)-C(33)	123.0(5)
C(35)-C(34)-H(34)	118.5
C(33)-C(34)-H(34)	118.5
C(34)-C(35)-C(36)	120.3(6)
C(34)-C(35)-H(35)	119.9
C(36)-C(35)-H(35)	119.9
C(37)-C(36)-C(35)	122.5(6)
C(37)-C(36)-C(41)	118.9(5)
C(35)-C(36)-C(41)	118.6(5)
C(38)-C(37)-C(36)	121.6(6)
C(38)-C(37)-H(37)	119.2
C(36)-C(37)-H(37)	119.2

Table A.33 continued

C(37)-C(38)-C(39)	119.6(6)
C(37)-C(38)-H(38)	120.2
C(39)-C(38)-H(38)	120.2
C(40)-C(39)-C(38)	121.5(6)
C(40)-C(39)-H(39)	119.2
C(38)-C(39)-H(39)	119.2
C(39)-C(40)-C(41)	120.3(6)
C(39)-C(40)-H(40)	119.9
C(41)-C(40)-H(40)	119.9
C(40)-C(41)-C(36)	118.0(5)
C(40)-C(41)-C(32)	122.0(5)
C(36)-C(41)-C(32)	120.0(5)
O(5)-C(42)-H(42A)	109.5
O(5)-C(42)-H(42B)	109.5
H(42A)-C(42)-H(42B)	109.5
O(5)-C(42)-H(42C)	109.5
H(42A)-C(42)-H(42C)	109.5
H(42B)-C(42)-H(42C)	109.5
O(4)-C(43)-H(43A)	109.5
O(4)-C(43)-H(43B)	109.5
H(43A)-C(43)-H(43B)	109.5
O(4)-C(43)-H(43C)	109.5
H(43A)-C(43)-H(43C)	109.5
H(43B)-C(43)-H(43C)	109.5

Table A.34. Anisotropic displacement parameters ($Å^2$x 10^3) for sm67a. The anisotropic displacement factor exponent takes the form: $-2 \pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Co(1)	19(1)	19(1)	32(1)	-3(1)	11(1)	0(1)
O(1)	28(3)	21(2)	39(3)	0(2)	19(2)	7(2)
O(2)	16(2)	12(2)	25(2)	-6(2)	8(2)	3(2)
O(3)	13(2)	23(2)	30(3)	-4(2)	10(2)	-2(2)
O(4)	39(3)	32(3)	98(5)	-21(3)	44(3)	-11(2)
O(5)	33(3)	37(3)	37(3)	-14(2)	20(2)	-8(2)
N(1)	28(3)	10(2)	17(3)	-2(2)	10(2)	-6(2)
C(1)	32(4)	5(3)	27(4)	6(3)	19(3)	7(2)
C(2)	18(3)	11(3)	25(4)	-3(3)	11(3)	-3(2)
C(3)	24(4)	15(3)	21(3)	-7(3)	9(3)	-7(3)
C(4)	20(4)	13(3)	23(3)	-4(3)	8(3)	-2(2)
C(5)	29(4)	5(3)	23(3)	3(2)	16(3)	-1(2)
C(6)	12(3)	13(3)	19(3)	2(2)	9(3)	2(2)
C(7)	20(4)	20(3)	29(4)	-1(3)	10(3)	-4(3)
C(8)	23(4)	34(4)	47(4)	-3(3)	15(3)	-12(3)
C(9)	27(4)	29(4)	42(4)	-5(3)	7(3)	-5(3)
C(10)	26(4)	27(4)	36(4)	-4(3)	2(3)	7(3)
C(11)	33(4)	11(3)	29(4)	-8(3)	14(3)	3(3)
C(12)	47(5)	18(3)	38(4)	-3(3)	24(3)	2(3)
C(13)	36(4)	20(3)	41(4)	-3(3)	15(3)	-5(3)
C(14)	17(4)	32(4)	45(4)	-12(3)	7(3)	12(3)
C(15)	24(4)	9(3)	24(3)	2(3)	10(3)	1(2)
C(16)	27(4)	12(3)	21(3)	4(3)	13(3)	-4(2)
C(17)	14(3)	12(3)	28(4)	2(3)	8(3)	3(2)
C(18)	19(4)	14(3)	30(4)	-3(3)	10(3)	3(2)
C(19)	20(4)	20(3)	24(4)	2(3)	3(3)	3(3)
C(20)	16(3)	17(3)	38(4)	10(3)	9(3)	7(3)
C(21)	25(4)	12(3)	27(4)	4(3)	15(3)	9(2)

Table A.34 continued

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(22)	13(3)	11(3)	30(4)	-6(3)	12(3)	-6(2)
C(23)	7(3)	18(3)	23(3)	1(3)	10(2)	4(2)
C(24)	13(3)	8(3)	28(4)	-3(3)	5(3)	-4(2)
C(25)	22(4)	21(3)	28(4)	3(3)	13(3)	8(3)
C(26)	23(4)	18(4)	46(5)	8(3)	14(3)	-4(3)
C(27)	15(4)	20(4)	47(5)	2(3)	4(3)	5(3)
C(28)	24(4)	25(4)	36(4)	-14(3)	8(3)	5(3)
C(29)	15(3)	18(3)	28(4)	-2(3)	9(3)	-1(2)
C(30)	24(4)	21(4)	28(4)	-8(3)	13(3)	7(3)
C(31)	21(4)	22(4)	21(3)	3(3)	11(3)	0(2)
C(32)	22(4)	11(3)	21(3)	2(2)	14(3)	2(2)
C(33)	11(3)	19(3)	26(4)	3(3)	9(3)	2(2)
C(34)	18(4)	17(3)	32(4)	0(3)	-2(3)	-1(3)
C(35)	17(4)	21(3)	20(3)	1(3)	8(3)	2(3)
C(36)	14(4)	20(3)	25(4)	8(3)	8(3)	6(2)
C(37)	22(4)	31(4)	31(4)	9(3)	24(3)	8(3)
C(38)	8(3)	17(3)	42(4)	4(3)	12(3)	-4(2)
C(39)	15(4)	17(3)	39(4)	2(3)	9(3)	-1(2)
C(40)	17(4)	10(3)	31(4)	-7(3)	3(3)	3(2)
C(41)	17(3)	7(3)	26(4)	5(3)	12(3)	5(2)
C(42)	31(4)	54(5)	35(4)	-1(4)	6(3)	-10(3)
C(43)	32(4)	41(5)	58(5)	-6(4)	7(4)	-3(3)

Table A35. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10 ^{3}) for sm67a.

	x	y	z	U(eq)
H(4)	465	2065	4654	77
H(5)	828	-1214	5242	40
H(3)	1666	-3055	2331	24
H(8A)	-139	-2900	3122	51
H(8B)	-822	-1965	2822	51
H(8C)	-72	-1782	3503	51
H(9A)	574	-2015	1662	49
H(9B)	-443	-1994	1717	49
H(9C)	171	-3003	1981	49
H(10A)	490	-131	2977	46
H(10B)	-280	-327	2310	46
H(10C)	738	-230	2265	46
H(12A)	2696	-3545	1708	48
H(12B)	3684	-4003	1787	48
H(12C)	3543	-2796	1982	48
H(13A)	2203	-4884	2451	47
H(13B)	2864	-5221	3148	47
H(13C)	3111	-5499	2452	47
H(14A)	4598	-4572	2860	47
H(14B)	4336	-4317	3554	47
H(14C)	4647	-3378	3135	47
H(15)	3926	-1479	4701	22
H(18)	3999	1891	6642	24
H(19)	5449	1207	6989	27
H(20)	5883	-243	6405	28
H(21)	4881	-1012	5496	24
H(25)	2566	4703	4445	27
H(26)	2335	6499	4642	34
H(27)	2145	7062	5705	34

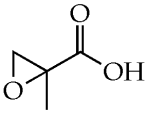
Table A.35 continued

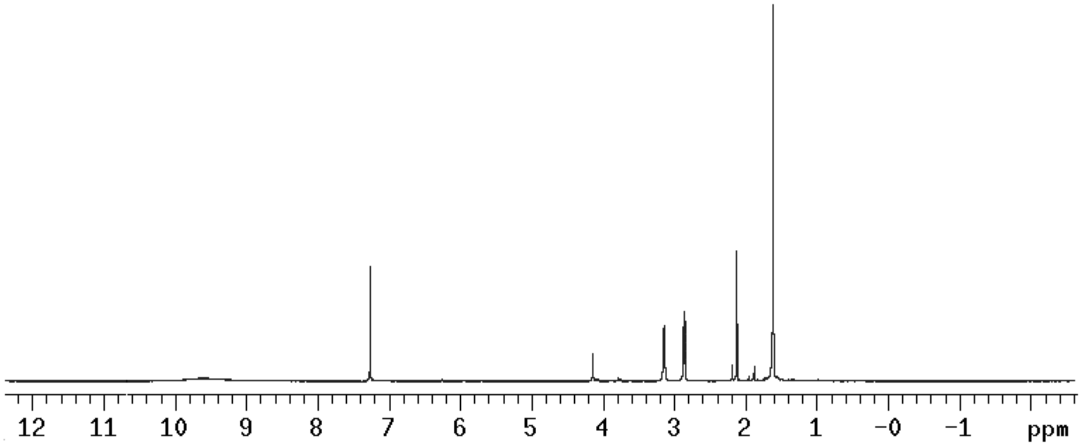
	x	y	z	U(eq)
H(28)	2073	5820	6541	34
H(30)	2048	3894	6906	28
H(31)	2204	2077	6690	24
H(34)	1864	1311	3214	29
H(35)	3116	1869	2870	23
H(37)	4650	2752	3154	30
H(38)	5781	3637	3914	26
H(39)	5621	4017	5007	28
H(40)	4284	3674	5310	24
H(42A)	1429	72	6285	60
H(42B)	479	-511	6120	60
H(42C)	576	641	5815	60
H(43A)	635	3323	5435	67
H(43B)	-429	3293	5321	67
H(43C)	9	3700	4732	67

APPENDIX B

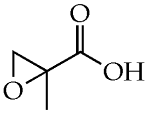
EPOXIDATIONS USING NICKEL OXIDE HYDROXIDE

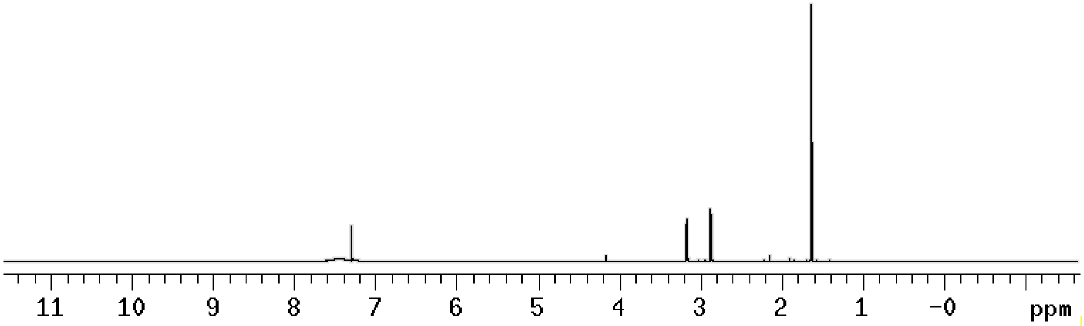
^{1}H NMR of 2-methyl-oxirane-2-carboxylic acid, crude, Table 3.1, entry 1.



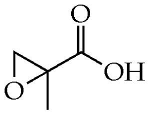


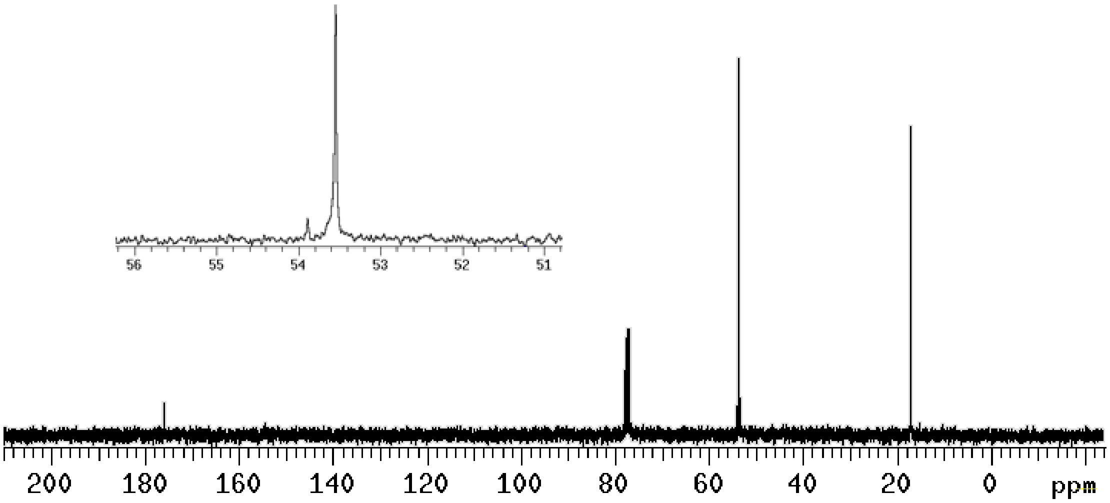
^{1}H NMR of 2-methyl-oxirane-2-carboxylic acid, pure, Table 3.1, entry 1.



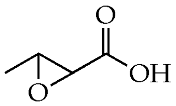


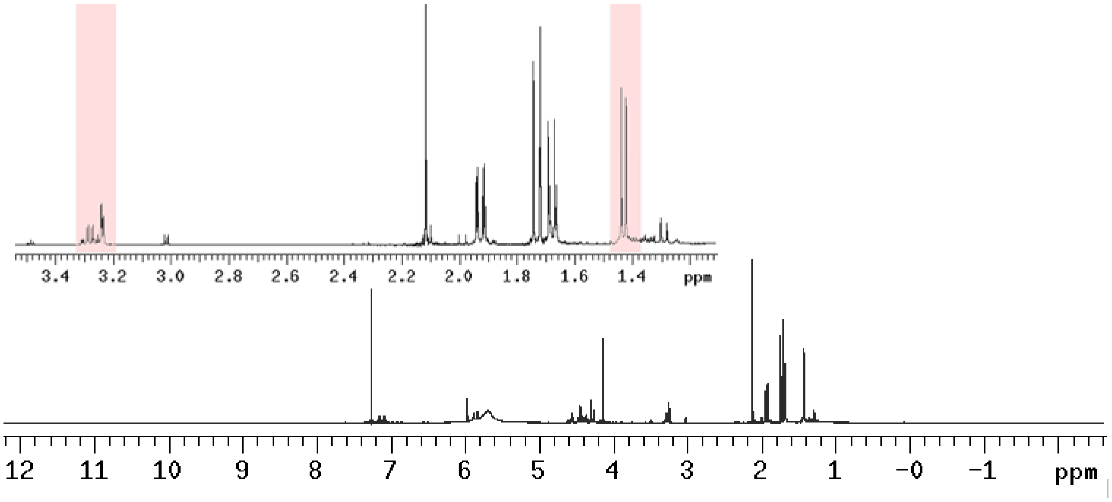
^{13}C NMR of 2-methyl-oxirane-2-carboxylic acid, pure, Table 3.1, entry 1.



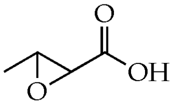


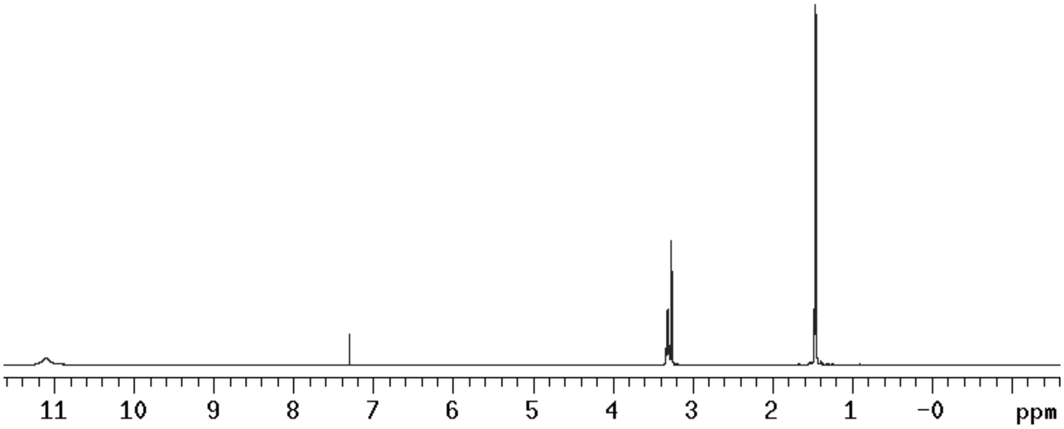
^{1}H NMR of 3-methyl-oxirane-2-carboxcylic acid, crude, Table 3.1, entry 2.



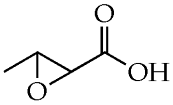


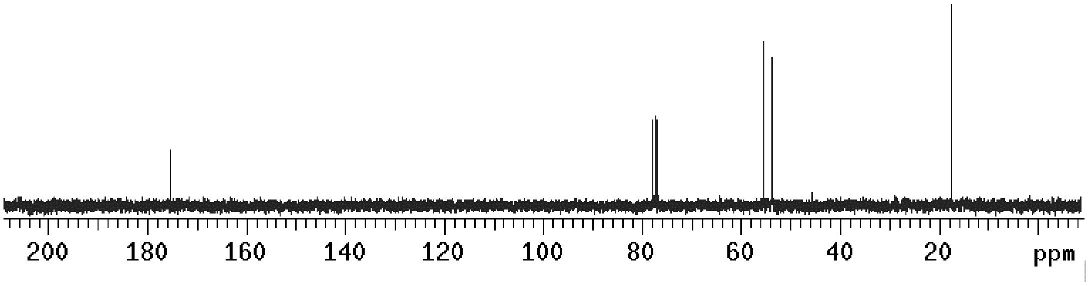
^{1}H NMR of 3-methyl-oxirane-2-carboxcylic acid, pure, Table 3.1, entry 2.



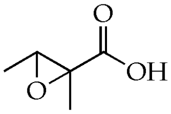


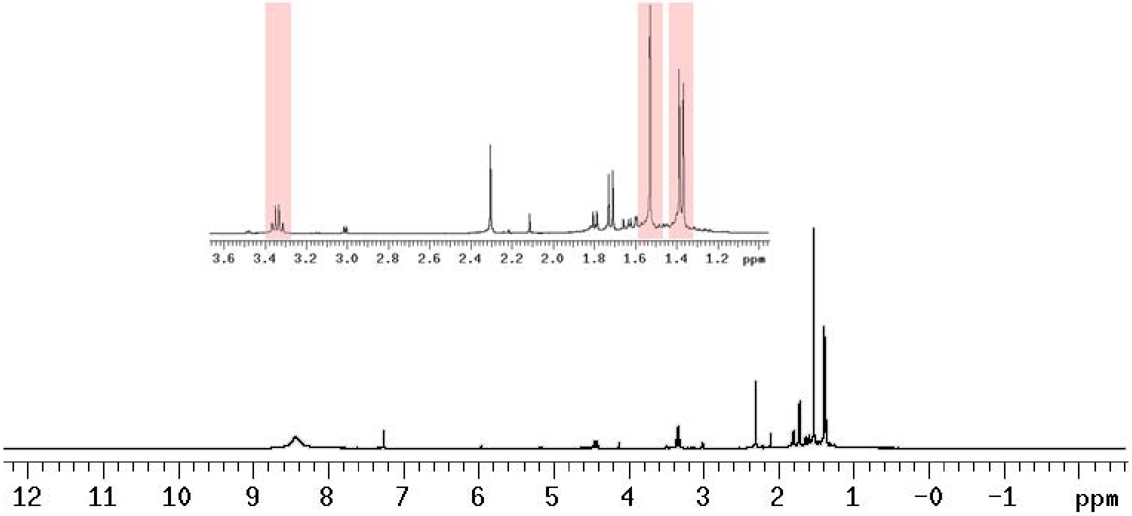
^{13}C NMR of 3-methyl-oxirane-2-carboxcylic acid, pure, Table 3.1, entry 2.



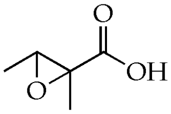


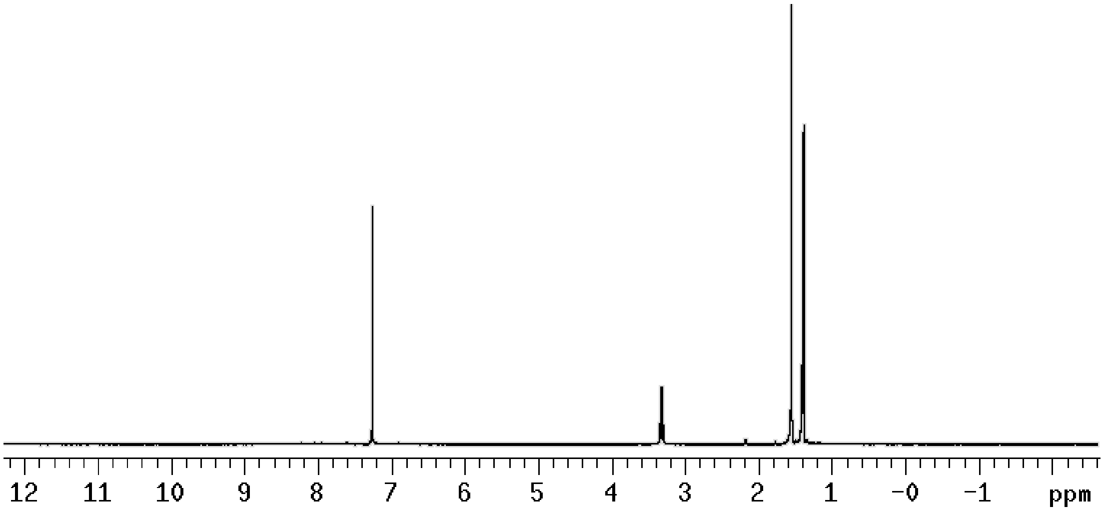
^{1}H NMR of 2,3-dimethyl-oxirane-2-carboxylic acid, crude, Table 3.1, entry 3.



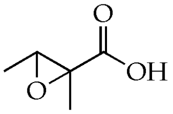


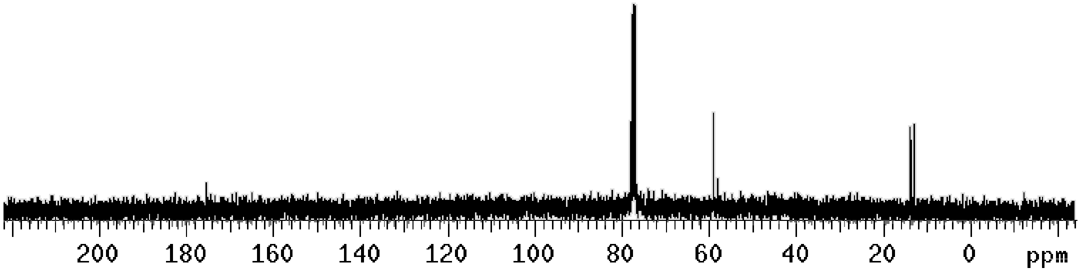
^{1}H NMR of 2,3-dimethyl-oxirane-2-carboxylic acid, pure, Table 3.1, entry 3.



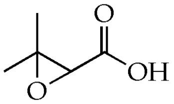


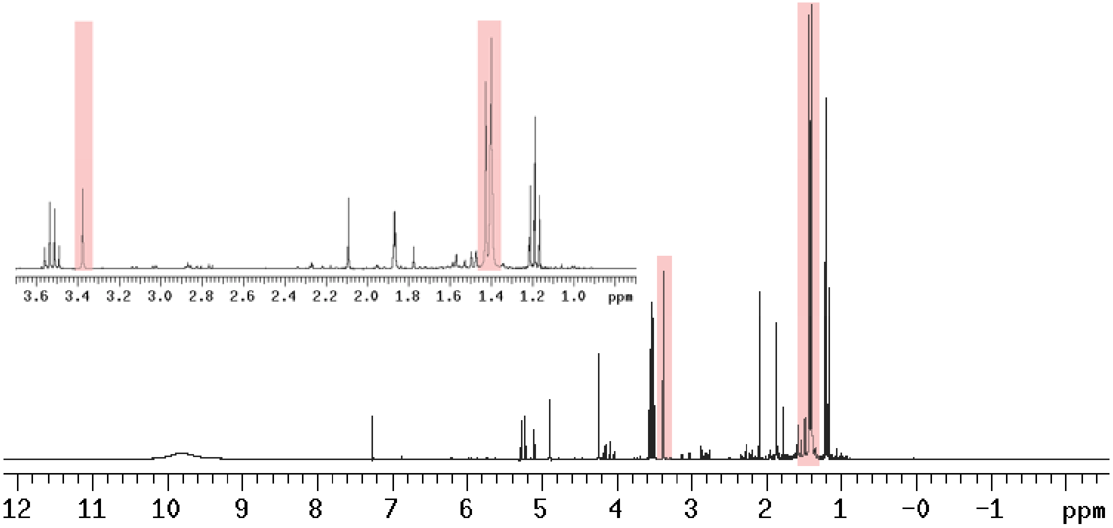
^{13}C NMR of 2,3-dimethyl-oxirane-2-carboxylic acid, pure, Table 3.1, entry 3.



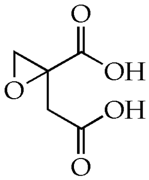


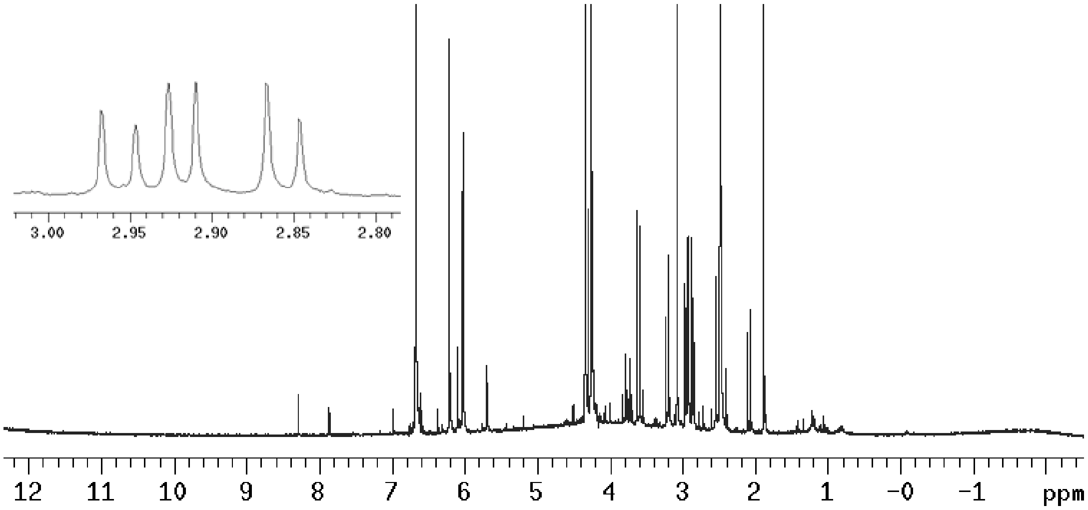
^{1}H NMR of 3,3-dimethyl-oxirane-2-carboxylic acid, crude, Table 3.1, entry 4.





^{1}H NMR of 2-carboxymethyl-oxirane-2-carboxylic acid, crude, Table 3.1, entry 5.

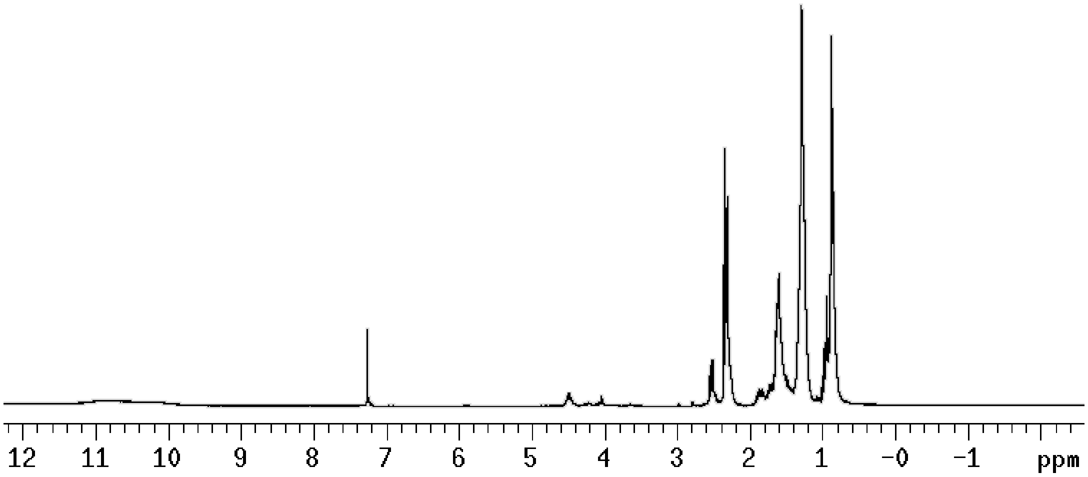




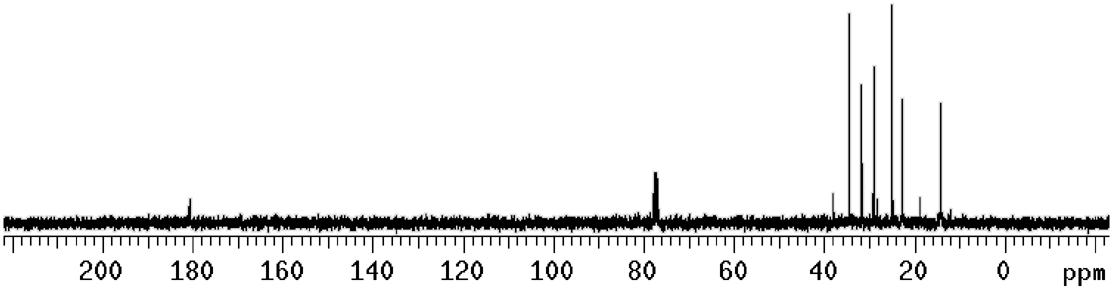
APPENDIX C

OTHER OXIDATIONS USING NICKEL OXIDE HYDROXIDE

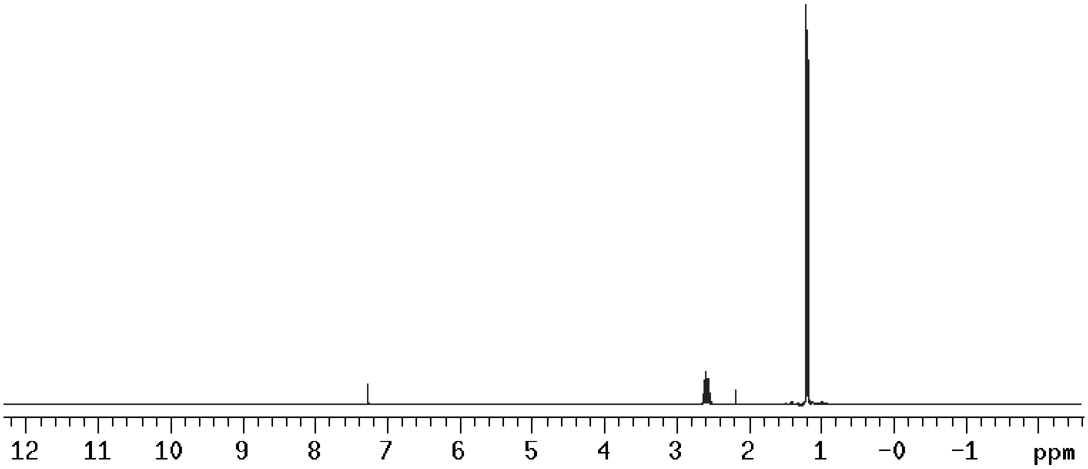
^{1}H NMR spectrum of heptanoic acid. Table 4.1, entry 1.



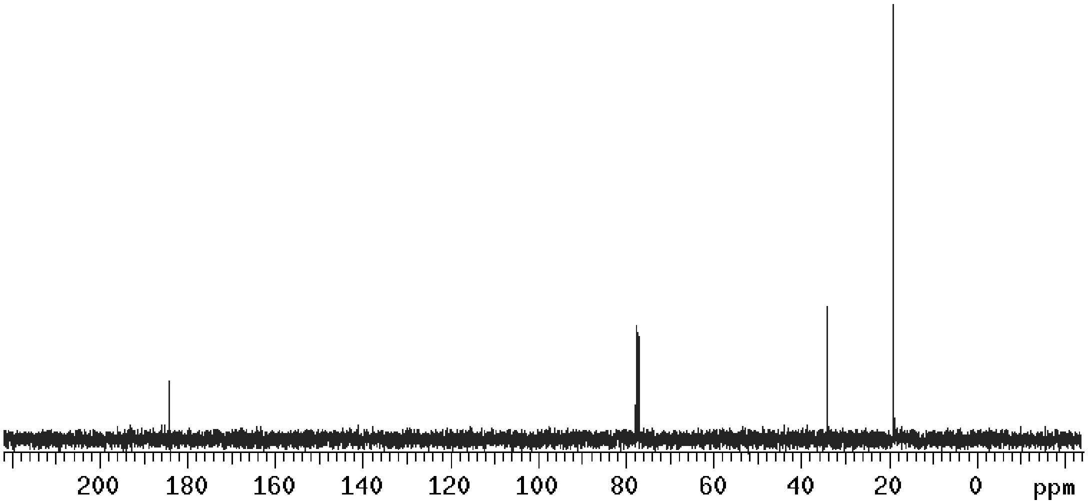
^{13}C NMR spectrum of heptanoic acid, Table 4.1, entry 1.



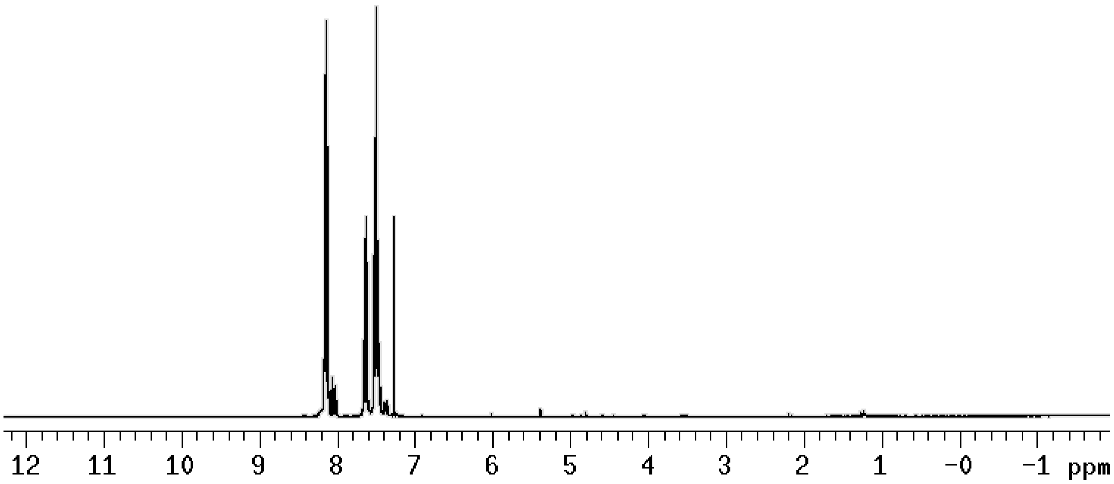
^{1}H NMR spectrum of 3-methyl buteric acid. Table 1, entry 2.



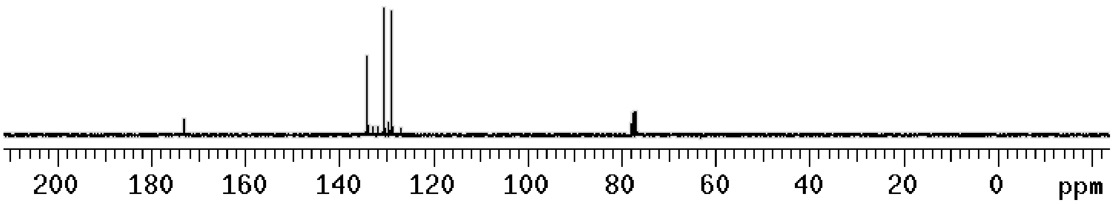
^{13}C NMR spectrum 3-methyl buteric acid, Table 1, entry 2.



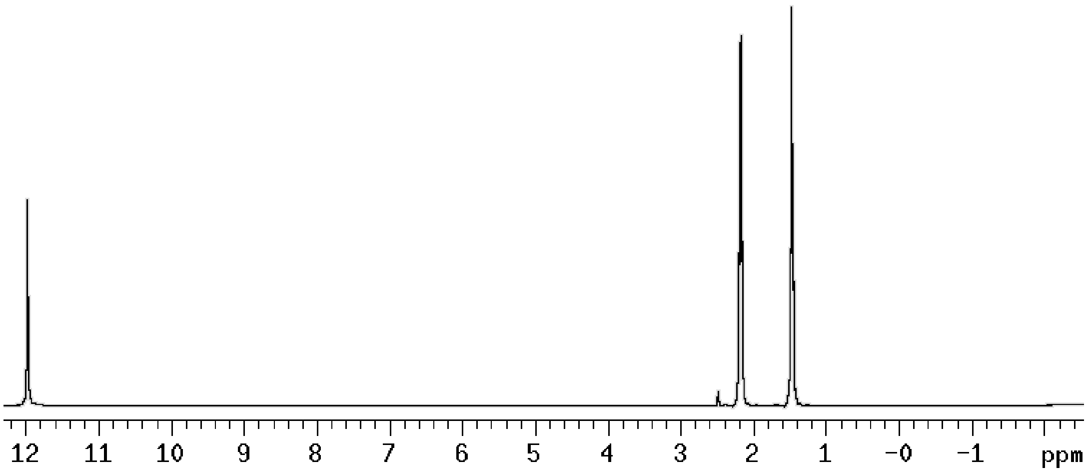
^{1}H NMR spectrum of benzoic acid. Table 1, entry 3.



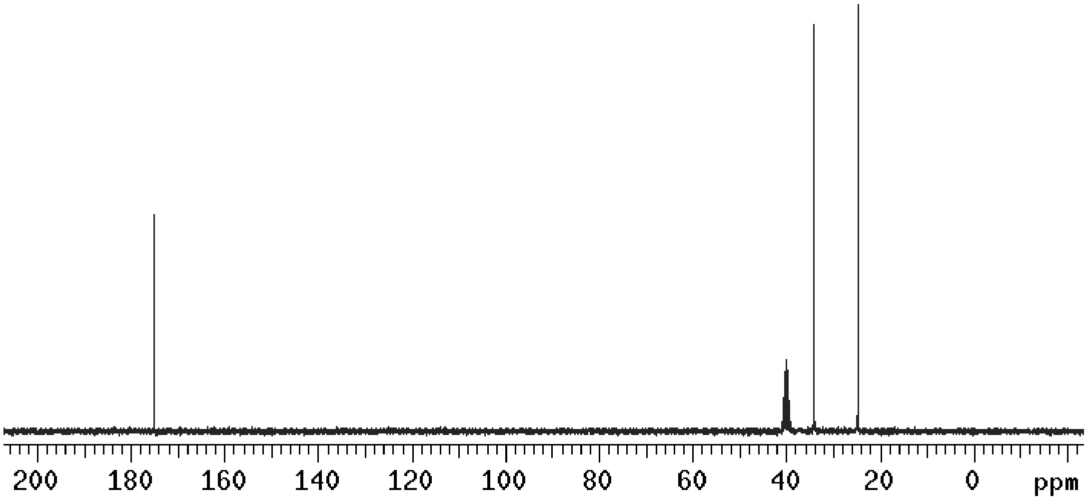
^{13}C NMR spectrum of benzoic acid. Table 1, entry 3.



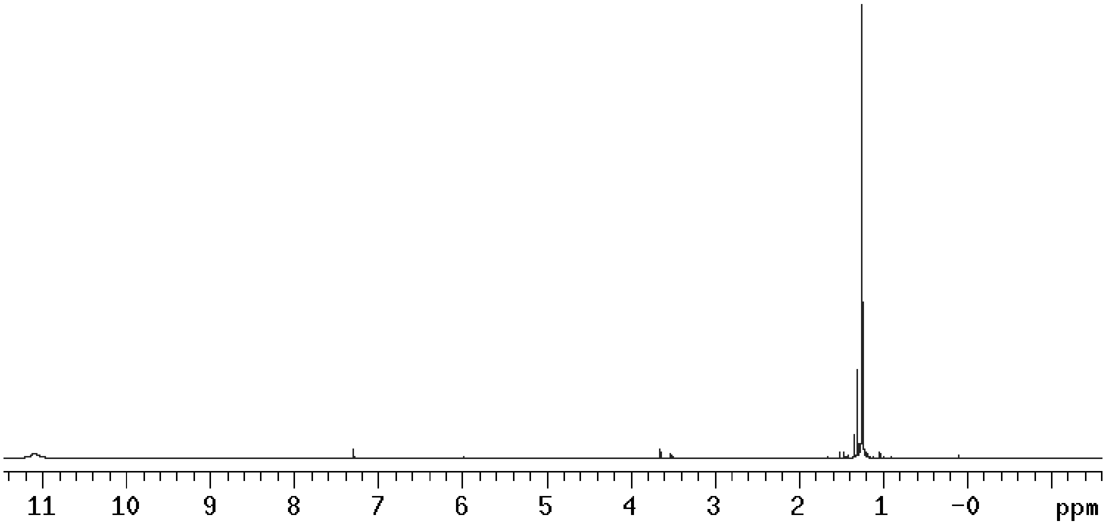
^{1}H NMR spectrum of adipic acid. Table 1, entry 4.



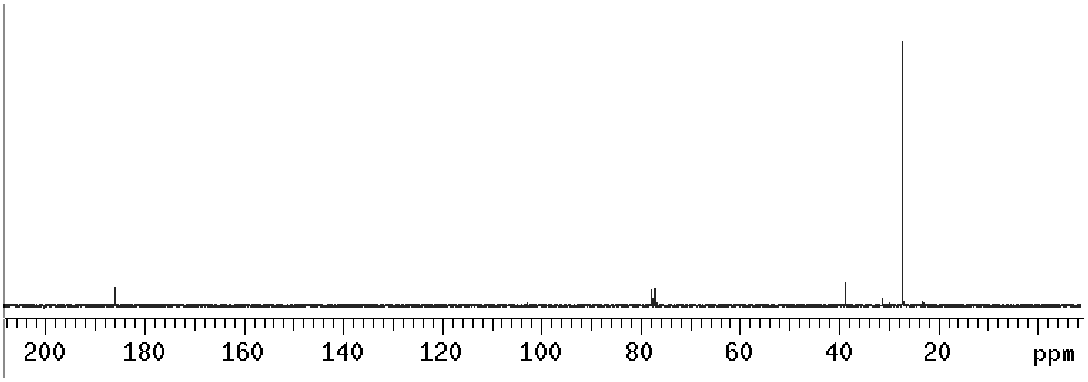
^{13}C NMR spectrum of adipic acid. Table 1, entry 4.



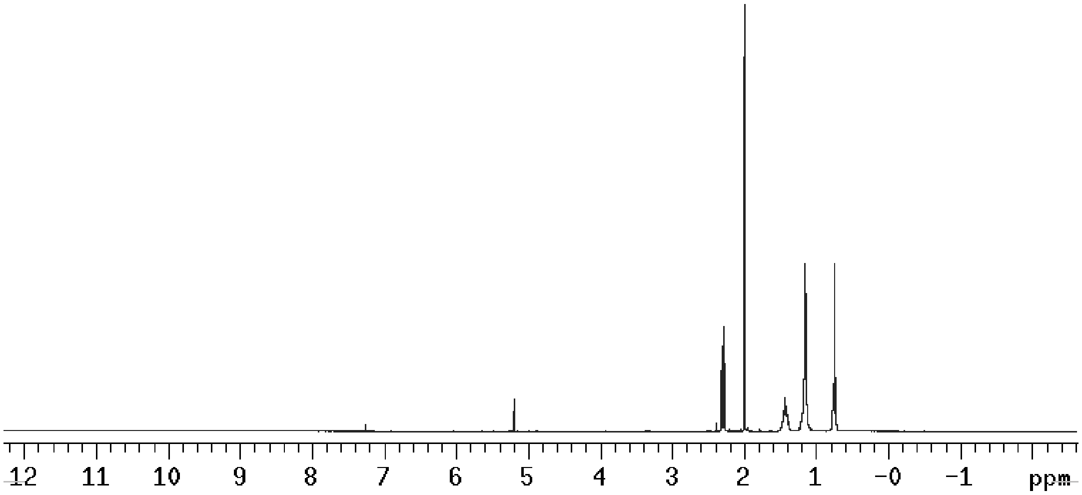
^{1}H NMR spectrum of trimethylacetic acid. Table 1, entry 6.



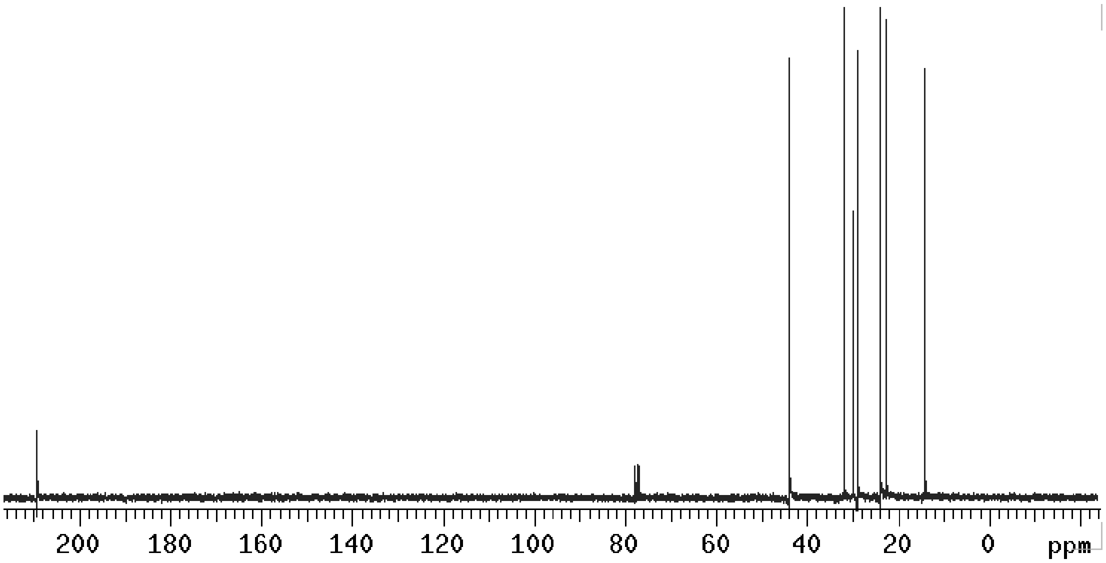
^{13}C spectrum of trimethylacetic acid. Table 1, entry 6.



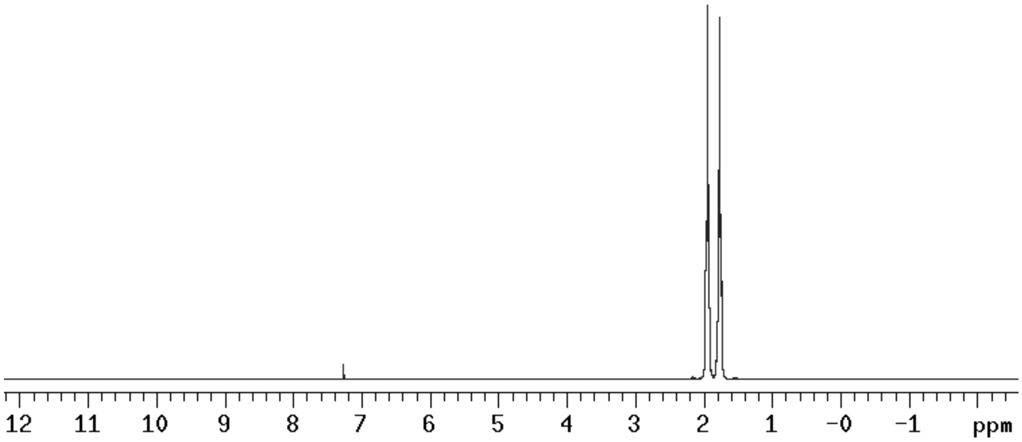
^{1}H NMR spectrum of 2-octanone. Table 3, entry 1.



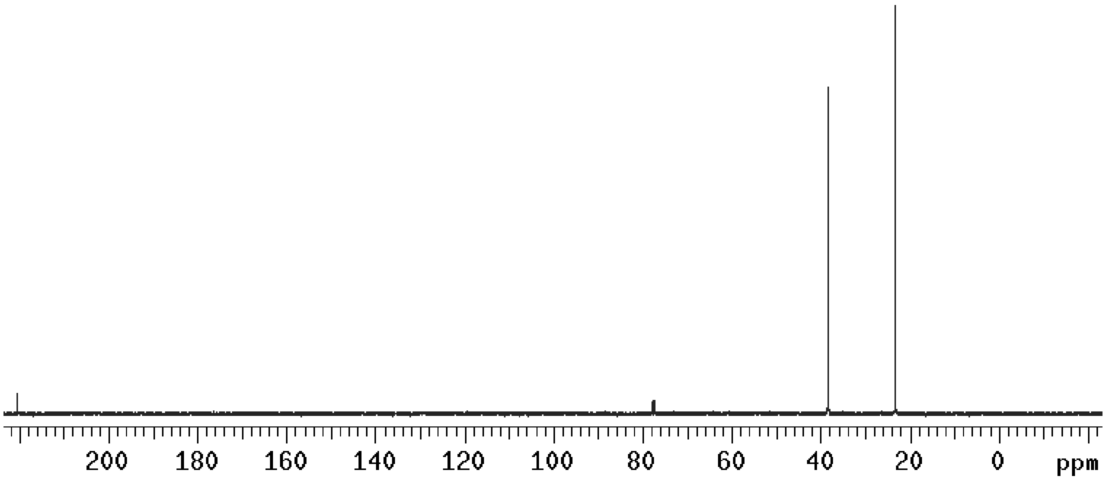
^{13}C spectrum of 2-octanone. Table 3, entry 1.



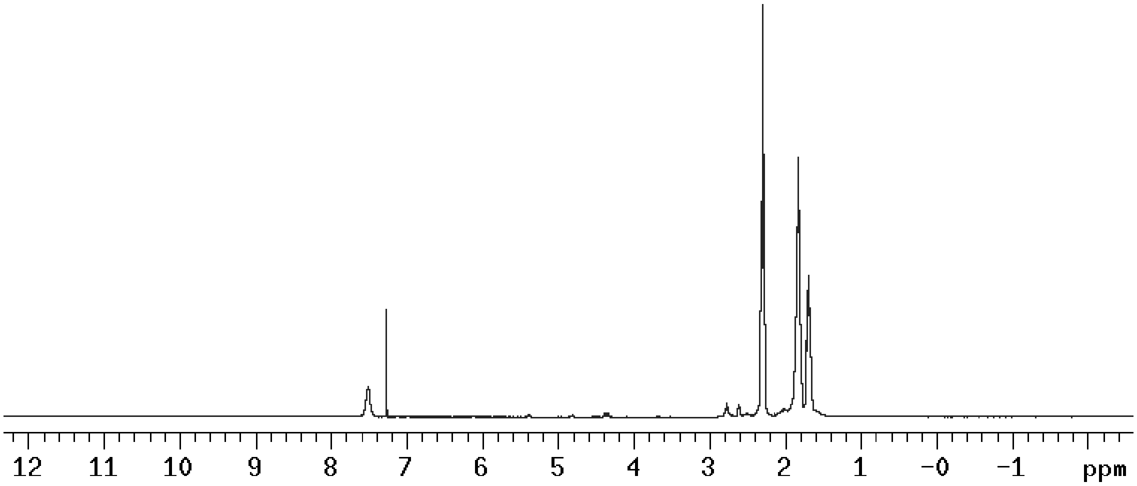
^{1}H NMR spectrum of cyclopentanone. Table 3, entry 2.



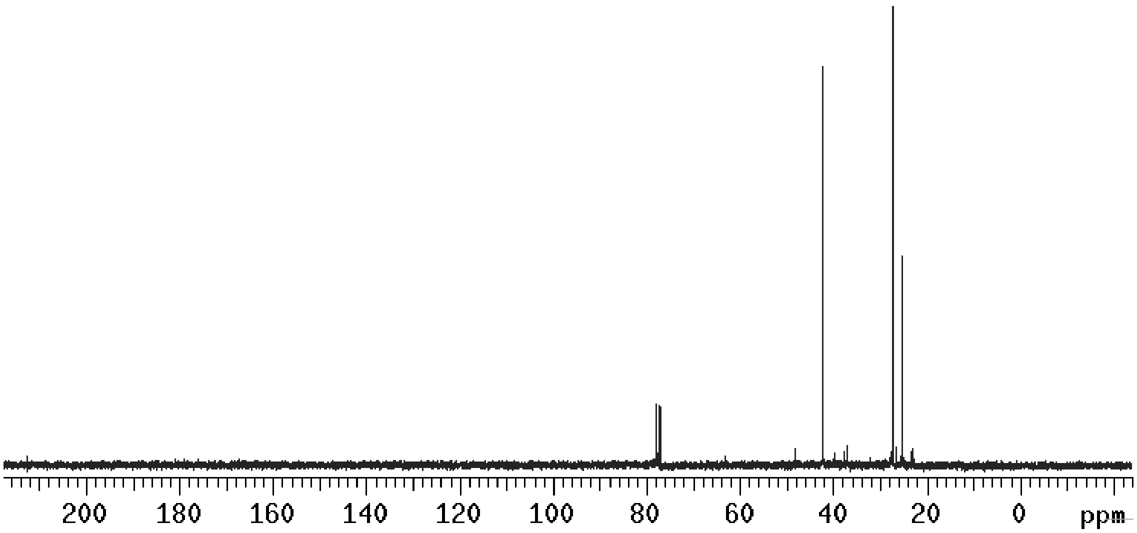
^{13}C spectrum of 2-octanone. Table 3, entry 2.



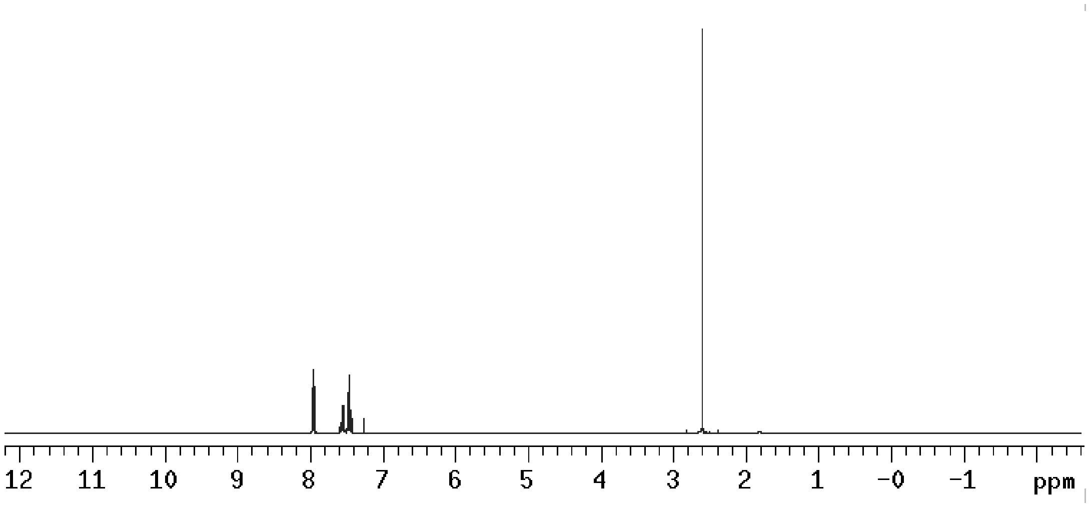
^{1}H NMR spectrum of cyclohexanone. Table 3, entry 3.



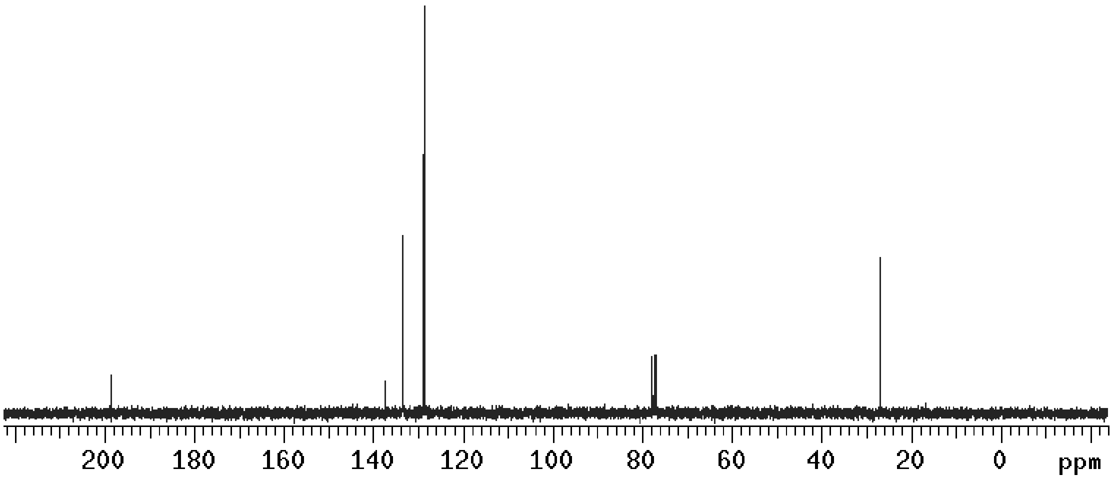
^{13}C spectrum of cyclohexanone. Table 3, entry 3



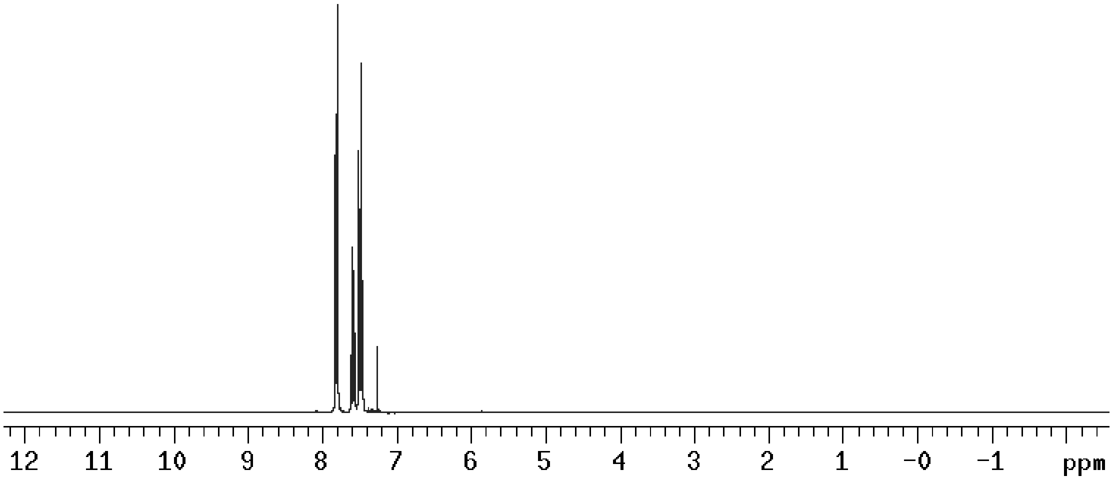
^{1}H NMR spectrum of acetophenone. Table 3, entry 4.



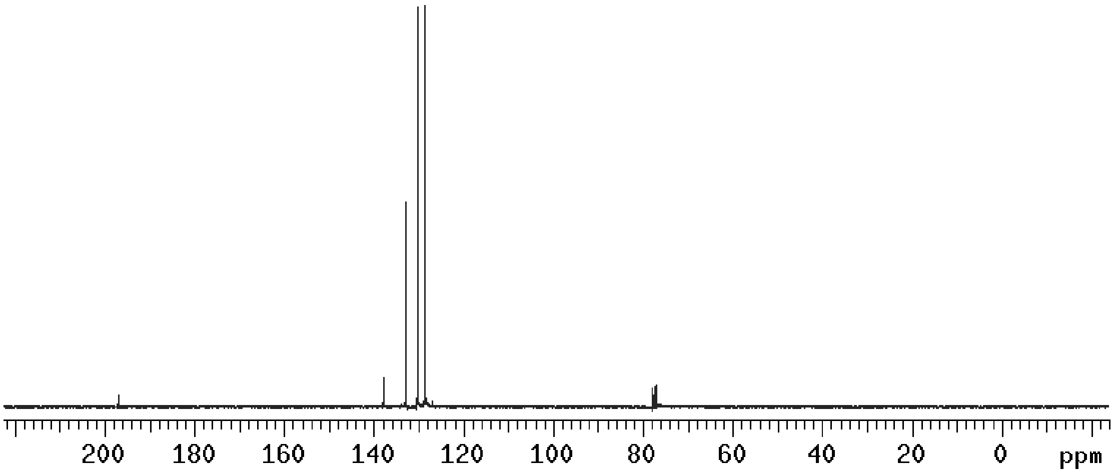
^{13}C spectrum of acetophenone. Table 3, entry 4.



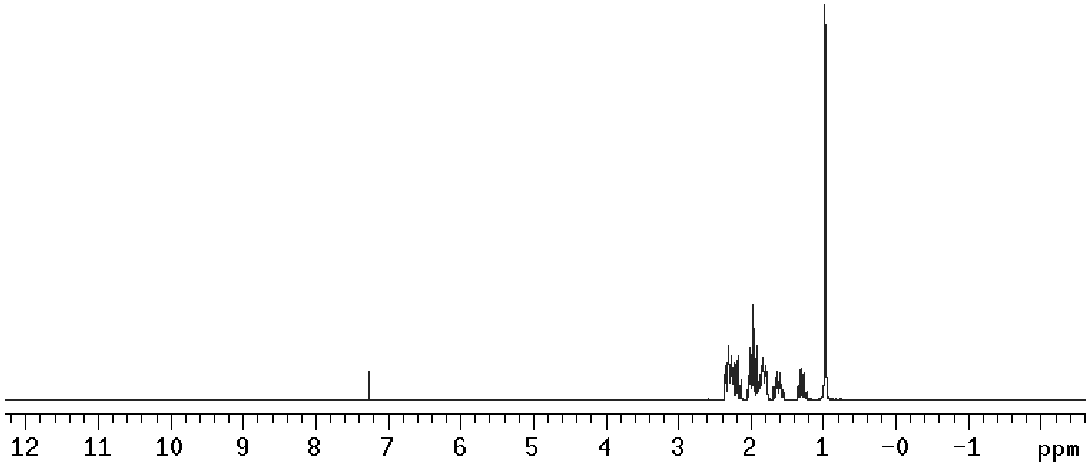
^{1}H NMR spectrum of benzophenone. Table 3, entry 5.



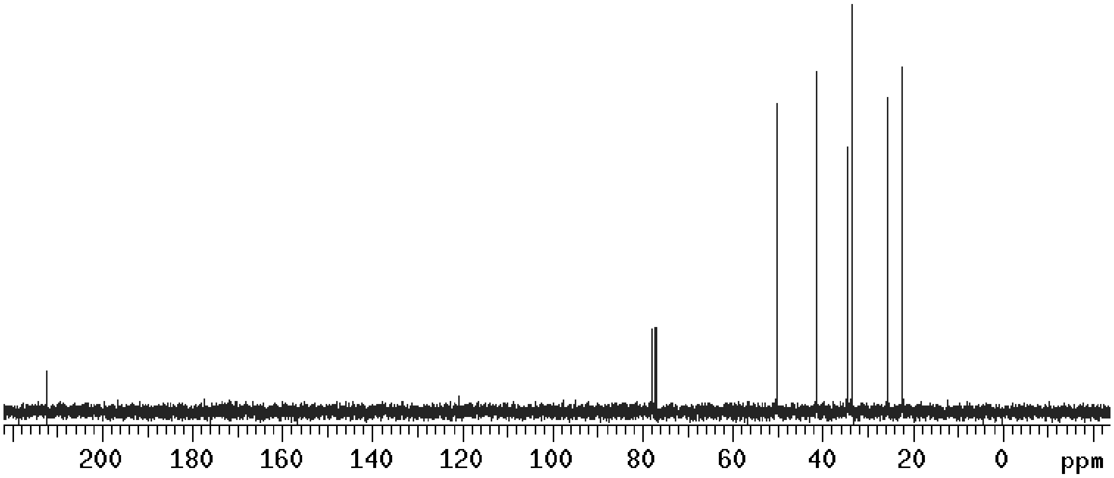
^{13}C NMR spectrum of benzophenone. Table 3, entry 5.



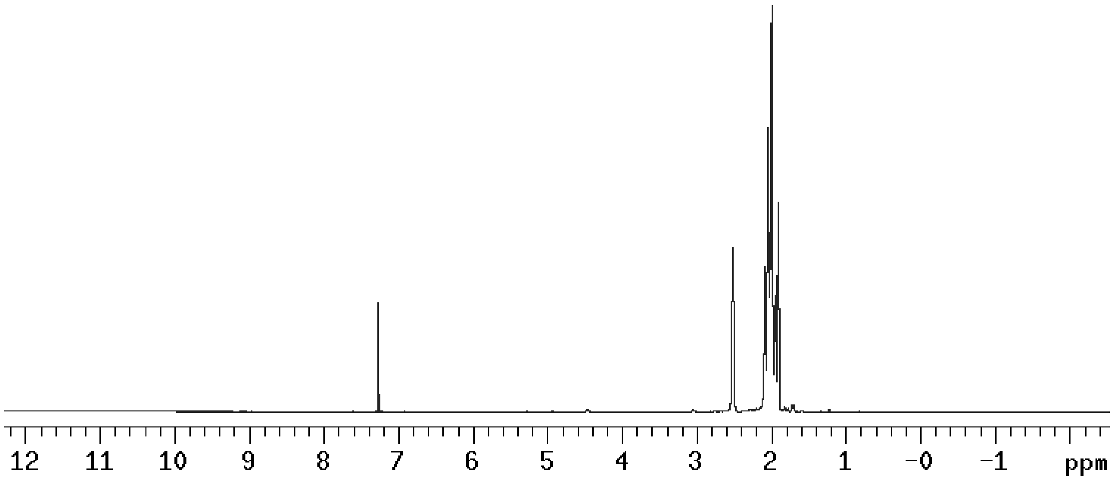
^{1}H NMR spectrum of 3-methylcyclohexanone. Table 3, entry 6.



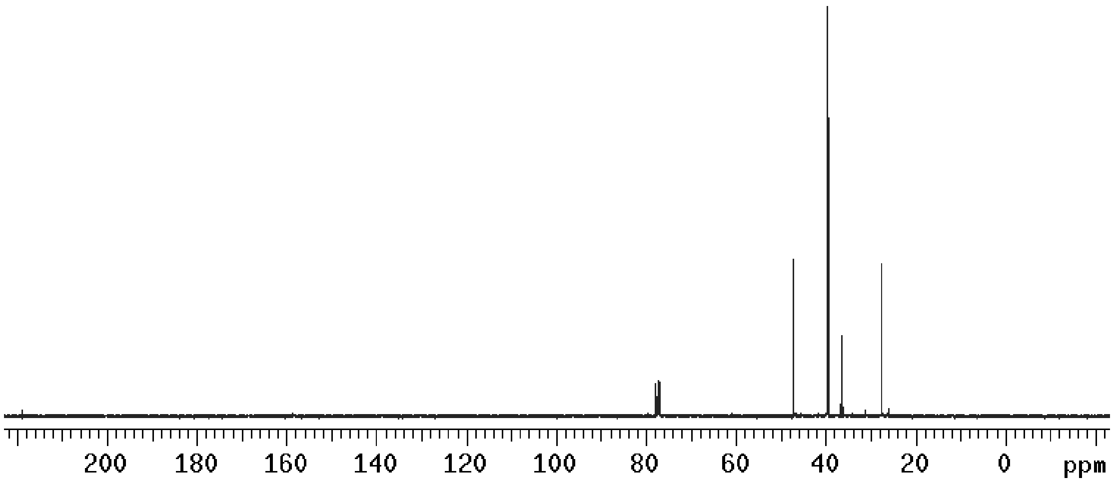
^{13}C NMR spectrum of 3-methylcyclohexanone. Table 3, entry 6.



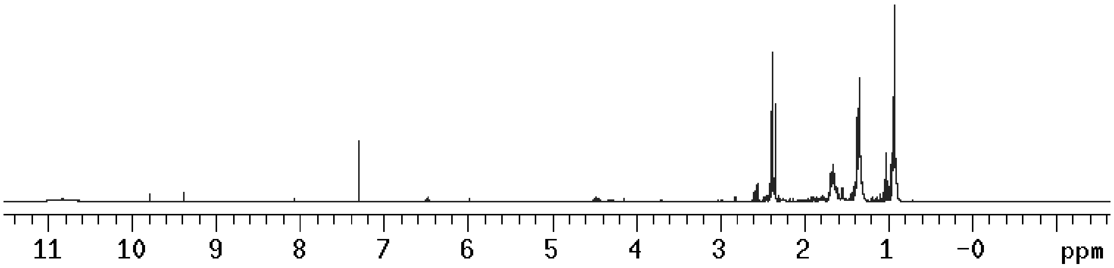
^{1}H NMR spectrum of adamantanone. Table 3, entry 7.



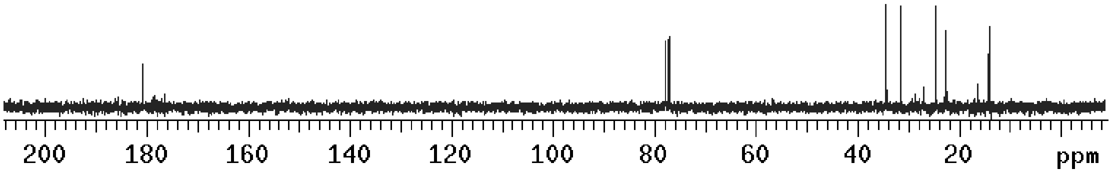
^{13}C NMR spectrum of adamantanone. Table 3, entry 7.



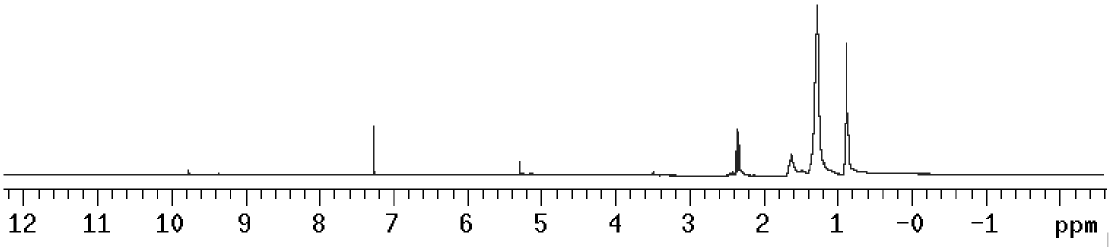
^{1}H NMR spectrum of hexanoic acid. Table 6, entry 1.



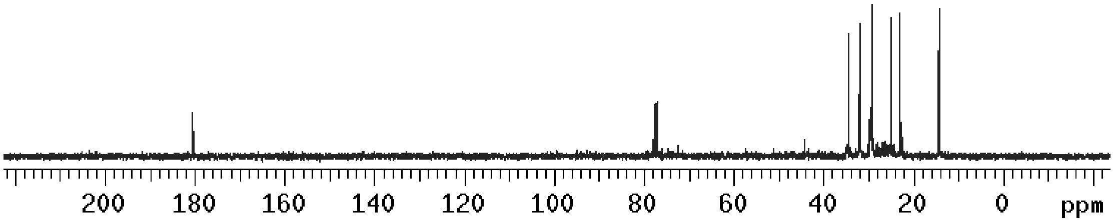
^{13}C NMR spectrum of hexanoic acid. Table 6, entry 1.



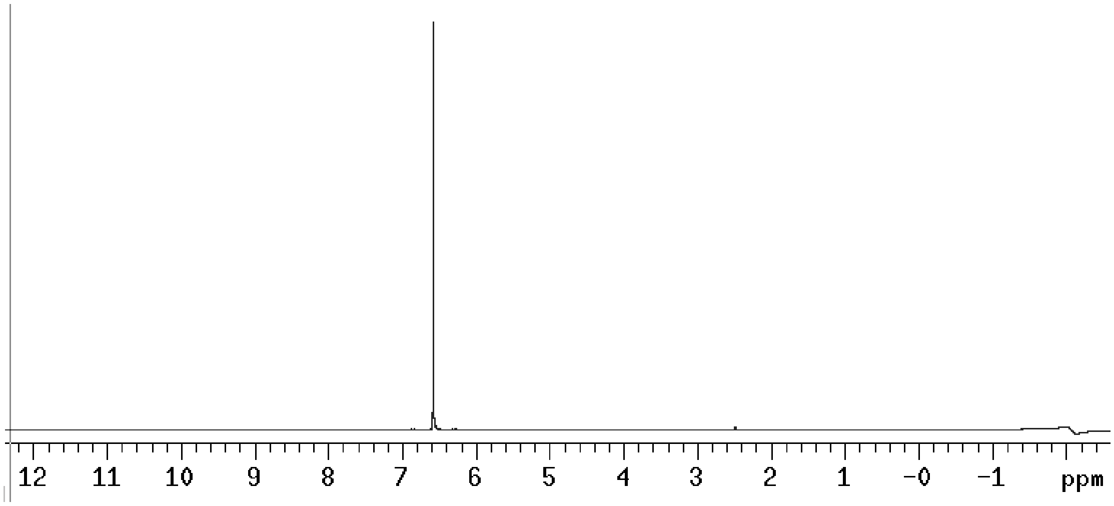
^{1}H NMR spectrum of octanoic acid. Table 6, entry 2.



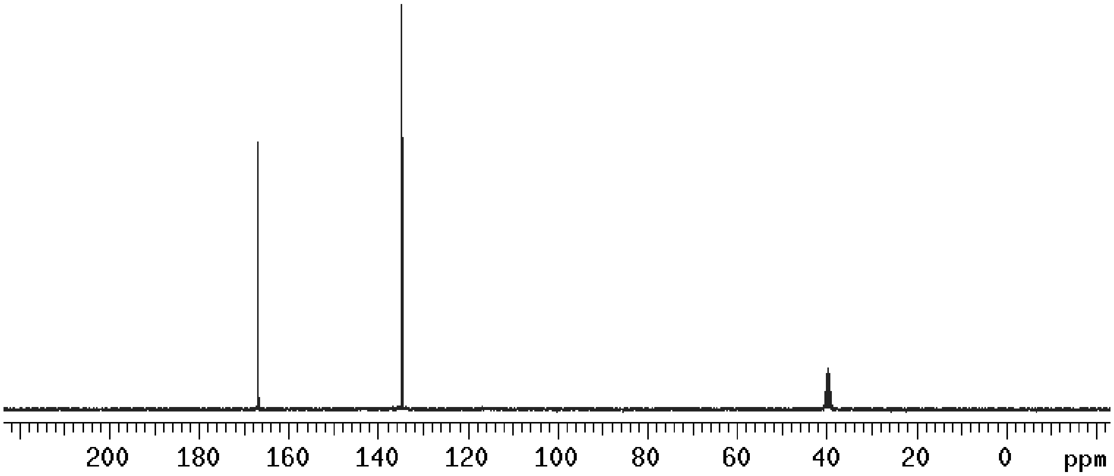
^{13}C NMR spectrum of octanoic acid. Table 6, entry 2.



^{1}H NMR spectrum of fumaric acid.



^{13}C NMR spectrum of fumaric acid.



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