

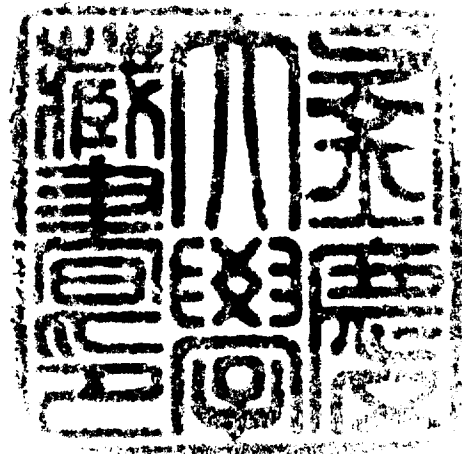
Studies of Supramolecular Chemistry
with Macrocyclic Ligands and
Cobalt-Dioxygen Complex
Chemistry

거대고리분자를 이용한 초분자와
코발트-산소 착화합물에
관한 연구

Advisor : Ju Chang Kim

by

Jaeheung Cho



A thesis submitted in partial fulfillment of the requirements for the degree of

Master of Science

in the Department of Chemistry, Graduate School,
Pukyong National University

February 2002

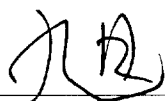
Studies of Supramolecular Chemistry with Macrocyclic Ligands
and Cobalt-Dioxygen Complex Chemistry

A Dissertation

by

Jaeheung Cho

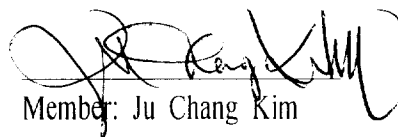
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February 2002

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**Studies of Supramolecular Chemistry with Macrocyclic Ligands
and Cobalt-Dioxygen Complex Chemistry**

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Abstract

A series of new one-dimensional coordination polymers based on macrocyclic ligands by additional pendent groups with bridging ligands-chromate, molybdate, oxalate, and terephthalate-have been synthesized and characterized. Two noble trans-bis(dicyanamido)nickel(II) macrocyclic complexes have also been synthesized and structurally characterized by X-ray crystallographic methods. All these complexes were prepared in order to understand supramolecular systems such as self-assemblies, molecular recognitions, and intermolecular interactions. Especially, in most of these cases the presence of water molecules is crucial to lead supramolecular arrays.

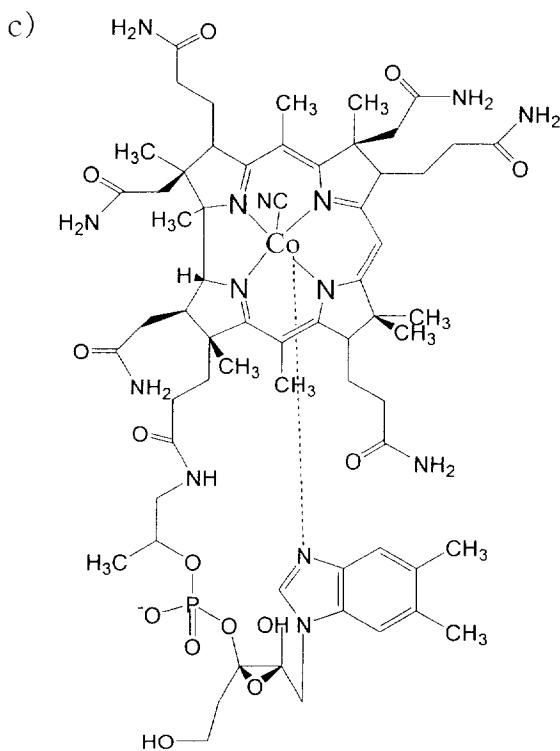
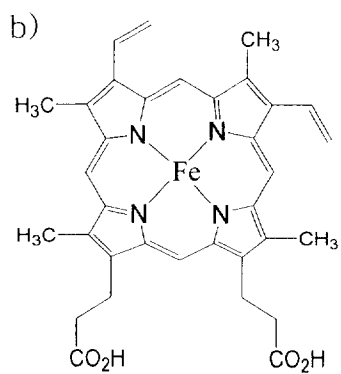
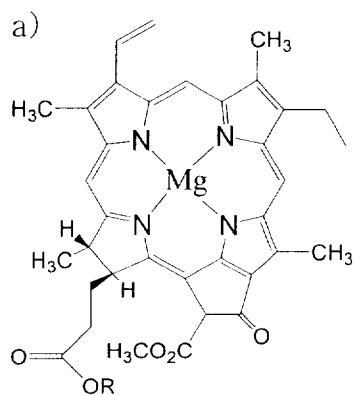
To comprehend the process of non-heme enzymes which can activate dioxygen in biological system, a biomimetic model complex and its functionalized complexes have been synthesized and structurally characterized by a combination of analytical, spectroscopic, and crystallographic methods. The role of transition metal species in this system ranges widely from incorporation of dioxygen and substrates into the coordination sphere to chemical transformations leading to oxygenated products.

General Introduction

Macrocyclic polyamines and their metal complexes have been the theme of extensive studies for several decades [1,2]. Macrocyclic compounds are found extensively in nature, playing a role in some important biological processes [1]. Special attention and great efforts have been devoted to the studies of tetraaza macrocycles, because of their potential relationship to the naturally occurring porphyrins and porphyrin-analogs [2]. For examples, the conversion of light energy from the sun into electrical and chemical energy in photosynthesis depends on a magnesium containing macrocycle, chlorophyll, oxygen is transported through the blood by heme, and a vitamin B12 contains cobalt ions (Scheme 1). The naturally occurring molecules are often very complex and difficult to study due to their association with several proteins. One approach used to help understanding the processes is to make the model compounds which have characteristics similar to the molecules found in nature. Model compounds can often provide insight into the important factors of the structure of the naturally occurring complexes as well as giving information into the design of systems which can mimic biological behavior.

Macrocyclic ligands are defined as cyclic molecules usually consisting of organic frames where heteroatoms, capable of binding to substrates, have been

Scheme 1. a) chlorophyll, b) heme, c) vitamin B12

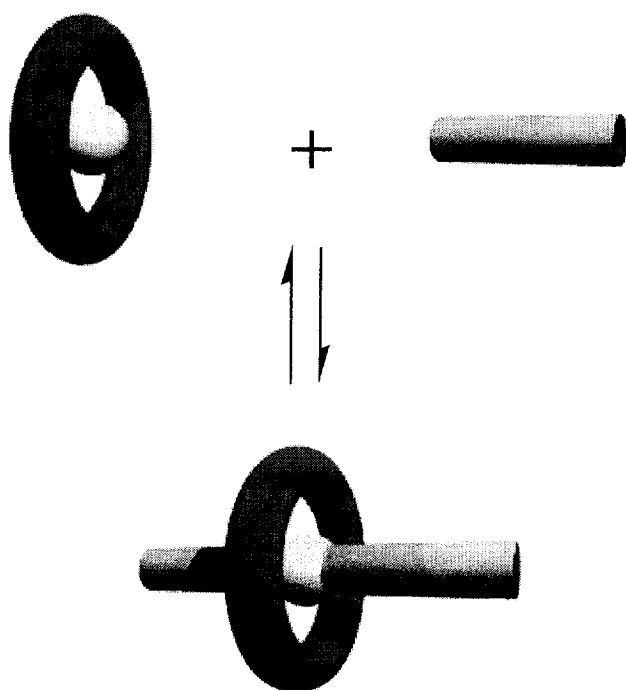


interspersed [1]. Since its advent, the development of macrocyclic chemistry has been proceeded along two lines: as models of the naturally occurring macrocyclic systems, containing predominantly nitrogen donor atoms, such as porphyrins, corrins, and chlorins; and as receptors designed for molecular recognition and supramolecular chemistry, with a variety of donor atoms and recognition capabilities.

The self-assembly of infinite metal complexes with distinct network topologies have also been interested due to their potential for supramolecular chemistry and crystal engineering. Non-covalent intermolecular interactions such as electrostatics, hydrogen bonds, π - π stacking interactions, van der Waals forces, and hydrophobic effects provide supramolecular assemblies through the formation of one-dimensional and multi-dimensional networks.

Consequently, we used macrocyclic ligands and several bridging ligands as building blocks to mimic biological system and to investigate intermolecular interactions which have an effect on their structures and properties (Scheme 2). In this thesis, we report the syntheses and properties of noble one-dimensional Ni(II) and Cu(II) complexes with polyaza macrocyclic ligands where each complex is bridged by chromate, molybdate, oxalate, terephthalate, or dicyanamide. The influences of the bridging ligands on structures and electronic properties of each complex have been studied, and X-ray crystal structures have been determined in

Scheme 2.



detail.

In the meantime, dioxygen activation chemistry by transition metal complexes also has great importance for understanding the reaction mechanisms of dioxygen activating metalloproteins in biological systems and utilizing metal complexes as oxidation catalysts [3,4]. In biological systems, heme and non-heme iron enzymes such as cytochrome P-450 [3] and methane monooxygenase (MMO) [4], catalyze the hydroxylation of alkanes, affording corresponding alcohols. To describe the mechanism of dioxygen activation by metal ions, the structure and reactivity of transition metal complexes with activated oxygen species have attracted increasing attention. In this thesis, cobalt complex with hydrogen peroxide species has also been investigated as biomimetic models.

Overall, this thesis is composed of four chapters. Chapter 1 – chapter 3 describe the Ni(II) and Cu(II) complexes with macrocyclic ligands which are of supramolecular structures. The works in these chapters were carried out at the Pukyong National University in Korea. Chapter 4 deals with the details of the Cobalt-Dioxygen chemistry, which were done at the Kanazawa University in Japan under the supervision of Professor Masatatsu Suzuki.

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CHAPTER I

Structures and magnetic properties of *catena*-(μ - $\text{MO}_4\text{-O,O}'$) [$\text{Ni}^{\text{II}}(\text{L})$] $\cdot 5\text{H}_2\text{O}$ ($\text{M} = \text{Cr, Mo}$; $\text{L} = 3,10\text{-bis}(2\text{-hydroxyethyl})\text{-}$ $1,3,5,8,10,12\text{-hexaazacyclotetradecane}$)

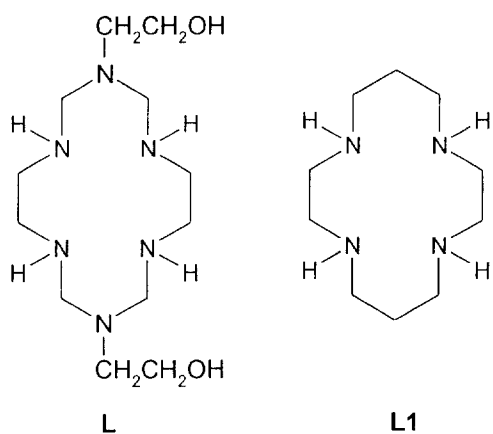
Abstract

The new compounds *catena*-(μ - $\text{CrO}_4\text{-O,O}'$)[$\text{Ni}^{\text{II}}(\text{L})$] $\cdot 5\text{H}_2\text{O}$ and *catena*-(μ - $\text{MoO}_4\text{-O,O}'$)[$\text{Ni}^{\text{II}}(\text{L})$] $\cdot 5\text{H}_2\text{O}$ have been synthesized and structurally characterized by spectroscopies, magnetic susceptibility and X-ray crystallography, where **L** is 3,10-bis(2-hydroxyethyl)-1,3,5,8,10,12-hexaazacyclotetradecane. The nickel ions of the one-dimensional chain complexes are bridged by tetraoxometalate ($[\text{CrO}_4]^{2-}$ or $[\text{MoO}_4]^{2-}$) unit. The magnetic properties of the chain complexes in the temperature range of 5-300 K indicate that there is a weak ferromagnetic intrachain interactions among the nickel ions. The electronic as well as infrared spectral properties of the title complexes are also reported and discussed.

Introduction

Various kinds of bridging ligands are now known to mediate magnetic exchange interactions between paramagnetic metal ions. These include the pseudo halides [1], oxalato and related groups [2], and tetraoxometalate anions [3,4] etc.. From the above systems it has been understood that the magnetic exchange depends upon the nature of the bridging species, symmetry of the frontier orbitals, and/or stereochemical factors of the ligands. Usually, the magnetic orbital overlap of the bridging ligands between the paramagnetic metal ions mediates antiferromagnetic interactions. On the other hand, if the magnetic orbitals are orthogonal to each other, ferromagnetic interactions can be resulted. It has been extensively studied that the one-dimensional nickel(II) systems with antiferromagnetic intrachain interactions [5-7]. In contrast, only a few one-dimensional nickel(II) chain systems with intrachain ferromagnetic interactions have been reported. Examples of ferromagnetic one-dimensional chain systems are the *catena*-(μ -CrO₄-O,O')[Ni^{II}(L1)].2H₂O ($J = 0.6 \text{ cm}^{-1}$; $H = -J\sum S_i \cdot S_{i+1}$) [3], end-on azido-bridged nickel(II) complexes ($J = 11.9 - 21.7 \text{ cm}^{-1}$; $H = -2J\sum S_i \cdot S_j$) [8], and *trans*-cyanato *catena* nickel(II) complex ($J = 2.3 \text{ cm}^{-1}$; $H = -2J\sum S_i \cdot S_{i+1}$) [9]. Magnetic interactions between the metal ions mediated through

tetraoxometalate anions have been understood [3,4,10], but examples are still rare. Herein, we report the structures and magnetic properties of one-dimensional nickel(II) systems in which paramagnetic nickel(II) centers bridged by the tetraoxometalates exhibit ferromagnetic interactions.



Experimental

Materials and physical measurements

All chemicals obtained from commercial sources were reagent grade and were used without further purification. Distilled water was used for all procedures. Infrared spectra of solid samples were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer between 4000 and 400 cm^{-1} as Nujol mulls on KBr discs.

Solid state electronic spectra were measured by diffuse reflectance method on a Varian Cary 1C UV-Vis spectrophotometer. Magnetic susceptibility data were collected in the temperature range 5.0 – 300 K in an applied field of 1 T with the use of a Quantum Design Model MPMS SQUID magnetometer. Diamagnetic corrections were estimated from Pascal tables. Solution spectra were obtained on a Varian Cary 1C UV-Vis spectrophotometer or a Milton Roy Spectronic 1201 recording spectrophotometer. Elemental Analysis was carried out by the Korea Research Institute of Chemical Technology, Taejon, Korea.

Preparation

The precursor complex $[\text{Ni}^{\text{II}}(\text{L})\text{Cl}_2]$ was prepared according to the literature procedures previously reported [11].

*Preparation of catena-(μ -CrO₄-O,O') $[\text{Ni}^{\text{II}}(\text{L})]\cdot 5\text{H}_2\text{O}$ (**1**)*

A solution of K₂CrO₄ (194 mg, 1 mmol) and triethylamine (101 mg, 1 mmol) in water (20 mL) was added to a solution of the $[\text{Ni}^{\text{II}}(\text{L})\text{Cl}_2]$ (430 mg, 1 mmol) in water (20 mL). After the solution was left to stand overnight, reddish orange blocks of **1** were filtered out and one of them was subjected to the X-ray structural

analysis. Anal. Calcd. for $C_{12}H_{40}N_6O_{11}CrNi$: C, 25.94; H, 7.20; N, 15.13. Found C, 25.57; H, 7.17; N, 15.01.

*Preparation of catena-(μ -MoO₄-O,O')[Ni^{II}(L)]·5H₂O (**2**)*

Faint lilac tinted **2** was prepared and isolated in a similar manner using K₂MoO₄ instead of K₂CrO₄. Anal. Calcd. for $C_{12}H_{40}N_6O_{11}MoNi$: C, 24.03; H, 6.68; N, 14.02. Found C, 23.75; H, 6.99; N, 13.88.

X-ray crystallography

Crystal data, a summary of data collection, and details of structure refinement are given in Table 1.1. Single crystals of **1** and **2** were grown as described in Section 2.2. For **1** and **2**, data were collected at 107(1) K on a Nonius KappaCCD diffractometer, using graphite monochromated MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$). A combination of 1° phi and omega (with kappa offsets) scans were used to collect sufficient data. The data frames were integrated and scaled using the Denzo-SMN package [12]. The structures were solved and refined using the SHELXTL\PC V5.1 package [13]. Refinement was by full-matrix least squares on F² using all data (negative intensities included). Hydrogen atoms were included in

Table 1.1. Crystal data and structure refinement for $[\text{C}_{12}\text{H}_{30}\text{N}_6\text{O}_6\text{CrNi}][\text{H}_2\text{O}]_5$ (**1**) and $[\text{C}_{12}\text{H}_{30}\text{N}_6\text{O}_6\text{MoNi}][\text{H}_2\text{O}]_5$ (**2**)

	1	2
Empirical formula	$\text{C}_{12}\text{H}_{40}\text{CrN}_6\text{NiO}_{11}$	$\text{C}_{12}\text{H}_{40}\text{MoN}_6\text{NiO}_{11}$
Formula weight	555.21	599.15
Crystal system	Orthorhombic	Orthorhombic
Space group	$\text{Pna}2_1$	$\text{Pna}2_1$
a(Å)	13.0786(2)	13.4288(2)
b(Å)	8.7816(2)	8.7643(3)
c(Å)	19.9801(4)	19.9375(6)
V(Å ³)	2294.73(8)	2346.52(11)
Z	4	4
D _{calcd} (Mg/m ³)	1.607	1.696
Absorption coefficient(mm ⁻¹)	1.358	1.399
F(000)	1176	1248
Crystal size(mm)	0.35× 0.30× 0.25	0.35× 0.30× 0.25
Limiting indices	-16 ≤ h ≤ 16	-18 ≤ h ≤ 18
	-11 ≤ k ≤ 11	-12 ≤ k ≤ 12
	-25 ≤ l ≤ 25	-27 ≤ l ≤ 28

Table 1.1. Continued

	1	2
Completeness to θ	99.8 % ($\theta = 27.49$)	99.8 % ($\theta = 30.03$)
Data/restraints/parameters	4988/11/315	6402/11/315
Goodness-of-fit on F^2	0.892	1.033
Reflections collected	17189/4988[R(int)=0.039]	18702/6402[R(int)=0.0000]
Final R indices [$I > 2\sigma(I)$]	R1=0.0293, wR2=0.0727	R1=0.0295, wR2=0.0669
R indices (all data)	R1=0.0336, wR2=0.0757	R1=0.0336, wR2=0.0689
Largest diff. peak and hole	0.428 and -0.468 e. \AA^{-3}	0.541 and -0.625 e. \AA^{-3}

$$R1 = \frac{\sum || F_o - F_c ||}{\sum | F_o |} \text{ and } wR2 = \left[\frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right]^{1/2}.$$

calculated positions except for the hydrogen atoms of the water molecule and those bonded to the nitrogen atoms, which were refined with isotropic thermal parameters. The structure in **2**, except for that Cr is substituted by Mo, is identical, atom by atom, to that of **1**. There are slight differences in the cell parameters but the space group is the same. To solve the structure of **2** the atom coordinates of **1** were used and simply changed the atom Mo instead of Cr then changed the cell parameters. For **1** and **2** there are five molecules of crystallization of water, which are involved in hydrogen bonding for every cation molecule, respectively.

Results and Discussion

Structures of 1 and 2

The structure of **1** consists of one-dimensional nickel-CrO₄ chains (Figure 1.1). The structure of the chain is shown in Figure 1.1. The important bond lengths and angles are listed in Table 1.2. In the chain structure, each nickel(II) atom is coordinated by one hexaaza macrocyclic ligand and two [CrO₄]²⁻ anions in a distorted octahedral *trans* arrangement. The four nickel-N(macrocyclic) bond lengths are in the range 2.052(2) - 2.070(3) Å and shorter than the two nickel-O

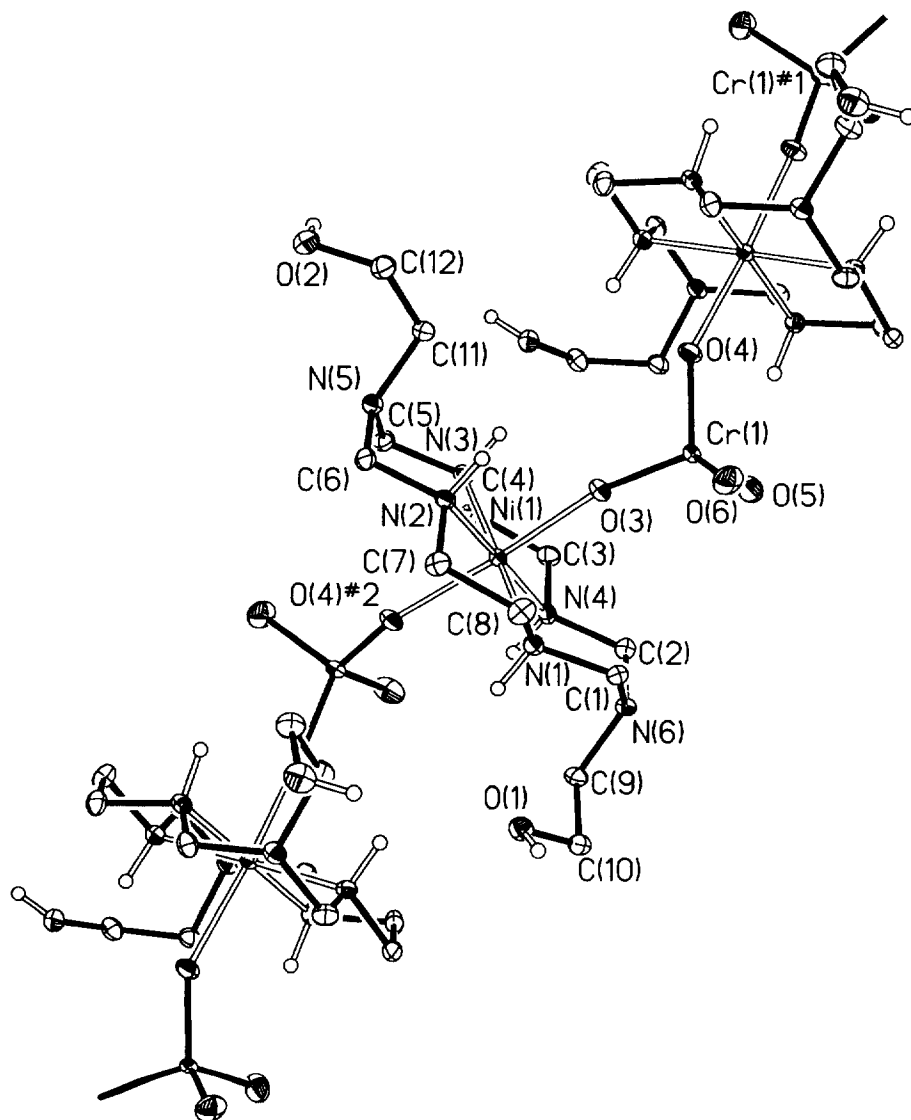


Figure 1.1. Molecular structure of *catena*-(μ -CrO₄-O,O')[Ni^{II}(L)]·5H₂O (**1**) with atom-labeling scheme. Hydrogen atoms are omitted for clarity.

Table 1.2. Selected bond lengths (Å) and angles (°) for [C₁₂H₃₀N₆O₆CrNi]
[H₂O]₅ (1)

Ni(1)-N(1)	2.051(2)	Ni(1)-N(2)	2.070(3)
Ni(1)-N(3)	2.052(2)	Ni(1)-N(4)	2.070(3)
Ni(1)-O(3)	2.0587(16)	Ni(1)-O(4)#1	2.0813(17)
Cr(1)-O(3)	1.6476(17)	Cr(1)-O(4)	1.6513(17)
Cr(1)-O(5)	1.633(2)	Cr(1)-O(6)	1.667(2)
<hr/>			
N(1)-Ni(1)-N(3)	178.79(9)	N(1)-Ni(1)-O(3)	92.28(7)
N(3)-Ni(1)-O(3)	88.41(7)	N(1)-Ni(1)-N(2)	86.03(8)
N(3)-Ni(1)-N(2)	95.00(8)	O(3)-Ni(1)-N(2)	87.18(8)
N(1)-Ni(1)-N(4)	93.18(8)	N(3)-Ni(1)-N(4)	85.78(8)
O(3)-Ni(1)-N(4)	93.30(8)	N(2)-Ni(1)-N(4)	179.10(9)
N(1)-Ni(1)-O(4)#1	86.96(7)	N(3)-Ni(1)-O(4)#1	92.44(7)
O(3)-Ni(1)-O(4)#1	174.80(8)	N(2)-Ni(1)-O(4)#1	87.64(8)
N(4)-Ni(1)-O(4)#1	91.88(8)	Cr(1)-O(3)-Ni(1)	167.78(11)
Cr(1)-O(4)-Ni(1)#2	145.95(11)		

Symmetry transformations used to generate equivalent atoms:

#1 $x+1/2, -y+1/2, z$ #2 $x-1/2, -y+1/2, z$

bond lengths (2.0587(16) and 2.0813(17) Å), giving an axially elongated octahedron in the chain direction. The four N atoms of the hexaaza macrocyclic ligand and the nickel atom are in the same plane. The coordination geometry around the Cr is pseudotetrahedral, where Cr-O bond lengths are within the range 1.633(2) - 1.667(2) Å with O-Cr-O bond angles of 108.94(10) – 110.02(12)°. The structure of **2** is isostructural to **1** with four nickel-N(macrocyclic) bond lengths of 2.047(2) - 2.077(3) Å two nickel-O bond lengths of 2.0615(17) and 2.0880(18) Å (Figure 1.2). The coordination geometry around Mo is similar to that of **1** with Mo-O bond lengths of 1.746(2) - 1.785(2) and O-Mo-O bond angles of 107.99(10) – 110.60(9)°. Selected bond lengths and bond angles are listed in Table 1.3.

Spectral and magnetic properties of 1 and 2

The infrared spectra of the two compounds contain the typical bands originated from the macrocyclic ligands and the bridging $[\text{MO}_4]^{2-}$ units. In **1** the spectrum consists of a strong sharp band at 833 cm^{-1} and additional strong bands at 858, 883, and 896 cm^{-1} , which were tentatively assigned to the ν_1 and ν_3 modes on the basis of previously studied comparable systems [10,14]. A coordinated secondary

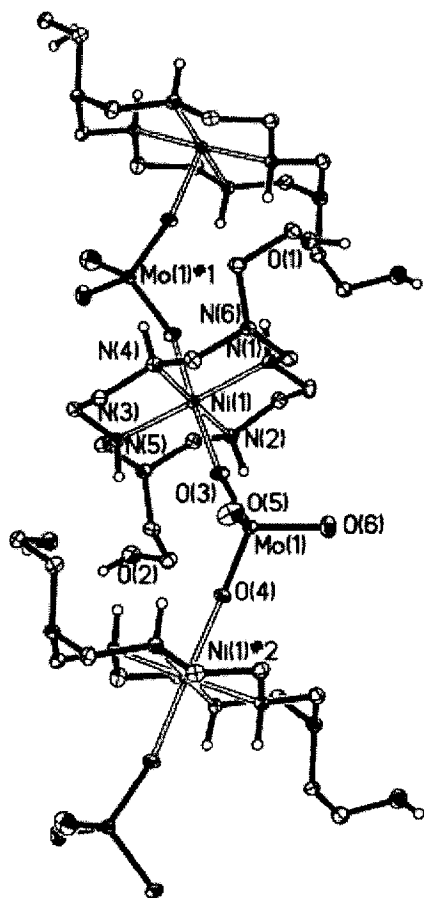


Figure 1.2. Molecular structure of *catena*-(μ -MoO₄-O,O')[Ni^{II}(L)]·5H₂O (**2**).

Atom-labeling scheme for the macrocycle is identical to that of **1**. Hydrogen atoms are omitted for clarity.

Table 1.3. Selected bond lengths (Å) and angles (°) for [C₁₂H₃₀N₆O₆MoNi][H₂O]₅ (2)

Ni(1)-N(1)	2.052(2)	Ni(1)-N(2)	2.077(3)
Ni(1)-N(3)	2.047(2)	Ni(1)-N(4)	2.068(2)
Ni(1)-O(3)	2.0615(17)	Ni(1)-O(4)#1	2.0880(18)
Mo(1)-O(3)	1.7644(17)	Mo(1)-O(4)	1.7635(18)
Mo(1)-O(5)	1.746(2)	Mo(1)-O(6)	1.785(2)
N(1)-Ni(1)-N(3)	178.46(9)	N(1)-Ni(1)-O(3)	92.09(8)
N(3)-Ni(1)-O(3)	89.25(8)	N(1)-Ni(1)-N(2)	85.81(9)
N(3)-Ni(1)-N(2)	95.00(8)	O(3)-Ni(1)-N(2)	87.15(8)
N(1)-Ni(1)-N(4)	93.26(9)	N(3)-Ni(1)-N(4)	85.91(9)
O(3)-Ni(1)-N(4)	93.81(8)	N(2)-Ni(1)-N(4)	178.69(9)
N(1)-Ni(1)-O(4)#1	86.43(8)	N(3)-Ni(1)-O(4)#1	92.30(8)
O(3)-Ni(1)-O(4)#1	174.34(8)	N(2)-Ni(1)-O(4)#1	87.29(8)
N(4)-Ni(1)-O(4)#1	91.73(9)	Mo(1)-O(3)-Ni(1)	168.95(11)
Mo(1)-O(4)-Ni(1)#2	148.00(12)		

Symmetry transformations used to generate equivalent atoms:

#1 $x+1/2, -y+1/2, z$ #2 $x-1/2, -y+1/2, z$

$\nu(\text{NH})$ stretching band at 3270 cm^{-1} and $\nu(\text{HOH})$ bending vibration at 1620 cm^{-1} were also observed in the spectrum. In **2**, strong $\nu(\text{MoO})$ bands were observed at 802 , 831 , 861 , and 885 cm^{-1} , indicating that Cr-O bonds are more covalent than Mo-O bonds. Similarly to the spectrum of **1** a weak band at 3270 cm^{-1} and a medium band at 1650 cm^{-1} in **2** were assigned to $\nu(\text{NH})$ and $\nu(\text{HOH})$, respectively.

Solid state electronic spectra of **1** and **2**, which were obtained by the diffuse reflectance method, are depicted in Figure 1.3. In **1**, the absorption bands at 265 and 404 nm with a broad shoulder at 500 nm were observed, where the bands at 265 and 404 nm were assigned to the LMCT ($\text{O} \rightarrow \text{Cr}$) transitions. A broad shoulder at $\sim 500\text{ nm}$ can be assigned to the LMCT ($\text{O} \rightarrow \text{Ni}$) transition [3,4]. In **2**, the interpretation of the electronic spectrum which contains four bands at 254 , ~ 340 (shoulder), 508 , and $\sim 680\text{ nm}$ (shoulder) is obscured due to the overlap in the region of expected LMCT ($\text{O} \rightarrow \text{Ni}$) and d-d transitions (at $\sim 500\text{ nm}$). A strong band at 254 nm is tentatively assigned to one of the LMCT ($\text{O} \rightarrow \text{Mo}$) bands. The rest of the band basically resemble to those of a typical high-spin nickel(II) system. Another LMCT ($\text{O} \rightarrow \text{Mo}$) band which is expected to appear in the higher energy region due to the energy mismatching of the molybdenum d- and oxygen p- orbitals were not observed in the scan range [15-18].

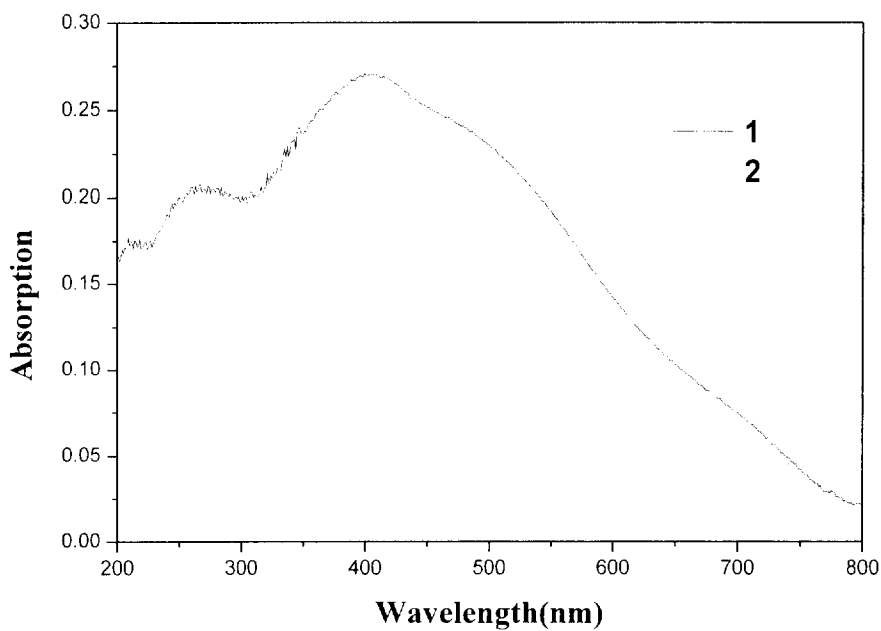


Figure 1.3. Solid state electronic absorption spectra of **1** (-) and **2** (...) in BaSO₄ by diffuse reflectance method at room temperature.

The magnetic susceptibility data for **1** and **2** are shown in the form of $\chi_m T$ vs T and χ_m vs T (Figures 1.4 and 1.5). The shape of the susceptibility plot reveals behavior typical of a ferromagnetically coupled one-dimensional chain compound. The observed ferromagnetic interactions are analyzed by Fisher's model for the classical spin chain system ($S = 1$ and $H_{\text{chain}} = -J \sum S_i \cdot S_{i+1}$) [19].

$$\chi_m = \frac{Ng^2 \beta^2 S(S+1) (1+u)}{3kT (1-u)}$$

$$u = \coth \left[\frac{JS(S+1)}{kT} \right] - \left[\frac{kT}{JS(S+1)} \right]$$

In **1** and **2** $\chi_m T$ values gradually increase as the temperature is lowered up to 30 K and 170 K, respectively, indicating ferromagnetic interactions between the nickel ions. The fitting of the observed data afforded to $J = 1.127 \text{ cm}^{-1}$ and $g = 2.275$ for **1**, $J = 0.666 \text{ cm}^{-1}$ and $g = 2.276$ for **2**. The $\chi_m T$ values below ~ 9 K (for **1**) and ~ 35 K (for **2**) show sudden decrease which is believed to be an antiferromagnetic interchain interactions [3]. The ferromagnetic interactions between the nickel ions through the oxometalates can be explained by the means of orbital topology of the frontier orbitals, which is recently developed by Oshio et al. [3].

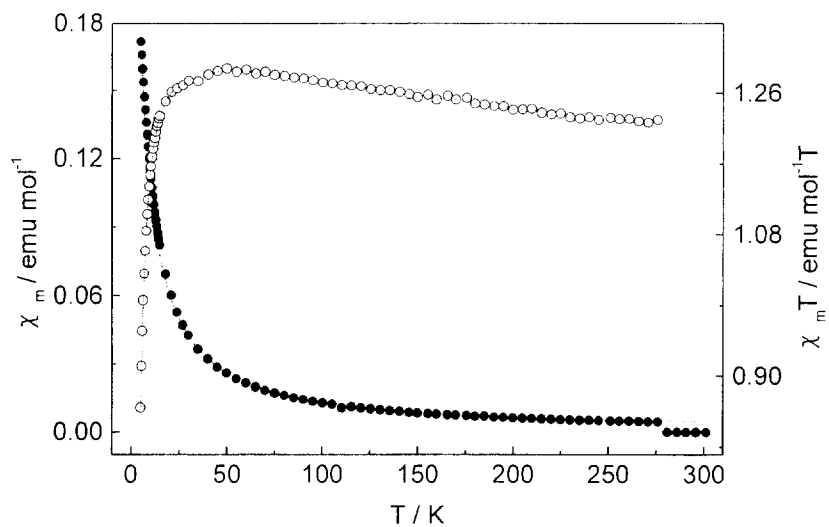


Figure 1.4. Plot of magnetic susceptibility vs. temperature for **1**.

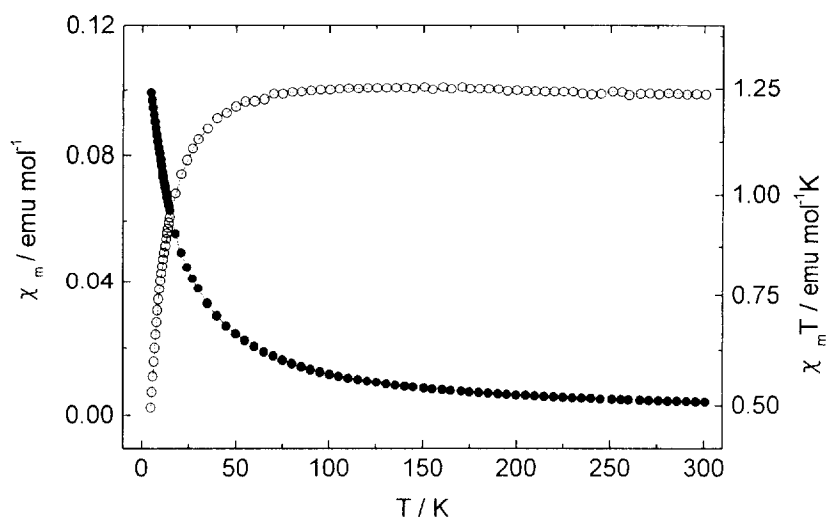


Figure 1.5. Plot of magnetic susceptibility vs. temperature for **2**.

Supplementary Material

Full crystal data and structure refinement details, atomic coordinates and equivalent isotropic displacement parameters, full interatomic distances and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters for **1** and **2** are available from the Cambridge Crystallographic Data Center, citing the deposition numbers 137387 for **1** and 137388 for **2**.

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CHAPTER II

Synthesis and characterization of trans-bis(dicyanamido) nickel(II) complexes with polyaza macrocyclic ligands

Abstract

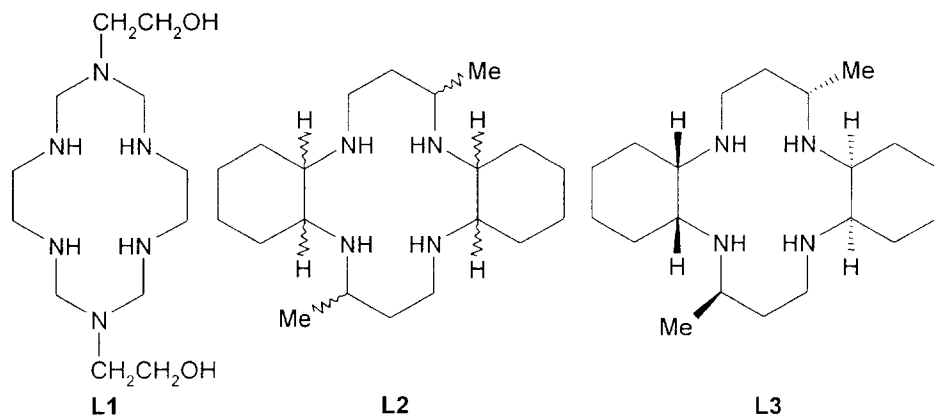
Two new trans-bis(dicyanamido)nickel(II) macrocyclic complexes, $[\text{Ni}(\text{II})(\mathbf{L1})\{\text{N}(\text{CN})_2\}_2] \cdot \text{H}_2\text{O}$ (**1**) and $[\text{Ni}(\text{II})(\mathbf{L3})\{\text{N}(\text{CN})_2\}_2]$ (**2**), where **L1** is 3,10-bis(2-hydroxyethyl)-1,3,5,8,10,12-hexaazacyclotetradecane and **L3** is 3,14-dimethyl-2,6,13,17-tetraazatricyclo[14,4,0^{1,18},0^{7,12}]docosane, have been synthesized and structurally characterized by spectroscopic and X-ray crystallographic methods. In **1** and **2**, each central nickel(II) ion possesses a distorted octahedral geometry with four equatorial nitrogen atoms from the macrocycle and two axial nitrogen atoms from dicyanamide anions, which are terminally bonded to the central nickel atom. The solid state electronic spectra of **1** and **2** using the diffuse reflectance method show a characteristic high-spin d^8 nickel(II) ion in a distorted octahedral environment.

Introduction

Many nickel(II) complexes of polyaza macrocyclic ligands undergo a square-planar low-spin and octahedral high-spin equilibrium in aqueous solutions [1-3]. Although this equilibrium has been reported to be susceptible to various factors, it is difficult to shift the equilibrium completely to the octahedral side [3-5]. A yellow square-planar nickel(II) complex is usually isolated in the presence of perchlorate or hexafluorophosphate anions [1]. We reported earlier polymeric octahedral nickel(II) complexes, bridged through oxalato or molybdate ligands with polyaza macrocyclic ligands [6,7]. The successful isolation of blue octahedral nickel(II) complexes in these cases may be attributed to the formation of insoluble nickel(II) coordination polymers in aqueous solutions. By the use of dicyanamide anion $[\text{N}(\text{CN})_2]^-$ with corresponding nickel(II) macrocycles (**L1** and **L2**), although not forming insoluble coordination polymers, we were able to isolate the blue high-spin octahedral nickel(II) complexes. Numerous metal complexes with dicyanamide ligand have been reported [8-11], however to our knowledge, no monomeric dicyanamide nickel(II) complex with a polyaza macrocyclic ligand **L1** or **L2** has been prepared.

In this thesis we report the synthesis and properties of two new dicyanamide

nickel(II) complexes with polyaza macrocyclic ligands. The dicyanamide anion, potentially tridentate, commonly prefers to coordinate as a bidentate mode, but acts as a monodentate ligand through lone pair donation of the terminal cyano N atoms to an octahedral metal center in **1** and **2**.



Experimental

Materials and physical measurements

All chemicals, obtained from commercial sources, were reagent grade and were used without further purification. Distilled H₂O was used for all procedures. I.R. spectra were measured as Nujol mulls between KBr plates using a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer over the range 4000 and 400 cm⁻¹.

UV/Vis diffuse reflectance spectra using samples diluted with BaSO₄ were recorded with a Shimadzu 2401 PC UV-Vis recording spectrophotometer. Elemental analyses were performed by the analytical laboratory of Korea Research Institute of Chemical Technology, Taejon, Korea.

The precursor complexes [Ni(II)(**L1**)]·2ClO₄ and [Ni(II)(**L2**)]·2ClO₄ were prepared according to slight modifiable literature procedures previously reported [3,12]. The macrocyclic ligand **L3** in complex **2** having both of the ethylene bridges replaced by cis-cyclohexane is one of the 16 possible diastereoisomers of **L2**. *Caution!* The perchlorate salts used in this study potentially are explosive and should be handled in small quantities.

Preparation

*Preparation of [Ni(**L1**){N(CN)₂}₂]·H₂O (**1**)*

An H₂O solution (10 cm³) of sodium dicyanamide (27 mg, 0.3 mmol) was added to a DMF (5 cm³) solution of [Ni(II)(**L1**)]·2ClO₄ (69 mg, 0.15 mmol). After several weeks, pale grey crystals were obtained while they were wet. Suitable crystals of **1** for X-ray diffraction studies and subsequent spectroscopic measurements were manually collected under the microscope. (Found: C, 39.1; H,

6.7; N, 34.0; C₁₆H₃₂N₁₂O₃Ni calcd.: C, 38.5; H, 6.4; N, 33.7 %.)

Preparation of [Ni(L3){N(CN)₂}₂] (2)

Violet plate crystals of **2** was prepared and isolated in a similar manner using [Ni(II)(L2)]·2ClO₄ (89.13 mg, 0.15 mmol) instead of [Ni(II)(L1)]·2ClO₄ (69 mg, 0.15 mmol). Although 16 different diastereoisomers are possible with the ligand L2, the nickel(II) complex with L3 in which the cyclohexane rings are cis-fused is always the isolated product. (Found: C, 55.9; H, 7.8; N, 27.1; C₂₄H₄₀N₁₀Ni calcd.: C, 54.6; H, 7.6; N, 26.6 %.)

X-ray crystallography

A summary of selected crystallographic data for **1** and **2** is given in Table 2.1. X-ray Data were collected on a STOE STADI4 four-circle-diffractometer using planar graphite monochromator (Mo K α , λ = 0.71073 Å) at 298(1) K. Cell parameters and an orientation matrix for data collection were obtained from least-squares refinement, using 24 reflections (for **1**) and 30 reflections (for **2**) in $9.6^\circ < \theta < 10.3^\circ$ (for **1**) and $10.24^\circ < \theta < 12.36^\circ$ (for **2**). Intensities were collected using ω scan technique. Three standard reflections were monitored every 1 hour of X-

Table 2.1. Crystal data and structure refinement for **1** and **2**

	1	2
Empirical formula	C ₁₆ H ₃₂ N ₁₂ NiO ₃	C ₂₄ H ₄₀ N ₁₀ Ni
Formula weight	499.25	527.37
Temperature (K)		298(2)
Wavelength (Å)		0.71069
Crystal system	Triclinic	Triclinic
Space group	P 1-	P 1-
a (Å)	8.1839(8)	8.223(5)
b (Å)	9.929(3)	8.338(4)
c (Å)	8.1008(12)	10.717(6)
α (°)	110.923(11)	72.74(4)
β (°)	105.848(18)	71.42(5)
γ (°)	93.68(3)	77.50(4)
V(Å ³)	581.8(2)	659.0(6)
Z	1	1
D _{calcd} (Mg/m ³)	1.425	1.329
Absorption coefficient(mm ⁻¹)	0.878	0.769
F(000)	264	282
Crystal size(mm)	0.5× 0.5× 0.2	0.50× 0.35× 0.20
θ range for data collection	5.19 to 27.44°	2.07 to 27.49°
Index ranges	-10 ≤ h ≤ 9 -12 ≤ k ≤ 11 1 ≤ l ≤ 10	-9 ≤ h ≤ 10 -10 ≤ k ≤ 10 0 ≤ l ≤ 13
Reflections collected	2236	3740
Independent reflections	2236 [R(int) = 0.0000]	2911 [R(int) = 0.0244]
Completeness to θ	83.9 % (θ = 27.44°)	96.3%(θ = 27.49°)
Refinement method	Full-matrix least-squares on F ²	

Table 2.1. Continued

	1	2
Data/restraints/parameters	2236/0/152	2911/0/160
Goodness-of-fit on F^2	1.082	1.128
Final R indices [$I > 2\sigma(I)$]	R1=0.0277, wR2=0.0751	R1=0.0314, wR2=0.0771
R indices (all data)	R1=0.0287, wR2=0.0763	R1=0.0363, wR2=0.0813
Largest diff. peak and hole	0.366 and -0.368 e. Å ⁻³	0.199 and -0.420 e. Å ⁻³

ray exposure and no significant decay was observed. All data were corrected for Lorentz and polarization effects, and absorption correction was applied. The structure was solved by direct method [13] and refined [14] on F^2 by full-matrix least-squares for all non-hydrogen atoms. Hydrogen atoms were included in calculated positions with isotropic displacement parameters. The final agreement factor values are $R1 = 0.0277$, $wR2 = 0.0751$ ($I > 2\sigma$); $R1 = 0.0287$, $wR2 = 0.0763$ (all data), $R1 = (||F_o|| - |F_c|) / \Sigma |F_o|$ and $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2 / \Sigma[w(F_o^2)^2]]]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.0417P)^2 + 0.2242P]$ where $P = (F_o^2 + 2 F_c^2)/3$ (for **1**), and $R1 = 0.0314$, $wR2 = 0.0771$ ($I > 2\sigma$); $R1 = 0.0363$, $wR2 = 0.0813$ (all data), $R1 = (||F_o|| - |F_c|) / \Sigma |F_o|$ and $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2 / \Sigma[w(F_o^2)^2]]]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.0370P)^2 + 0.1724P]$ where $P = (F_o^2 + 2 F_c^2)/3$ (for **2**).

Results and Discussion

Structures of 1 and 2

The single crystal X-ray structures were determined to establish the coordination nature of cyanamide ligands in the complexes in the solid state. In each case the composition of the structure was confirmed by microanalysis.

A view of molecules **1** and **2** is described in Figures 2.1 and 2.3, and the selected interatomic distances and angles are presented in Table 2.2 and 2.3. The ligand geometries of the present macrocycles adopt the most stable *trans III* configuration. An inversion center exists on the nickel(II) ion in both complexes. In **1** and **2** the coordination environment around nickel(II) centers reveals the expected distorted octahedral arrangement with the four nitrogen atoms from the macrocycle and the two dicyanamide anions in *trans*-positions from the nitrogen atoms of the terminal cyano groups. Although the dicyanamide anion can act as a monodentate [15-18], bidentate [19-21], or even tridentate [22], it usually prefers to coordinate as a bridging bidentate through both terminal cyano nitrogens. However, in the present cases, the monomeric complexes **1** and **2** always even in different molar ratios of $[\text{Ni(II)(L1)}] \cdot 2\text{ClO}_4$ or $[\text{Ni(II)(L2)}] \cdot 2\text{ClO}_4$ and $\text{Na}[\text{N(CN)}_2]$. The nickel-nitrogen (macrocycle) atom distances vary from 2.0534(13) to 2.0777(16) Å in **1** [2.0814(19) - 2.0980(18) Å in **2**]. These values lie well within the general trend that weaker nickel-nitrogen bonds are involved in the octahedral species (Ni-N = 2.07-2.10 Å) than in the square-planar species (Ni-N = 1.88-1.91 Å) [23]. The longer nickel-nitrogen (dicyanamide) distance in **2** than that in **1** may be most reasonably explained by the increased steric effect of the macrocycle **L3**. The end-bonded $[\text{N(CN)}_2]^-$ anion maintains C_{2v}

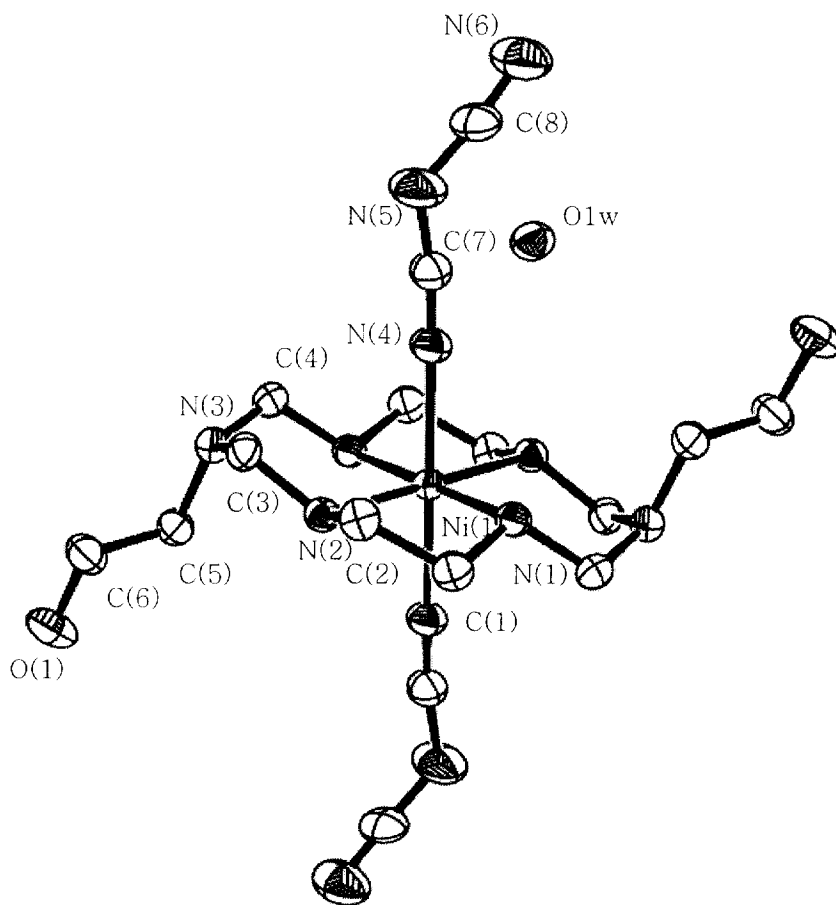


Figure 2.1. Molecular structure of **1** with atom-labeling scheme. Hydrogen atoms are omitted for clarity.

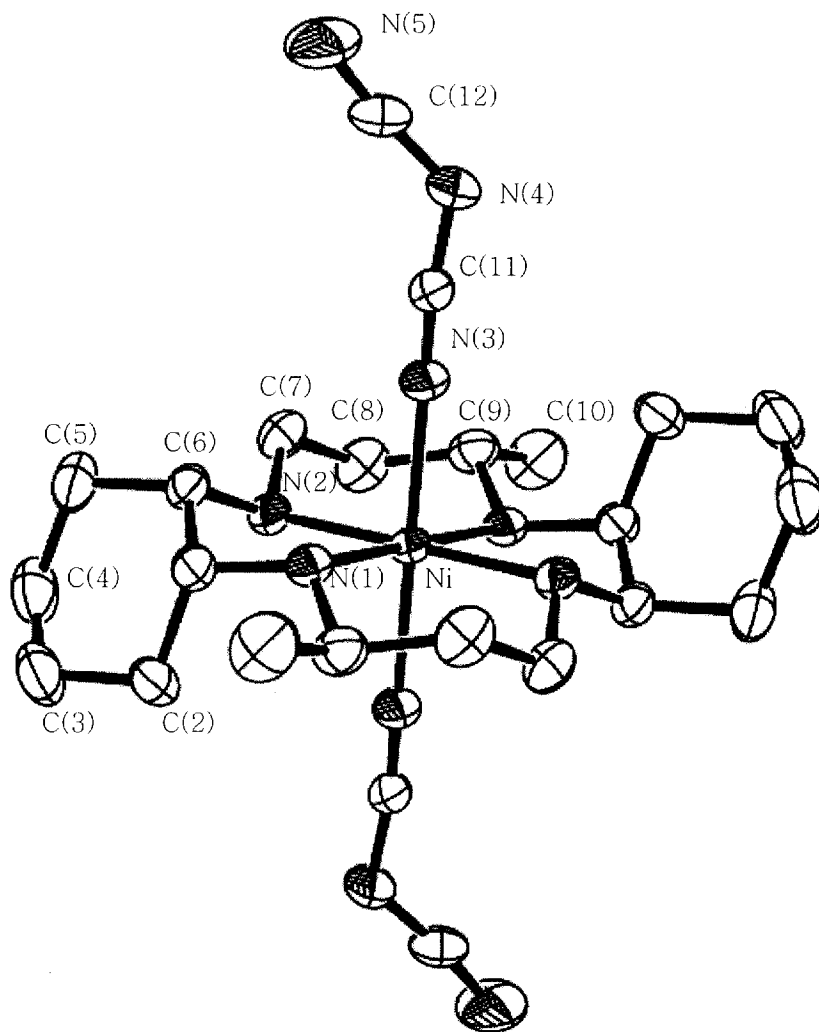


Figure 2.3. Molecular structure of **2** with atom-labeling scheme. Hydrogen atoms are omitted for clarity.

Table 2.2. Selected bond lengths (Å) and angles (°) for [Ni(L1){N(CN)₂}₂].H₂O (1)

Ni(1)-N(1)	2.0777(16)	Ni(1)-N(2)	2.0534(13)
Ni(1)-N(4)	2.1635(15)	N(4)-C(7)	1.144(2)
N(5)-C(8)	1.303(3)	N(5)-C(8)	1.303(3)
N(6)-C(8)	1.147(3)		
N(2)#1-Ni(1)-N(2)	180.0	N(2)#1-Ni(1)-N(1)	94.09(6)
N(2)-Ni(1)-N(1)	85.91(6)	N(1)#1-Ni(1)-N(1)	180.0
N(2)#1-Ni(1)-N(4)	89.13(6)	N(1)-Ni(1)-N(4)	88.83(6)
C(7)-N(4)-Ni(1)	179.02(16)	N(4)-C(7)-N(5)	171.3(2)
C(7)-N(5)-C(8)	124.1(2)	N(6)-C(8)-N(5)	172.9(2)
N(4)-Ni(1)-N(4)#1	180.0		

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

Table 2.3. Selected bond lengths (Å) and angles (°) for [Ni(L3){N(CN)₂}₂] (2)

Ni-N(1)	2.0980(18)	Ni-N(2)	2.0814(19)
Ni-N(3)	2.1220(19)	N(4)-C(11)	1.290(2)
N(4)-C(12)	1.294(3)	N(3)-C(11)	1.149(3)
N(5)-C(12)	1.138(3)		
<hr/>			
N(2)#1-Ni-N(2)	180.0	N(2)#1-Ni-N(1)	96.36(7)
N(2)-Ni-N(1)	83.64(7)	N(1)#1-Ni-N(1)	180.0
N(2)#1-Ni-N(3)	89.90(7)	N(1)-Ni-N(3)	86.86(7)
C(11)-N(3)-Ni	176.53(15)	N(3)-C(11)-N(4)	172.27(19)
C(11)-N(4)-C(12)	123.81(18)	N(5)-C(12)-N(4)	173.5(2)
N(3)-Ni-N(3)#1	180.0		

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

symmetry with N(5)-C(7) and N(5)-C(8) bond distances of 1.296(3) and 1.303(3) Å in **1** [N(4)-C(11) = 1.290(2) and N(4)-C(12) = 1.294(3) in **2**]. In **1**, the average C-N and C≡N bond distances are 1.300 and 1.146 Å [1.292 and 1.144 Å in **2**], respectively, as commonly observed in [N(CN)₂]⁻ anions. The lack of significant electron density near the amide nitrogen results in longer C-N bond distances, suggesting a small degree of π conjugation within the [N(CN)₂]⁻ backbone. The [N(CN)₂]⁻ ligand skeleton in **2** is isostructural to that of **1**. All other structural features are as typical of the [N(CN)₂]⁻ anions in **1** and **2**. In **1**, the molecules are further extended resulting in a two-dimensional network through hydrogen-bonding interactions involving the nitrogen atoms of the secondary and tertiary amines, the hydroxyl group, the lattice water molecule, and one of the terminal nitrogen atom of [N(CN)₂]⁻ ligand [O(1w)...O(1)#1 = 2.721(2) Å, O(1w)...N(6)#2 = 2.888(3) Å, O(1w)...N(3)#3 = 2.929(2) Å, N(2)...O(1)#4 = 2.842(2) Å] (Figures 2.1 and 2.2) [24].

*Spectroscopic properties of **1** and **2***

The I.R. spectra of **1** and **2** contain three ν(C≡N) stretching bands at 2156, 2217, and 2272 cm⁻¹ for **1**, and at 2162, 2210, and 2265 cm⁻¹ for **2**, whose

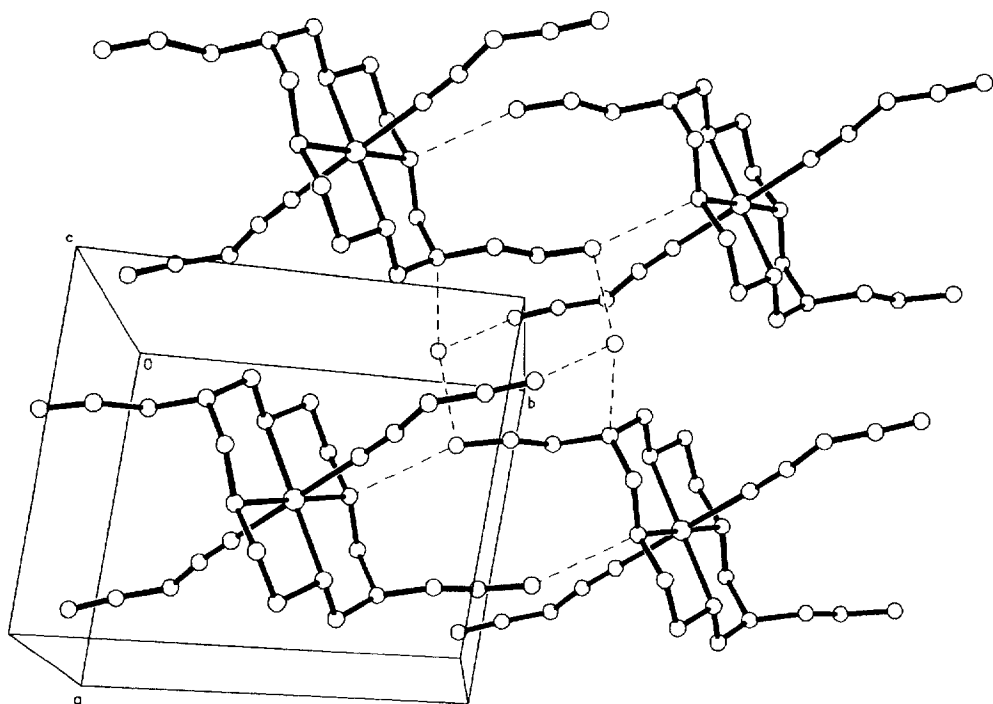


Figure 2.2. Crystal packing diagram of **1** showing the two-dimensional structure with the hydrogen-bonding interactions. Dotted lines indicate hydrogen bonds. Hydrogen atoms are omitted for clarity.

positions are in good agreement of those reported in the literature [25]. They are slightly shifted to lower frequencies compared to those of the free Na[N(CN)₂] ($\nu(\text{C}\equiv\text{N}) = 2179, 2232, \text{ and } 2286 \text{ cm}^{-1}$), indicating the presence of terminally coordinated dicyanamide groups. In addition, broad bands above 3100 cm^{-1} and ca. 1600 cm^{-1} were observed in **1** due to a molecule of lattice water (stretching and bending of O-H).

The Nujol mull diffuse reflectance absorption spectra of **1** and **2** over the range 300-800 nm show three absorption bands [329, 488, and 683 nm for **1**, and 337, 513, and 699 nm for **2**] (Figure 2.4). These are the characteristic spectra expected for a high-spin d^8 nickel(II) ion in a distorted octahedral environment, and can be attributed to ${}^3\text{B}_{1g} \rightarrow {}^3\text{E}_g$, ${}^3\text{B}_{1g} \rightarrow {}^3\text{E}_g$, ${}^3\text{B}_{1g} \rightarrow {}^3\text{B}_{2g} + {}^3\text{B}_{1g} \rightarrow {}^3\text{A}_{2g}$ transitions, respectively [1,2,23]. However, the electronic spectra for **1** or **2** dissolved in water show a single broad absorption band ca. 460 nm, indicating that the square-planar species is predominant over octahedral species.

Supplementary Material

Crystallographic data have been deposited at the Cambridge Crystallographic Data Center (CCDC), CCDC No. 163651 for **1** and CCDC No. 163652 for **2**.

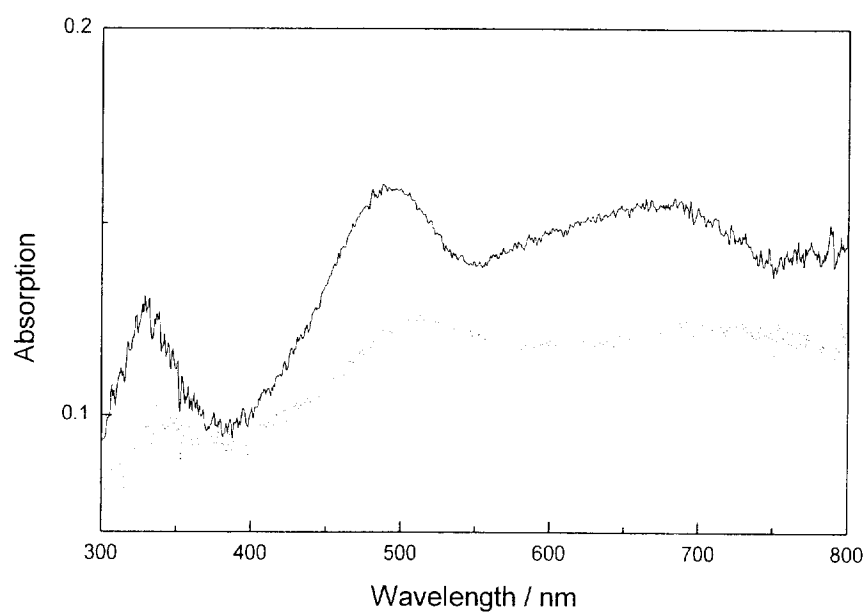


Figure 2.4. Solid state electronic absorption spectra of **1** (—) and **2** (...) in BaSO₄ by the diffuse reflectance method at room temperature.

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CHAPTER III

Syntheses, isolation, and structures of nickel(II) and copper(II) coordination polymers with a tetraaza macrocyclic ligand

Abstract

The one-dimensional coordination polymers $[\text{Ni}(\mathbf{L1})(\text{oxalato})]_n \cdot n\text{H}_2\text{O}$ (**1**) and $[\text{Cu}(\mathbf{L1})(\text{terephthalato})]_n \cdot 2n\text{H}_2\text{O}$ (**2**) have been synthesized and structurally characterized by a combination of analytical, spectroscopic, and crystallographic methods. The complex **1** exhibits a novel one-dimensional polymeric structure with nickel(II) centers and bridging oxalato ligands. Two important features are observed in **1** when regarding the structure of the oxalato bridge: first, it has an unusual bis-monodentate coordination mode to nickel(II) ions; and second, it is not planar, the distortion arising forms a twisting about the carbon-carbon bond of the oxalato ligand. In **2**, the ligand conformation is planar, and the distorted octahedral coordination about the copper(II) ion is completed by two bis-monodentate terephthalato ligands. The copper(II) ions in the complex are bridged

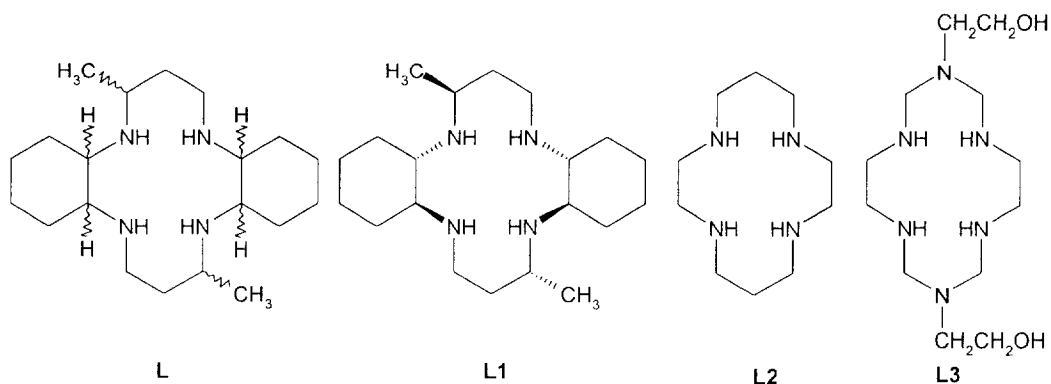
by the terephthalato anions to form infinite linear chains, and each chain is linked by interchain hydrogen bonding interactions mediated through water molecules. The presence of water molecules is crucial to lead supramolecular arrays in both complexes.

Introduction

The design and synthesis of molecular solids containing specific network topologies have been extensively studied in recent years [1-4]. Some interests lie in the construction of channel or cavity containing multi-dimensional frameworks [5-7], others in the understanding of structures and magnetic properties in low-dimensional polymeric systems [8-10]. The success of construction of these structures largely has been depend on the nature of the bridging ligand, as well as the availability of interchain hydrogen bonding interactions. Indeed, a number of examples of polymeric structures have been reported by the use of various bridging ligands. These include the oxalate [7], terephthalate [5], halide and pseudo halide [10,11], and tetraoxometalate [9] etc.

During studies aimed at constructing such one-dimensional networks using bridging ligands, novel complexes of an oxalato-bridged macrocyclic nickel(II)

coordination polymer, $[\text{Ni}(\mathbf{L1})(\text{oxalato})]_n \cdot n\text{H}_2\text{O}$ (**1**) and a terephthalato-bridged macrocyclic copper(II) coordination polymer, $[\text{Cu}(\mathbf{L1})(\text{terephthalato})]_n \cdot 2n\text{H}_2\text{O}$ (**2**) have been isolated. In **1**, each bridging oxalate anion binds two nickel(II) ions in a bis-monodentate fashion. In spite of numerous studies on oxalato-bridged nickel(II) complexes, bis-bidentate dimeric structures are predominant [12-15]. To the best of our knowledge, **1** is the first example of a bis-monodentate oxalato-bridged nickel(II) coordination polymer with tetraaza macrocyclic ligand. In **2**, each bridging terephthalate anion coordinates to two copper(II) ions in a bis-monodentate mode, resulting in the formation of infinite one-dimensional chains, where each chain is further extended by the interchain hydrogen bonding interactions mediated through water molecules. In this report, the syntheses and crystal structures of **1** and **2** are reported, where the bridging ligands are stabilized by hydrogen bonding interactions with pre-organized macrocycles and lattice water molecules.



Experimental

Materials and physical measurements

All chemicals were obtained from commercial sources, were reagent grade, and were used without further purification. Distilled water was used for all procedures. Infrared spectra of solid samples were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer between 4000 cm^{-1} and 400 cm^{-1} as Nujol mulls on KBr discs or as KBr pellets. Solid state electronic spectra were measured by the diffuse reflectance method using samples diluted with BaSO_4 with a Shimadzu 2401 PC UV/Vis recording spectrophotometer. The analytical laboratory of Korea Research Institute of Chemical Technology, Taejon, Korea, performed elemental analyses.

Preparation

The free ligand **L** and the precursor complexes $[\text{Ni}(\text{L})]\cdot 2\text{ClO}_4$ and $[\text{Cu}(\text{L})]\cdot 2\text{ClO}_4$ were synthesized by previously reported methods [16].

Caution! The perchlorate salts used in this study potentially are explosive and

should be handled in small quantities.

Preparation of [Ni(L1)(oxalato)]_n·nH₂O (1)

To a DMF (10 mL) solution of [Ni(L)]·2ClO₄ (594 mg, 1.0 mmol) was added a stoichiometric amount of sodium oxalate (134 mg, 1.0 mmol) dissolved in water (10 mL), which was allowed to stand in an open beaker at ambient temperature. After several weeks, purple crystals were obtained. Suitable crystals of **1** for X-ray diffraction studies and subsequent spectroscopic measurements were manually collected under the microscope. Anal. Calcd. for C₂₅H₄₉N₅O₆Ni: C, 52.24; H, 8.53; N, 12.18. Found C, 51.98; H, 8.14; N, 12.18.

Preparation of [Cu(L1)(terephthalato)]_n·2nH₂O (2)

An aqueous solution of sodium terephthalate (52.5 mg, 0.25 mmol) was added to an aqueous solution of [Cu(L)]·2ClO₄ (150 mg, 0.25 mmol). After standing for a week, violet crystals were obtained. Suitable crystals of **2** for X-ray diffraction studies and subsequent spectroscopic measurements were manually collected under the microscope. Anal. Calcd. for C₂₈H₄₈N₄O₆Cu : C, 55.98; H, 7.99; N, 9.33. Found C, 55.87; H, 8.12; N, 9.53.

X-ray crystallography

A summary of selected crystallographic data for **1** and **2** is given in Table 3.1. X-ray data were collected on a Nonius KappaCCD diffractometer, using graphite monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). A combination of 1° phi and omega (with kappa offsets) scans were used to collect sufficient data. The data frames were integrated and scaled using the Denzo-SMN package [17]. The structures were solved and refined, using the SHELXTL\PC V5.1 package [18]. Refinement was by full-matrix least squares on F^2 , using all data (negative intensities included). Hydrogen atoms were included in calculated positions, except for those involving hydrogen bonding specifically for the hydrogen atoms of the water molecule and those bonded to the nitrogen atoms, which were refined with isotropic thermal parameters. For **1** there are two independent centrosymmetric macrocycles in the structure. There is some electron density, which was disordered about an inversion center. Presumably, this was DMF solvent, but could not model the density to fit this type of molecule, which was eventually removed the contribution from the data using program SQUEEZE [19]. There is a molecule of crystallization of water, which is involved in hydrogen bonding for each cation and anion. For **2** the Cu containing cation and the anion

Table 3.1. Crystal data and structure refinement for [Ni(L1)(oxalato)]_n·nH₂O (**1**) and [Cu(L1)(terephthalato)]_n·2nH₂O (**2**)

	1	2
Empirical formula	C ₂₂ H ₄₂ N ₄ NiO ₅	C ₂₈ H ₄₈ CuN ₄ O ₆
Formula weight	501.31	600.24
Temperature(K)	113(2)	100.0(1)
Wavelength(Å)	0.71073	
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a (Å)	9.6798(5)	8.9701(5)
b (Å)	11.0018(5)	9.2486(5)
c (Å)	12.7679(2)	9.2555(5)
α (°)	103.087(3)	89.314(4)
β (°)	102.613(3)	68.834(3)
γ (°)	97.914(3)	85.487(3)
V (Å ³)	1267.15(9)	713.71(7)
Z	2	1
D _{calcd} (Mg/m ³)	1.314	1.397
Absorption coefficient(mm ⁻¹)	0.803	0.813
F(000)	540	321
Crystal size(mm)	0.25 x 0.20 x 0.10	0.25 x 0.20 x 0.20
θ range for data collection	2.63 to 27.49°	4.42 to 27.50°
Index ranges	0 ≤ h ≤ 12 -14 ≤ k ≤ 14 -16 ≤ l ≤ 15	-11 ≤ h ≤ 0 -12 ≤ k ≤ 11 -12 ≤ l ≤ 10
Reflections collected	21381	9357
Independent reflections	5738 [R(int) = 0.032]	3245 [R(int) = 0.054]
Completeness to θ	98.3 % (θ = 27.49°)	99.2 % (θ = 27.50°)

Table 3.1. Continued

	1	2
Absorption correction	multi-scan (Denzo-SMN)	
Max. and min. transmission	0.9240 and 0.8244	0.8542 and 0.8225
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	5738/3/302	3245/0/195
Goodness-of-fit on F^2	1.065	1.024
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0440, wR2 = 0.1044 R1 = 0.0381, wR2 = 0.0875	
R indices (all data)	R1 = 0.0696, wR2 = 0.1123 R1 = 0.0546, R2 = 0.0918	
Largest diff. peak and hole	0.430 and -0.392 e. \AA^{-3}	0.496 and -0.473 e. \AA^{-3}

$R1 = \frac{\sum || F_o - F_c ||}{\sum | F_o |}$ and $wR2 = \left[\frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right]^{1/2}$.

have crystallographic inversion symmetry and there is one anion for each cation. There are two molecules of crystallization of water for each cation molecule.

Results and Discussion

Structures of 1 and 2

The macrocyclic ligand **L1** in **1** and **2** adopts the classical *trans III* conformation in which both of the ethylene bridges in the macrocycle have been replaced by *trans*-cyclohexane. The ligand **L1** is one of the 16 possible diastereoisomers of **L**.

The structure of **1**, as illustrated in Figure 3.1, consists of a basic nickel-oxalate unit with an included water molecule. The coordination environment around the nickel(II) ion is a distorted octahedron with four Ni-N bonds and two Ni-O bonds. The average Ni-O interatomic distance of 2.139 Å is longer than the average Ni-N interatomic distance of 2.081 Å. Selected interatomic distances and angles of **1** are listed in Table 3.2. The oxalate ion in this complex coordinates to two nickel(II) ions in an unusual bis-monodentate mode. The uncoordinated oxygen atoms {O(2) and O(3)} of the carboxylate groups and the secondary amines of the macrocycle

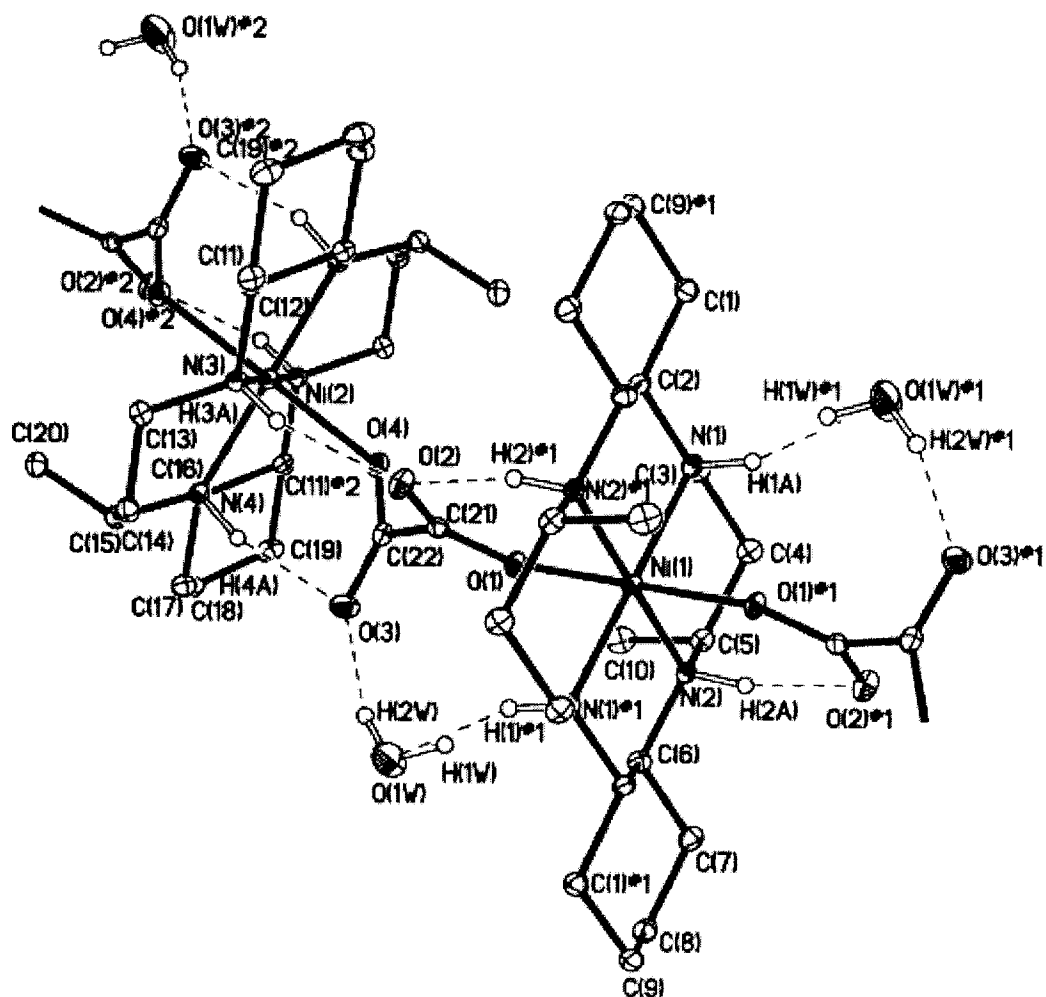


Figure 3.1. Molecular structure of $[\text{Ni}(\text{L1})(\text{oxalato})]_n \cdot n\text{H}_2\text{O}$ with atom-labeling scheme. Hydrogen atoms other than those participating in hydrogen bonding are omitted for clarity.

Table 3.2. Selected interatomic distances (Å) and angles (°) for [Ni(L1)(oxalato)]_n· nH₂O (1)

Ni(1)-N(1)	2.0745(19)	Ni(1)-N(2)	2.0793(17)
Ni(1)-O(1)	2.1273(15)	Ni(2)-N(3)	2.0628(18)
Ni(2)-N(4)	2.1088(18)	Ni(2)-O(4)	2.1504(15)
O(1)-C(21)	1.257(3)	O(2)-C(21)	1.258(3)
O(3)-C(22)	1.249(3)	O(4)-C(22)	1.270(3)
C(21)-C(22)	1.531(3)		
N(1)#1-Ni(1)-N(1)	180.00(10)	N(1)-Ni(1)-N(2)#	184.20(7)
N(1)#1-Ni(1)-N(2)	84.20(7)	N(1)-Ni(1)-N(2)	95.80(7)
N(2)#1-Ni(1)-N(2)	180.00(7)	N(1)-Ni(1)-O(1)#	189.02(7)
N(2)-Ni(1)-O(1)#1	89.53(6)	N(1)-Ni(1)-O(1)	90.98(7)
N(2)-Ni(1)-O(1)	90.47(6)	O(1)#1-Ni(1)-O(1)	180.0
N(3)-Ni(2)-N(3)#2	180.00(10)	N(3)-Ni(2)-N(4)#2	84.23(7)
N(3)-Ni(2)-N(4)	95.77(7)	N(4)#2-Ni(2)-N(4)	180.00(15)
N(3)-Ni(2)-O(4)	89.48(7)	N(4)-Ni(2)-O(4)	85.72(6)
N(3)-Ni(2)-O(4)#2	90.52(7)	N(4)-Ni(2)-O(4)#2	94.28(6)
O(4)-Ni(2)-O(4)#2	180.0	C(21)-O(1)-Ni(1)	137.39(15)
C(22)-O(4)-Ni(2)	128.46(15)	O(1)-C(21)-O(2)	127.3(2)
O(1)-C(21)-C(22)	116.3(2)	O(2)-C(21)-C(22)	116.4(2)
O(3)-C(22)-O(4)	126.0(2)	O(3)-C(22)-C(21)	118.4(2)
O(4)-C(22)-C(21)	115.48(19)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1, -y+1, -z+1 #2 -x, -y+1, -z

involve in the formation of stable 6-membered, and 7-membered hydrogen bonded rings. In addition, one {O(3)} of the oxygen atoms of the oxalato group forms a third type of hydrogen bonded ring with a secondary amine and a lattice water molecule (Figure 3.1, Table 3.4). Two important interesting features are observed in **1** when regarding the structure of the oxalato bridge: first, it has a bis-monodentate coordination mode to nickel(II) ions; second, it is not planar, the distortion arising forms a twisting about the carbon-carbon {C(21)-C(22)} bond of the oxalato ligand, which leads to a dihedral angle of $-103.0(3)^\circ$ between the O(1), C(21), O(2) and O(3), C(22), O(4) planes. Two combined effects are believed to be the origin of these unusual phenomena: first, complex **1** has an unequivalence of hydrogen bonding interactions involving the uncoordinated oxygen atoms of the oxalate anions with pre-organized macrocycles (Figure 3.1, Table 3.4); second, complex **1** contains sterically hindered cyclohexane groups as well as methyl groups on the macrocycle **L1** which force the bridging oxalato ligand to twist in a manner of the minimization of the steric hindrance. Numerous investigators have reported oxalato-bridged metal complexes with various metal ions. However, binuclear metal complexes were predominant with planar bis-bidentate oxalato ligands [7,12-14]. This is especially true in macrocyclic nickel(II) complexes. Binuclear complex, $[\{\text{Ni}(\mathbf{L2})\}_2(\text{oxalato})](\text{NO}_3)_2$ (**L2** = 1,4,8,11-

Table 3.4. Hydrogen bonds for [Ni(L1)(oxalato)]_n·nH₂O (1) [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...O(1W)#1	0.93	2.36	3.239(3)	158.4
N(2)-H(2A)...O(2)#1	0.93	2.04	2.940(2)	161.5
N(3)-H(3A)...O(2)	0.93	2.19	3.096(2)	163.3
N(4)-H(4A)...O(3)	0.93	2.21	3.092(2)	157.6
O(1W)-H(2W)...O(3)	0.839(5)	2.095(11)	2.908(3)	163(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 -x,-y+1,-z

tetraazacyclotetradecane, cyclam) is one of the examples [20]. In this complex the oxalate ion acts as a bis-bidentate ligand bridging two macrocyclic nickel(II) units with the ligand **L2**, adopting a folded conformation. The structure of oxalato-bridged nickel(II) complex with **L3** (**L3** = 3,10-bis(2-hydroxyethyl)-1,3,5,8,10,12-hexaazacyclotetradecane) also has been determined [21], where the structure is similar to that of $[\{\text{Ni}(\mathbf{L2})\}_2(\text{oxalate})](\text{NO}_3)_2$ except for the slightly longer distances of Ni-O in the former structure. In both cases, the macrocycles in nickel(II) complexes of **L2** and **L3** are flexible and foldable when the bridging oxalate anion binds to the nickel(II) ions, occupying the oxalate anion *cis*-positions in the coordination sphere of the nickel(II) ion, and producing dimeric structures. In the present ligand **L1**, however, the rigidity of the macrocycle has been increased considerably by the introduction of two cyclohexane rings and two methyl groups on **L2**, and a folded macrocycle is not anticipated with **L1**. Indeed, the nickel(II) complex of **L1** with oxalato bridging ligand produces an unusual polymeric complex **1** rather than a binuclear complex with folded macrocycles. In **1**, the closest Ni...Ni distance in the one dimensional chain is 7.12 Å.

The structure of **2** shows a terephthalato-bridged one-dimensional chain structure with interchain interactions (Figure 3.2). Water molecules mediate hydrogen bonding interactions between the chains. The intrachain Cu...Cu

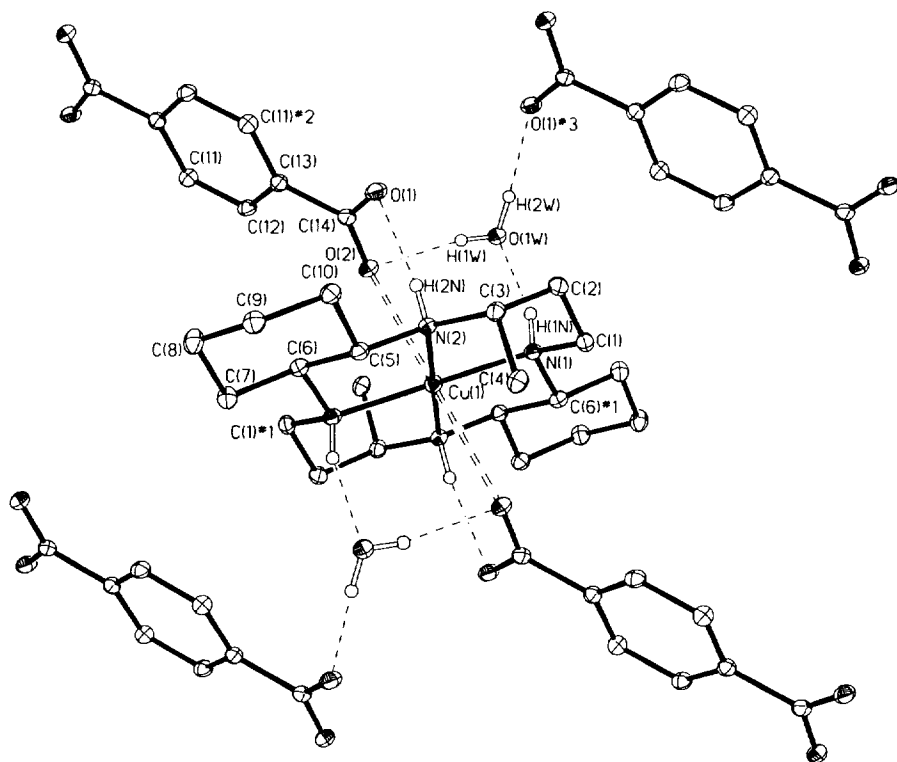


Figure 3.2. Molecular structure of $[\text{Cu}(\text{L1})(\text{terephthalato})]_n \cdot 2n\text{H}_2\text{O}$ with atom-labeling scheme. Hydrogen atoms other than those participating in hydrogen bonding are omitted for clarity.

distance is 8.970 Å and the interchain Cu...Cu distance is 9.225 Å. The copper coordination geometry of compound **2** shows a strong Jahn-Teller distortion with oxygen atoms of terephthalate anions occupying the axial sites. The four Cu-N(macrocycle) interatomic distances vary from 2.0225(16) to 2.0294(16) Å with an average distance of ~ 2.026 Å. The Cu-O interatomic distances of 2.7323(12) Å are well outside of any previously determined distances in related systems {Cu-O(maleato) = 2.3601(18) Å in [Cu(L1)(H₂O)(maleato); Cu-O(formato) = 2.2343(15) Å in [Cu(L1)(O₂CH)][ClO₄] [22,23]. The average Cu-O distance of 1.966±0.030 Å, determined for five structures, is found in a previous report [24]. It thus appears, that the Cu-O interactions in the present compound are essentially ionic in nature. Selected bond distances and angles for **2** are listed in Table 3.3. The hydrogen bonding interactions present in **2** are summarized in Table 3.5. In **2** the oxygen atoms of the terephthalate anions participate in the hydrogen bonding interactions with secondary amines and water molecules. Water molecules in **2** involve in mediating chain link. The secondary amine hydrogen H(2N) intramolecularly interacts to the uncoordinated oxygen atom of the terephthalate anion to form a stable 6-membered ring {Cu(1), O(2), C(14), O(1), H(2N), N(2)}. Additional hydrogen bonding interactions are observed by an intervention of water molecule, resulting in the formation of another 6-membered chelate

Table 3.3. Selected interatomic distances (Å) and angles (°) for [Cu(L1) (terephthalato)]_n·2nH₂O (2)

Cu(1)-N(1)	2.0225(16)	Cu(1)-N(2)	2.0294(16)
Cu(1)-O(2)	2.7323(12)	O(2)-C(14)	1.260(2)
N(1)#1-Cu(1)-N(1)	180.00(10)	N(1)#1-Cu(1)-N(2)#1	95.28(6)
N(1)-Cu(1)-N(2)#1	84.72(6)	N(2)#1-Cu(1)-N(2)	180.00(13)
N(1)#1-Cu(1)-O(2)#1	95.70(5)	N(1)-Cu(1)-O(2)#1	84.30(5)
N(2)#1-Cu(1)-O(2)#1	82.81(5)	N(2)-Cu(1)-O(2)#1	97.19(5)
O(2)#1-Cu(1)-O(2)	180.00(7)		

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z #2 -x+1,-y-1,-z

Table 3.5. Hydrogen bonds for [Cu(L1)(terephthalato)]_n·2nH₂O (**2**) [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1N)...O(1W)	0.84(2)	2.09(2)	2.902(2)	162(2)
N(2)-H(2N)...O(1)	0.85(2)	2.01(2)	2.8602(19)	171(2)
N(2)-H(2N)...O(2)	0.85(2)	2.61(2)	3.1932(19)	126.9(18)
O(1W)-H(1W)...O(2)	0.76(3)	2.05(3)	2.806(2)	170(3)
O(1W)-H(2W)...O(1)#3	0.85(3)	1.88(3)	2.729(2)	177(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z #2 -x+1,-y-1,-z #3 -x+1,-y,-z

ring{Cu(1), O(2), H(1W), O(1W), H(1N), N(1)}, as well as interchain link{O(1W), H(2W), O(1)#3} (Table 3.5).

Synthesis and spectroscopic characterization of 1 and 2

By reacting nickel(II) complex $[\text{Ni}(\mathbf{L})]\cdot 2\text{ClO}_4$ with sodium oxalate in DMF/H₂O solutions, a novel one-dimensional nickel(II) coordination polymer $[\text{Ni}(\mathbf{L1})(\text{oxalato})]_n \cdot n\text{H}_2\text{O}$ (**1**) has been isolated. The formation of this compound is partly a consequence of the high rigidity of the macrocyclic ligand **L1** which prevents *cis*-coordination of the oxalate ligand to the nickel(II) ion. The solid state IR spectrum of $[\text{Ni}(\mathbf{L1})(\text{oxalato})]_n \cdot n\text{H}_2\text{O}$ displays characteristic strong bands of the oxalate ligand at 1556 ($\nu_{\text{as}}\text{COO}$) cm^{-1} and 1284 ($\nu_{\text{s}}\text{COO}$) cm^{-1} . The large difference of 272 cm^{-1} between the two bands indicates that the carboxylate group of the oxalate ligand coordinates to the nickel ion in a monodentate fashion [25]. The solid state IR spectrum in the νNH and νOH stretching region shows medium intensity bands at 3169 cm^{-1} and 3315 cm^{-1} as expected. Compound **2** was synthesized by reacting copper complex $[\text{Cu}(\mathbf{L})]\cdot 2\text{ClO}_4$ with sodium terephthalate in an aqueous solution. In the solid state IR spectrum of **2**, a strong ($\nu_{\text{as}}\text{COO}$) band was observable at 1573 cm^{-1} with a medium band at 3332 (νOH) and 1660

cm^{-1} (vHOH), respectively. Solid state electronic spectrum of **1** over the range 200-800 nm is composed of three bands at 351, 539, and 712 nm. All three bands are expected from a high-spin d^8 nickel(II) ion in a distorted octahedral environment (${}^3B_{1g} \rightarrow {}^3E_g$, ${}^3B_{1g} \rightarrow {}^3E_g$, ${}^3B_{1g} \rightarrow {}^3B_{2g} + {}^3B_{1g} \rightarrow {}^3A_{2g}$). The spectrum of **2** shows maximum absorptions at 243, 275, and 532 nm. The lower energy band (532 nm) in the visible region is believed to be a composite of the three possible transitions d_{xy} , d_{xz} , $d_{yz} \rightarrow d_{x^2-y^2}$ [26]. The other two bands at higher energy region may be from the terephthalate ligand. The lowest energy absorption $d_{z^2} \rightarrow d_{x^2-y^2}$ transition arising from the tetragonal splitting of the formally octahedral e_g orbitals was not observed in the visible region.

In summary, one-dimensional coordination polymers have been constructed by the reaction of nickel(II) macrocyclic complex and oxalato ligand (**1**), and copper(II) macrocyclic complex and terephthalato ligand (**2**). The oxalato-bridged nickel(II) coordination polymer **1** has an unusual twist structure in oxalato bridge which is stabilized by hydrogen bonding interactions with the pre-organized nickel(II) macrocyclic ligand, the oxalato ligand, and the water molecule. The terephthalato-bridged copper(II) complex **2** has a tetragonally elongated octahedral geometry about the copper(II) ion. The infinite chains in **2** are also stabilized by hydrogen bonding interactions composed of the secondary amines,

the oxygen atoms of the terephthalato ligand, the water molecules, and the central copper(II) atom. Water molecule is a versatile molecule in **1** and **2** with a potential to play as hydrogen bond donors and acceptors. Oxalato and terephthalato ligands in **1** and **2** show a tendency to bridging metal ions by coordination to form infinite chains, as well as to play a role as hydrogen bond acceptors. In both complexes the ligand skeleton adopts the most stable *trans III* conformations [27].

Supplementary Material

Full crystal data and refinement details, atomic coordinates and equivalent isotropic displacement parameters, interatomic distances and angles, anisotropic displacement parameters, hydrogen atom coordinates and isotropic displacement parameters, and hydrogen bond parameters for **1** and **2** are available from the Cambridge Crystallographic Data Centre. Deposition numbers 158651 for **1** and 158652 for **2**.

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CHAPTER IV

Biomimetic non-heme catalysts for aliphatic C-H bond functionalization with a cobalt complex

Abstract

An aliphatic C-H bond functionalization into carboxylate is attained by hydrogen peroxide. A biomimetic precursor of the dinuclear Co(II) bis(μ -hydroxo) complex, $[\text{Co}^{\text{II}}_2(\text{Me}_3\text{-tpa})_2(\text{OH})_2]^{2+}$ (**1**), has been synthesized and structurally characterized by spectroscopy, elemental analysis, and X-ray crystallography, where Me₃-tpa is tris(6-methyl-2-pyridylmethyl)amine. The reaction of **1** with an excess amount of H₂O₂ yields two kinds of crystals of the ligand oxidized dinuclear Co(III) bis(μ -hydroxo) complexes, $[\text{Co}^{\text{III}}_2(\text{Me}_2\text{-tpa-COO})_2(\text{OH})_2]^{2+}$ (**2a**, **2b**), in which one of the methyl groups of Me₃-tpa is oxidized to carboxylate. The structural difference between **2a** and **2b** is characterized by spectroscopy and X-ray analysis. One of the pyridyl groups in asymmetric units of **2a** and **2b** is detached from metal due to the new bond formation between metal and oxygen of the ligand which is oxidized by H₂O₂.

The fixation of atmospheric CO₂ by **1** affords a μ-carbonato dinuclear Co(II) complex, [Co^{II}₂(Me₃-tpa)₂(CO₃)]²⁺ (**3**), which shows that a core of **1** is sufficiently nucleophilic. These results indicate that a plausible functionalization pathway of aliphatic C-H bond to carboxylate may be progressed via metal-oxo species.

Introduction

In recent years, there has been great interest in dioxygen activation related to C-H bond functionalization, which is an important goal for biomimetic chemistry as well as chemical industry [1]. Dioxygen activation by transition metal-dioxygen species, M₂(μ-O)₂ (M = Cu [2-12], Fe [13-16]), has been investigated as biomimetic models. These studies show that M₂(μ-O)₂ is the intermediate state prior to be functionalized.

More recently, these kinds of researches have been extended to cobalt complexes in order to understand general metabolism of the dioxygen in an ecosystem [17-20], even if no O₂ carrier or oxygenase with cobalt metals has been found. For instance, Hikichi at al. have reported the cobalt-dioxygen complex chemistry surrounded by hydrotris(pyrazoly)borate ligands (Tp^R), and explained their reaction with HOOX (X = H, alkyl, acyl) species, which results in the C-H bond oxygenation by the spontaneous decomposition [21].

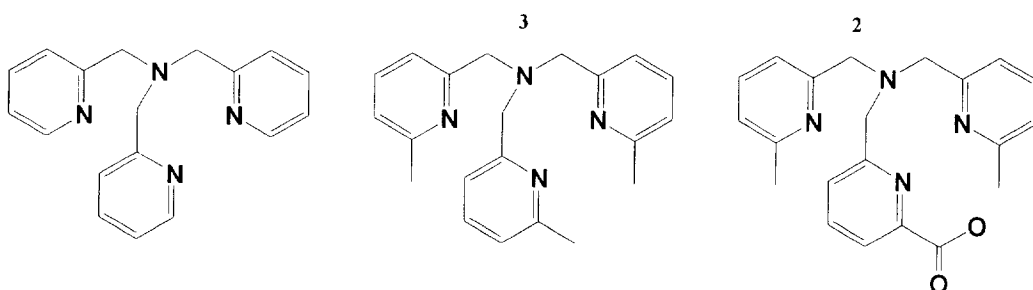
In the similar subject to alkane C-H bond oxygenation, Costas et al. have also demonstrated biomimetic nonheme iron catalysts for selective alkane oxidation using alkyl hydroperoxides or hydrogen peroxide as oxidants [22]. In spite of such an importance of the C-H bond functionalization, there are a few examples presented so far, compared with the aromatic/arene oxygenation [23-25].

Among the several transition metals, it is widely known that the cobalt ions have a tendency to be of a low-spin Co(III) oxidation state. In the transition metal-dioxygen chemistry, however, a lower oxidation state metal center is more susceptible to O-O bond activation, because the lower oxidation state metal is able to give high electron back-donation to the antibonding σ^* orbital (LUMO) of the peroxide, which abates the O-O bond. In this reason, we have focused on taking advantage of a bulky tetradentate tripodal ligand, Me₃-tpa, which also provides two vacant sites for O₂. Owing to its bulky substituents at 6-position of the pyridyl rings, the lower oxidation state of the cobalt metal can be stabilized. Moreover, such a bulky ligand may offer a hydrophobic cavity to the metal core so that unstable functional groups can be inhibited from decomposition.

By the reaction of a dinuclear Co(II) bis(μ -hydroxo) complex, [Co^{II}₂(Me₃-tpa)₂(OH)₂]²⁺ (**1**), with an excess amount of hydrogen peroxide, we have obtained and isolated the intramolecular ligand oxidized dinuclear Co(III) bis(μ -hydroxo) complexes, [Co^{III}₂(Me₂-tpa-COO)₂(OH)₂]²⁺ (**2a**, **2b**) (Scheme). Although ligand

functionalization to carboxylate has been reported in our group before [26], this kind of oxygenation is still rare. Herein, we report the structures of **1**, **2a**, **2b**, and **3**, and the reaction of intramolecular aliphatic C-H bond oxygenation.

Scheme.



Experimental

Materials and physical measurements

All chemicals obtained from commercial sources were reagent grade and used without further purification. All solvents were treated under nitrogen prior to use. Me₃-tpa was prepared according to the literature procedures previously reported [27]. All air-sensitive processes were performed in a vacuum atmospheres under nitrogen by standard Schlenk and vacuum line techniques. *Caution! The*

perchlorate salts in this study are potentially explosive and should be handled with care.

Electronic spectra were measured on a Shimatsu MultiSpec-1500 UV-Vis recording spectrophotometer for liquid measurement. UV/Vis diffuse reflectance spectra using solid samples diluted with BaSO₄ were recorded with a Hitachi U-3400 spectrophotometer. Infrared spectra were obtained by the KBr-disk method using a HORIBA FT-300 spectrophotometer over the range 4000 and 400 cm⁻¹. Mass and elemental analyses were performed by the analytical laboratory of Kanazawa University.

Preparation

*Preparation of [Co^{II}₂(Me₃-tpa)₂(OH)₂](ClO₄)₂ (**1**)*

To a mixture of Co(ClO₄)₂·6H₂O (36.6 mg, 0.1 mmol) and Me₃-tpa (33.2 mg, 0.1 mmol) in methanol was slowly added 2 equiv. of triethylamine (28 μL, 0.2 mmol) solution. The resultant mixture in a Schlenk ware was allowed to stand overnight under N₂ to give **1** as red-brown crystals, which were suitable for X-ray crystallography. Anal. Calcd. for C₄₂H₅₀N₈O₁₀Cl₂Co₂: C, 49.67; H, 4.96; N, 11.03. Found C, 49.53; H, 4.93; N, 11.22. UV-Vis (λ_{max}/nm (ε/M⁻¹cm⁻¹)) in acetonitrile at r.t.): 470(81), 493(72), 576(46). FT-IR (cm⁻¹): ν(C=C), 1604; ν(ClO₄), 1099.

*Preparation of [Co^{III}₂(Me₂-tpa-COO)₂(OH)₂](ClO₄)₂ (**2a**, **2b**)*

An excess amount of H₂O₂ was added to an ethanol suspension of **1** with rapid stirring. This green suspension turned dark brown solution. The resulting solution was standing for a day to afford **2a** and **2b** as blue-violet crystals and red-violet crystals, respectively, which were suitable for X-ray crystallography.

Spectroscopic data for **2a**·2H₂O: Anal. Calcd. for C₄₂H₄₈N₈O₁₆Cl₂Co₂ : C, 45.46; H, 4.36; N, 10.10. Found C, 45.66; H, 4.35; N, 10.04. UV-Vis (diffuse reflectance spectrum, λ_{max}): 584 nm. FT-IR (cm⁻¹): ν_a(COO), 1677; ν_s(COO), 1348; ν(ClO₄), 1095.

Spectroscopic data for **2b**·4H₂O: Anal. Calcd. for C₄₂H₅₂N₈O₁₈Cl₂Co₂ : C, 44.03; H, 4.57; N, 9.78. Found C, 43.62; H, 4.24; N, 9.77. UV-Vis (diffuse reflectance spectrum, λ_{max}): 594 nm. FT-IR (cm⁻¹): ν_a(COO), 1677; ν_s(COO), 1336; ν(ClO₄), 1087.

*Preparation of [Co^{II}₂(Me₃-tpa)₂(CO₃)](ClO₄)₂ (**3**)*

When the methanol solution of **1** was exposed to CO₂, the color change from green to pink was observed due to the formation of **3**. This solution was standing for several days to give pale brown crystals. Suitable crystals for X-ray crystallography were collected by filtration and washed with ether (Figure 4.1).

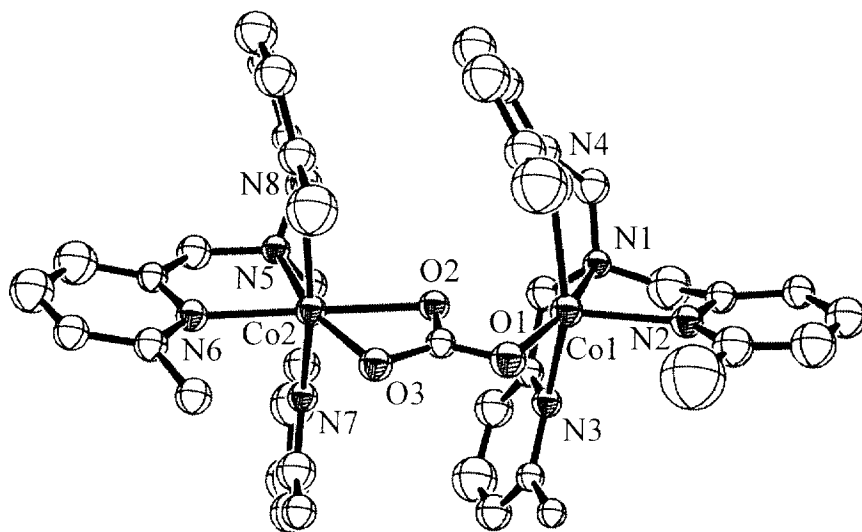


Figure 4.1. Thermal ellipsoid drawing of $[\text{Co}^{\text{II}}_2(\text{Me}_3\text{-tpa})_2(\text{CO}_3)]^{2+}$ (**3**) showing 20% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

X-ray crystallography

Data for **1** and **2b** were collected at $-150\text{ }^{\circ}\text{C}$ on a Quantum CCD area detector coupled with a Rigaku AFC7 diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069\text{ \AA}$). Crystal-to-detector distance was 35.98 mm. To determine the cell constants and the orientation matrix, seven oscillation photographs were taken with an oscillation angle of 0.5° for **1** and 0.25° for **2b**. Intensity data were collected by taking oscillation photographs using ω scans from -80.0° to 100.0° at $\chi = 45.0^{\circ}$ and $\varphi = 0.0^{\circ}$, and at $\chi = 45.0^{\circ}$ and $\varphi = 90.0^{\circ}$. The data were corrected for Lorentz and polarization effects, and empirically for the absorption effect.

Data for **2a** and **3** were collected on a Rigaku RAXIS-IV Imaging Plate diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71070\text{ \AA}$). Crystal-to-detector distance was 120 mm. To determine the cell constants and the orientation matrix, three oscillation photographs were taken with an oscillation angle of 2° . Intensity data were collected by taking oscillation photographs using ω scans (40 images with 4° oscillation for **2a** and 82 images with 2° oscillation for **3**). The data were corrected for Lorentz and polarization effects, but not for the absorption effect.

All structures were solved by a direct method [28] and expanded using a Fourier technique [29]. All calculations were performed using the teXsan [30] crystallographic software package of Molecular Structure Corporation. Hydrogen atoms were positioned at calculated positions. They were included, but not refined, in the final least-squares cycles [31].

Crystallographic data are summarized in Table 4.1. Tables of final atomic coordinates, thermal parameters, and full bond distances and angles are given in the Supplementary Material.

Results and Discussion

Generally, it has been revealed that Co(III) dioxygen complexes are produced by the reaction of Co(II) species and dioxygen or ROOH (R = H, alkyl), because a cobalt metal tends to be a low spin d^6 Co(III) state. Co(II)-bis(μ -hydroxo) complex, $[\text{Co}^{\text{II}}_2(\text{Me}_3\text{-tpa})_2(\text{OH})_2](\text{ClO}_4)_2$ (**1**), is basic enough to react with atmospheric CO_2 , which is testified by easily obtaining μ -carbonato dinuclear complex, $[\text{Co}^{\text{II}}_2(\text{Me}_3\text{-tpa})_2(\text{CO}_3)](\text{ClO}_4)_2$ (**3**), just standing the solution of complex **1** in the air [32]. Therefore the reaction of the Co(II)-bis(μ -hydroxo) complex and ROOH may yield Co(III) dioxygen complex, as expected.

Reaction of the complex **1** with an equimolar amount of H_2O_2 at -40°C afforded

Table 4.1. Crystallographic Data for $[\text{Co}^{\text{II}}_2(\text{Me}_3\text{-tpa})_2(\text{OH})_2](\text{ClO}_4)_2$ (**1**), $[\text{Co}^{\text{III}}_2(\text{Me}_2\text{-tpa-COO})_2(\text{OH})_2](\text{ClO}_4)_2$ (**2a**, **2b**), and $[\text{Co}^{\text{II}}_2(\text{Me}_3\text{-tpa})_2(\text{CO}_3)](\text{ClO}_4)_2$ (**3**)

	1	2a	2b	3
formula	$\text{C}_{42}\text{H}_{50}\text{N}_8\text{O}_{10}\text{Cl}_2\text{Co}_2$	$\text{C}_{42}\text{H}_{44}\text{N}_8\text{O}_{14}\text{Cl}_2\text{Co}_2$	$\text{C}_{46}\text{H}_{64}\text{N}_8\text{O}_{20}\text{Cl}_2\text{Co}_2$	$\text{C}_{43}\text{H}_{50}\text{N}_8\text{O}_{12}\text{Cl}_2\text{Co}_2$
temp, °C	-150	23	-150	23
MW	1015.68	1073.63	1237.83	1059.69
cryst system	triclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a , Å	11.6303(4)	10.945(4)	11.249(1)	10.3443(8)
b , Å	18.164(4)	18.626(5)	11.2127(8)	19.216(2)
c , Å	21.890(1)	11.673(7)	12.030(3)	23.330(1)
α , deg	97.457(3)	90	68.693(4)	90
β , deg	91.532(3)	110.57(3)	84.087(4)	94.187(8)
γ , deg	90.357(1)	90	70.387(2)	90

Table 4.1. Continued

	1	2a	2b	3
$V, \text{\AA}^3$	4583(1)	222(8)	1331.3(3)	4625.2(6)
Z	4	2	1	4
$2\theta_{max}$	55.0	51.4	55.0	51.3
$F(000)$	2158.0	1104.0	644.0	2192.0
$D_{calcd}, \text{g/cm}^3$	1.507	1.630	1.544	1.522
abs coeff, cm^{-1}	9.08	9.06	8.08	9.04
no. of reflcns colled	45036	3237	13665	4385
no. of indpt reflcns	12744 ($I \geq 3\sigma(I)$)	1886 ($I \geq 3\sigma(I)$)	3498 ($I \geq 3\sigma(I)$)	2523 ($I \geq 3\sigma(I)$)
no. of refined params	1159	307	352	575
GOF	1.35	1.92	1.17	1.61
largest peak / hole, e \AA^{-3}	1.29 / -0.74	0.40 / -0.67	0.60 / -0.35	0.64 / -0.57
R^a	0.054	0.089	0.048	0.070

Table 4.1. Continued

	1	2a	2b	3
R_w	0.077 ^b	0.124 ^c	0.063 ^d	0.095 ^e
^a $R = \Sigma[F_o - F_c]/\Sigma F_o $. ^b $R_w = [\Sigma w(F_o - F_c)^2/\Sigma w F_o ^2]^{1/2}$; $w = [\sigma^2_c(F_o) + p^2Fo^2/4]^{-1}$ ($p = 0.089$). ^c $R_w = [\Sigma w(F_o - F_c)^2/\Sigma w F_o ^2]^{1/2}$; $w = [\sigma^2_c(F_o) + p^2Fo^2/4]^{-1}$ ($p = 0.092$). ^d $R_w = [\Sigma w(F_o - F_c)^2/\Sigma w F_o ^2]^{1/2}$; $w = [\sigma^2_c(F_o) + p^2Fo^2/4]^{-1}$ ($p = 0.057$). ^e $R_w = [\Sigma w(F_o - F_c)^2/\Sigma w F_o ^2]^{1/2}$; $w = [\sigma^2_c(F_o) + p^2Fo^2/4]^{-1}$ ($p = 0.096$).				

a dark brown solution. Although the dark brown species were not isolated owing to their instability, the color change from green to dark brown suggested that the oxidation state of the metal was changed. An excess amount of H₂O₂ was then added to the brown solution and the mixture was warmed to room temperature. It was followed that blue-violet needle crystals, **2a**, and red-violet crystals which were block shape, **2b**, were obtained.

A thermal ellipsoid illustration of the [Co^{II}₂(Me₃-tpa)₂(OH)₂] (**1**) cation is shown in Figure 4.2, and selected bond lengths and angles are listed in Table 4.2. Complex **1** consists of a centrosymmetric core with a tetradentate ligand completing the distorted octahedral environment of each cobalt center. The bond distances of Co-O_{ave} (2.041 Å) and Co-N_{ave} (2.233 Å) and the Co...Co separation (3.129 Å) of **1** are quite similar but slightly longer than those of [Ni^{II}₂(Me₃-tpa)₂(OH)₂] (2.018, 2.181, and 3.090 Å, respectively) [26], which has the same coordination sphere around metals, and longer than those of [Co^{II}₂(Tp^{Me3})₂(OH)₂] (2.006, 2.105, and 3.141 Å, respectively) [18], where each metal center has less coordination environment than that of the complex **1**.

A structural comparison of two ligand oxidized products, [Co^{III}₂(Me₂-tpa-COO)₂(OH)₂](ClO₄)₂ (**2a**, **2b**), are shown in Figure 4.3, while selected bond lengths and angles are listed in Table 4.3.

The coordination geometries around each cobalt atom in **2a** and **2b** are the

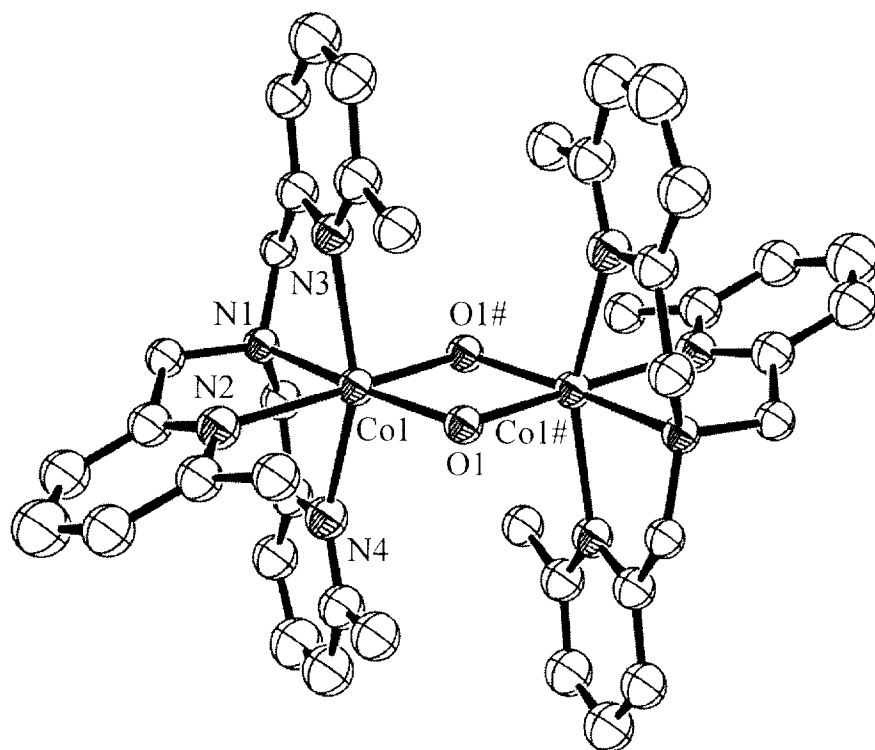


Figure 4.2. Thermal ellipsoid drawing of $[\text{Co}^{\text{II}}_2(\text{Me}_3\text{-tpa})_2(\text{OH})_2]^{2+}$ (**1**) showing 50% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

Table 4.2. Selected Bond Lengths (Å) and Bond Angles (°) for [Co^{II}₂(Me₃-tpa)₂(OH)₂](ClO₄)₂ (**1**)

Co1-O1	1.974(3)	Co1#-O1	2.102(3)
Co1-N1	2.155(4)	Co1-N2	2.241(4)
Co1-N3	2.273(4)	Co1-N4	2.270(4)
Co1...Co1#	3.130(1)	O1...O1#	2.610(4)
Co1-O1-Co1#	100.6(1)	O1-Co1-O1#	79.4(1)
O1-Co1-N1	169.4(1)	O1-Co1-N2	108.8(1)
O1-Co1-N3	106.2(1)	O1-Co1-N4	101.6(1)
O1#-Co1-N1	90.3(1)	O1#-Co1-N2	171.5(1)
O1#-Co1-N3	92.4(1)	O1#-Co1-N4	90.9(1)
N1-Co1-N2	81.6(1)	N1-Co1-N3	76.6(1)
N1-Co1-N4	75.7(1)	N2-Co1-N3	83.2(1)
N2-Co1-N4	89.6(1)	N3-Co1-N4	152.1(1)

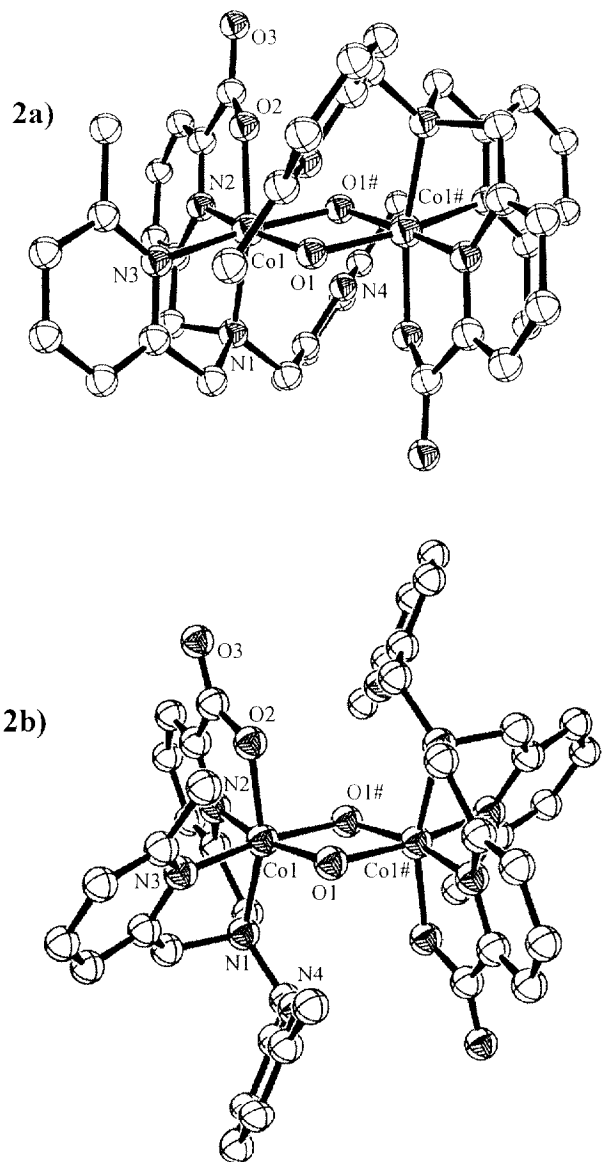


Figure 4.3. ORTEP drawings of $[\text{Co}^{\text{III}}_2(\text{Me}_2\text{-tpa-COO})_2(\text{OH})_2]^{2+}$ (**2a**, **2b**) showing 30% and 40% thermal ellipsoids, respectively. Hydrogen atoms have been omitted for clarity.

Table 4.3. Selected Bond Distances (Å) and Angles (°) of [Co^{III}₂(Me₂-tpa-COO)₂(OH)₂](ClO₄)₂ (**2a**, **2b**)

	2a		2b
Co1-O1	1.861(7)	Co1-O1	1.906(3)
Co1-O1#	1.839(7)	Co1-O1#	1.903(3)
Co1-O2	1.910(3)	Co1-O2	1.962(8)
Co1-N1	2.114(9)	Co1-N1	2.063(4)
Co1-N2	1.833(9)	Co1-N2	1.892(4)
Co1-N3	1.986(9)	Co1-N3	1.987(4)
Co1...Co1#	2.734(2)	Co1...Co1#	2.921(1)
O1...O1#	2.494(1)	O1...O1#	2.444(4)
N4...O1#	2.842(1)	N4...O1	2.729(5)
O1-Co1-O1#	84.8(3)	O1-Co1-O1#	79.8(1)
Co1-O1-Co1#	95.2(3)	Co1-O1-Co1#	100.2(1)

distorted octahedron where each cobalt metal is bound by three nitrogen atoms from a facially coordinated ligand and by three oxygen atoms from bridging hydroxides and an oxidized part of the ligand. These two cobalt(III) complexes are dimerized by a couple of hydroxides in which each complex has a rotational C_2 symmetry axis passing through the center of Co_2O_2 core. Therefore, the core is strictly planar due to the presence of the symmetry axis, and separation of each metal is 2.734 and 2.921 Å, respectively. These little difference of the separation is resulted from the position of the free pyridyl groups.

These Ortep diagrams show that a major difference is the position of intramolecular hydrogen bonds. In **2a**, each free nitrogen of pyridyl groups which are detached from metals forms a hydrogen bond with the oxygen atom of bridging hydroxo ($N4 \cdots O1\#$) which lies trans to the nitrogen of a non-oxidized pyridyl group. In the case of **2b**, however, the nitrogen forms a hydrogen bond with the other oxygen atom of bridging hydroxo ($N4 \cdots O1$) which lies trans to the nitrogen of an oxidized pyridyl group.

In the case of a monomer Ni(II) complex, $[Ni^{II}(Me_2-tpa-COO)(OH_2)]$, which has the same oxidized ligand reported by Shiren et al. [26], the Ni-O and average Ni-N bond distances (2.084 and 2.131 Å, respectively) are significantly longer than those in **2a** (Co-O;1.910 and Co-N;1.978 Å) and **2b** (Co-O;1.962 and Co-N;1.981 Å).

In Ni(III) μ -oxo complexes, the average core bond length of the $[\text{Ni}^{\text{III}}_2(\text{Me}_3\text{-tpa})_2(\text{O})_2]$ (2.052 Å) [26] is longer than those of the $[\text{Ni}^{\text{III}}_2(\text{Tp}^{\text{Me}_3})_2(\text{O})_2]$ (1.948 Å) [18], which is attributable to the difference of steric influence and/or Lewis acidity up to each ligand. Somewhat, in the case of $[\text{Co}^{\text{III}}_2(\text{Tp}^{\text{Me}_3})_2(\text{O})_2]$ [18], the average Co-O and Co-N bond distances are 1.790 and 2.049 Å. All these comparisons of the bond distances suggest that the intermediate brown species in the present study is very unstable sterically.

The electronic diffuse reflectance spectra of the compounds exhibit maximum absorptions at 584 nm for **2a** and 594 nm for **2b**, which also show the structural difference in the solid states. Each visible absorption feature is expected from a low-spin d^6 cobalt(III) ion in a distorted octahedral environment, which is assigned to the ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{1g}$ transition. When the compounds, however, were dissolved in acetonitrile, intramolecular hydrogen bonds decompose to be free, which are identified by the UV-Vis spectra showing the similar absorption bands ($\lambda_{\text{max}} = 583$ ($\epsilon = 564 \text{ M}^{-1}\text{cm}^{-1}$) and 584 (540) nm, respectively).

The reaction pathway for the formation of $\text{Me}_2\text{-tpa-COO}^-$ is not clear at present but it is possible that the $\text{Me}_3\text{-tpa}$ could be oxidized by dioxygen in the presence of a metal ion, which is initiated by hydrogen abstraction of a methyl group of the $\text{Me}_3\text{-tpa}$.

In conclusion, a Co(II)-bis(μ -hydroxo) complex, $[\text{Co}^{\text{II}}_2(\text{Me}_3\text{-tpa})_2(\text{OH})_2](\text{ClO}_4)_2$

(**1**), and Co(III)-bis(μ -hydroxo) complexes, $[\text{Co}^{\text{III}}_2(\text{Me}_2\text{-tpa-COO})_2(\text{OH})_2](\text{ClO}_4)_2$ (**2a**, **2b**), were synthesized and characterized by X-ray crystallography and physicochemical measurements. Complexes **2a** and **2b** were produced by the reaction of a complex **1** with an excess amount of H_2O_2 . The sterically demanding $\text{Me}_3\text{-tpa}$ ligand makes it possible to isolate the aliphatic C-H bond oxygenated complexes using hydrogen peroxide.

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$$w = 1/[\sigma^2(F_o)] = [\sigma_c^2(F_o) + p^2 F_o^2/4]^{-1}$$

$\sigma_c(F_o)$ = e.s.d. based on counting statistics

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Supplementary Material

Tables listing crystallographic experimental details, final atomic coordinates, thermal parameters, and full bond distances and angles for **1**, **2a**, **2b**, and **3**.

Supplementary Materials for Chapter IV

For complex 1.

A. Crystal Data

Empirical Formula	H ₅₀ C ₄₂ N ₈ O ₁₀ Cl ₂ Co ₂
Formula Weight	1015.68
Crystal Color, Habit	red-brown, plate
Crystal Dimensions	0.25 X 0.20 X 0.05 mm
Crystal System	triclinic
Lattice Type	Primitive
Lattice Parameters	a = 11.6303(4) Å b = 18.164(4) Å c = 21.890(1) Å α = 97.457(3) ^o β = 91.532(3) ^o γ = 90.357(1) ^o V = 4583(1) Å ³
Space Group	P $\bar{1}$ (No. 2)
Z value	4
D _{calc}	1.507 g/cm ³
F ₀₀₀	2158.00
μ(MoKα)	9.08 cm ⁻¹

B. Intensity Measurements

Diffractometer	Quantum CCD/Rigaku AFC7
Radiation	MoKα (λ = 0.71069 Å) graphite monochromated
Temperature	-150.0 °C
Voltage, Current	50 kV, 200 mA
Detector Aperture	70 mm x 70 mm
Data Images	720 exposures@20.0 seconds
ω Oscillation Range (χ=45.0, φ=0.0)	-80.0 - 100.0 ^o

	($\chi=45.0$, $\phi=90.0$)	-80.0 - 100.0 $^{\circ}$
Detector Position		35.96 mm
Detector Swing Angle		10.00 $^{\circ}$
$2\theta_{\max}$		55.0 $^{\circ}$
No. of Reflections Measured		Total: 45036 Unique: 19628 ($R_{\text{int}}=0.025$)
Corrections		Lorentz-polarization Empirical Absorption

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma w (F_o - F_c)^2$
Least Squares Weights	$1/\sigma^2(F_o) = 4F_o^2/\sigma^2(F_o^2)$
p-factor	0.0890
Anomalous Dispersion	All non-hydrogen atoms
No. of Observations ($I > 3.00\sigma(I)$, $2\theta < 54.97^{\circ}$)	12744
No. Variables	1159
Reflection/Parameter Ratio	11.00
Residuals: R; Rw	0.054 ; 0.077
Goodness of Fit Indicator	1.35
Max Shift/Error in Final Cycle	0.004
Maximum peak in Final Diff. Map	1.29 e $^{-}/\text{\AA}^3$
Minimum peak in Final Diff. Map	-0.74 e $^{-}/\text{\AA}^3$

Table 1. Atomic coordinates, $B_{\text{iso}}/B_{\text{eq}}$ and occupancy

atom	x	y	z	B_{eq}	occ
Co(1)	0.41161(5)	0.44168(3)	0.46654(3)	2.11(1)	1.0000
Co(2)	0.07801(5)	0.03681(3)	0.55509(3)	2.29(1)	1.0000
Co(3)	0.37009(5)	0.47732(3)	0.99245(3)	2.44(1)	1.0000
Co(4)	0.08192(5)	-0.05258(3)	0.95935(3)	2.23(1)	1.0000
O(1)	0.5798(3)	0.4563(2)	0.4759(1)	2.33(6)	1.0000

Table 1 (continued). Atomic coordinates, $B_{\text{iso}}/B_{\text{eq}}$ and occupancy

atom	x	y	z	B_{eq}	occ
O(2)	0.0300(3)	-0.0631(2)	0.5179(1)	2.54(6)	1.0000
O(3)	0.4703(3)	0.5440(2)	1.0485(1)	2.72(6)	1.0000
O(4)	-0.0854(3)	-0.0370(2)	0.9695(1)	2.45(6)	1.0000
N(1)	0.2266(3)	0.4418(2)	0.4705(2)	2.55(7)	1.0000
N(2)	0.3750(3)	0.3369(2)	0.4028(2)	2.55(7)	1.0000
N(3)	0.3560(3)	0.4967(2)	0.3831(2)	2.61(8)	1.0000
N(4)	0.3734(3)	0.3810(2)	0.5482(2)	2.47(7)	1.0000
N(5)	0.1104(4)	0.1517(2)	0.5826(2)	2.69(8)	1.0000
N(6)	0.2119(3)	0.0278(2)	0.6305(2)	2.60(8)	1.0000
N(7)	0.2399(3)	0.0590(2)	0.5020(2)	2.69(8)	1.0000
N(8)	-0.0567(3)	0.0675(2)	0.6241(2)	2.76(8)	1.0000
N(9)	0.2851(4)	0.4007(2)	0.9221(2)	2.68(8)	1.0000
N(10)	0.1935(4)	0.4784(2)	1.0305(2)	3.03(8)	1.0000
N(11)	0.3758(4)	0.3683(2)	1.0344(2)	2.81(8)	1.0000
N(12)	0.3147(3)	0.5494(2)	0.9206(2)	2.74(8)	1.0000
N(13)	0.2677(3)	-0.0531(2)	0.9580(2)	2.59(8)	1.0000
N(14)	0.1057(3)	-0.1416(2)	0.8794(2)	2.66(8)	1.0000
N(15)	0.1280(3)	-0.1313(2)	1.0257(2)	2.44(7)	1.0000
N(16)	0.1251(3)	0.0232(2)	0.8868(2)	2.63(8)	1.0000
C(1)	0.1808(4)	0.3693(3)	0.4393(2)	3.2(1)	1.0000
C(2)	0.2602(4)	0.3265(3)	0.3949(2)	3.00(10)	1.0000
C(3)	0.2104(5)	0.2737(4)	0.3506(3)	4.4(1)	1.0000
C(4)	0.2820(6)	0.2311(4)	0.3119(3)	5.2(2)	1.0000
C(5)	0.3988(6)	0.2400(3)	0.3196(3)	4.2(1)	1.0000
C(6)	0.4448(4)	0.2932(3)	0.3653(2)	2.94(10)	1.0000
C(7)	0.5726(5)	0.3012(3)	0.3755(2)	3.3(1)	1.0000
C(8)	0.1825(4)	0.5056(3)	0.4421(2)	3.08(10)	1.0000
C(9)	0.2477(4)	0.5224(3)	0.3878(2)	2.83(9)	1.0000
C(10)	0.2000(5)	0.5672(3)	0.3473(2)	3.5(1)	1.0000
C(11)	0.2642(6)	0.5869(3)	0.3005(2)	3.9(1)	1.0000

Table 1 (continued). Atomic coordinates, $B_{\text{iso}}/B_{\text{eq}}$ and occupancy

atom	x	y	z	B_{eq}	occ
C(12)	0.3754(5)	0.5587(3)	0.2936(2)	3.6(1)	1.0000
C(13)	0.4185(4)	0.5130(2)	0.3349(2)	2.90(9)	1.0000
C(14)	0.5345(5)	0.4787(3)	0.3270(2)	3.4(1)	1.0000
C(15)	0.1981(4)	0.4507(3)	0.5364(2)	2.75(9)	1.0000
C(16)	0.2708(4)	0.4020(2)	0.5720(2)	2.65(9)	1.0000
C(17)	0.2335(5)	0.3823(3)	0.6273(2)	3.2(1)	1.0000
C(18)	0.3061(5)	0.3431(3)	0.6615(2)	3.3(1)	1.0000
C(19)	0.4110(5)	0.3199(3)	0.6371(2)	3.06(10)	1.0000
C(20)	0.4422(4)	0.3388(2)	0.5806(2)	2.72(9)	1.0000
C(21)	0.5537(4)	0.3134(3)	0.5535(2)	3.01(10)	1.0000
C(22)	0.1822(5)	0.1610(3)	0.6402(2)	3.10(10)	1.0000
C(23)	0.2559(4)	0.0956(3)	0.6495(2)	2.76(9)	1.0000
C(24)	0.3584(4)	0.1069(3)	0.6827(2)	3.3(1)	1.0000
C(25)	0.4169(5)	0.0463(3)	0.6996(2)	3.7(1)	1.0000
C(26)	0.3716(5)	-0.0231(3)	0.6815(2)	3.6(1)	1.0000
C(27)	0.2693(4)	-0.0316(3)	0.6466(2)	3.2(1)	1.0000
C(28)	0.2186(6)	-0.1070(3)	0.6276(3)	4.1(1)	1.0000
C(29)	0.1663(5)	0.1834(3)	0.5321(2)	3.12(10)	1.0000
C(30)	0.2579(4)	0.1327(3)	0.5022(2)	2.86(9)	1.0000
C(31)	0.3495(5)	0.1617(3)	0.4740(3)	3.6(1)	1.0000
C(32)	0.4242(5)	0.1138(4)	0.4428(3)	4.1(1)	1.0000
C(33)	0.4083(5)	0.0386(3)	0.4422(2)	3.8(1)	1.0000
C(34)	0.3169(4)	0.0126(3)	0.4725(2)	3.09(10)	1.0000
C(35)	0.3000(5)	-0.0690(3)	0.4742(2)	3.4(1)	1.0000
C(36)	-0.0029(4)	0.1870(3)	0.5943(2)	3.01(10)	1.0000
C(37)	-0.0751(4)	0.1415(3)	0.6309(2)	2.94(9)	1.0000
C(38)	-0.1613(5)	0.1744(3)	0.6686(3)	3.8(1)	1.0000
C(39)	-0.2305(5)	0.1309(3)	0.6980(3)	4.0(1)	1.0000
C(40)	-0.2140(5)	0.0554(3)	0.6912(2)	3.7(1)	1.0000
C(41)	-0.1252(4)	0.0248(3)	0.6549(2)	3.09(10)	1.0000

Table 1 (continued). Atomic coordinates, $B_{\text{iso}}/B_{\text{eq}}$ and occupancy

atom	x	y	z	B_{eq}	occ
C(42)	-0.1017(5)	-0.0571(3)	0.6484(3)	3.8(1)	1.0000
C(43)	0.1601(4)	0.4036(3)	0.9306(2)	3.15(10)	1.0000
C(44)	0.1274(4)	0.4248(3)	0.9966(2)	3.02(10)	1.0000
C(45)	0.0307(5)	0.3950(3)	1.0195(3)	3.9(1)	1.0000
C(46)	0.0013(5)	0.4194(4)	1.0789(3)	4.5(1)	1.0000
C(47)	0.0657(5)	0.4741(4)	1.1132(3)	4.4(1)	1.0000
C(48)	0.1607(5)	0.5044(3)	1.0872(2)	3.6(1)	1.0000
C(49)	0.2278(6)	0.5670(4)	1.1226(3)	4.4(1)	1.0000
C(50)	0.3312(5)	0.3254(2)	0.9256(2)	3.10(10)	1.0000
C(51)	0.3506(4)	0.3098(3)	0.9912(2)	2.97(10)	1.0000
C(52)	0.3494(5)	0.2374(3)	1.0037(3)	3.7(1)	1.0000
C(53)	0.3759(5)	0.2234(3)	1.0631(3)	4.1(1)	1.0000
C(54)	0.4009(5)	0.2828(3)	1.1077(2)	3.7(1)	1.0000
C(55)	0.3998(4)	0.3554(3)	1.0925(2)	3.2(1)	1.0000
C(56)	0.4205(5)	0.4191(3)	1.1408(2)	3.7(1)	1.0000
C(57)	0.3138(5)	0.4259(2)	0.8626(2)	2.90(9)	1.0000
C(58)	0.2964(4)	0.5081(2)	0.8652(2)	2.70(9)	1.0000
C(59)	0.2660(5)	0.5390(3)	0.8128(2)	3.1(1)	1.0000
C(60)	0.2581(5)	0.6157(3)	0.8158(2)	3.5(1)	1.0000
C(61)	0.2782(5)	0.6581(3)	0.8716(3)	3.6(1)	1.0000
C(62)	0.3051(5)	0.6239(3)	0.9236(2)	3.2(1)	1.0000
C(63)	0.3212(5)	0.6698(3)	0.9857(3)	3.9(1)	1.0000
C(64)	0.3060(4)	-0.1127(3)	0.9106(2)	3.04(10)	1.0000
C(65)	0.2152(4)	-0.1405(2)	0.8616(2)	2.61(9)	1.0000
C(66)	0.2496(5)	-0.1687(3)	0.8034(2)	3.4(1)	1.0000
C(67)	0.1690(6)	-0.2046(3)	0.7621(2)	4.0(1)	1.0000
C(68)	0.0581(5)	-0.2098(3)	0.7803(3)	4.1(1)	1.0000
C(69)	0.0271(5)	-0.1774(3)	0.8394(2)	3.3(1)	1.0000
C(70)	-0.0942(5)	-0.1854(3)	0.8602(3)	4.1(1)	1.0000
C(71)	0.3110(4)	-0.0665(3)	1.0199(2)	2.91(10)	1.0000

Table 1 (continued). Atomic coordinates, $B_{\text{iso}}/B_{\text{eq}}$ and occupancy

atom	x	y	z	B_{eq}	occ
C(72)	0.2388(4)	-0.1228(2)	1.0460(2)	2.67(9)	1.0000
C(73)	0.2828(5)	-0.1594(3)	1.0934(2)	3.3(1)	1.0000
C(74)	0.2122(5)	-0.2056(3)	1.1208(2)	3.4(1)	1.0000
C(75)	0.0995(5)	-0.2154(3)	1.0997(2)	3.1(1)	1.0000
C(76)	0.0600(4)	-0.1784(2)	1.0514(2)	2.77(9)	1.0000
C(77)	-0.0617(4)	-0.1901(3)	1.0275(2)	3.2(1)	1.0000
C(78)	0.3054(4)	0.0209(3)	0.9452(2)	3.03(10)	1.0000
C(79)	0.2357(4)	0.0471(2)	0.8932(2)	2.76(9)	1.0000
C(80)	0.2837(5)	0.0973(3)	0.8581(2)	3.3(1)	1.0000
C(81)	0.2120(5)	0.1267(3)	0.8156(2)	3.7(1)	1.0000
C(82)	0.1004(5)	0.1015(3)	0.8075(2)	3.7(1)	1.0000
C(83)	0.0590(4)	0.0484(3)	0.8422(2)	2.93(10)	1.0000
C(84)	-0.0607(5)	0.0181(3)	0.8319(2)	3.5(1)	1.0000
Cl(1)	-0.1190(1)	0.29587(7)	0.46667(7)	4.09(3)	1.0000
Cl(2)	0.0338(1)	0.33780(6)	0.76374(5)	2.94(2)	1.0000
Cl(3)	0.5235(1)	0.26167(7)	0.79467(6)	3.39(2)	1.0000
Cl(4)	0.6014(1)	-0.06889(6)	0.82185(5)	2.89(2)	1.0000
O(5)	-0.1745(6)	0.3522(3)	0.4378(3)	8.0(2)	1.0000
O(6)	-0.0497(4)	0.3315(2)	0.5178(2)	5.0(1)	1.0000
O(7)	-0.0466(5)	0.2505(3)	0.4276(3)	6.9(1)	1.0000
O(8)	-0.2047(4)	0.2513(3)	0.4878(2)	5.8(1)	1.0000
O(9)	0.0681(5)	0.4136(2)	0.7796(2)	6.2(1)	1.0000
O(10)	0.0139(4)	0.3270(3)	0.6987(2)	5.0(1)	1.0000
O(11)	-0.0704(5)	0.3219(3)	0.7916(3)	7.1(2)	1.0000
O(12)	0.1239(4)	0.2910(2)	0.7802(3)	5.5(1)	1.0000
O(13)	0.4085(4)	0.2812(2)	0.7779(2)	4.22(9)	1.0000
O(14)	0.5968(5)	0.2641(4)	0.7441(3)	8.5(2)	1.0000
O(15)	0.5663(4)	0.3109(4)	0.8445(4)	9.8(2)	1.0000
O(16)	0.5235(5)	0.1889(3)	0.8095(3)	6.7(1)	1.0000
O(17)	0.6484(8)	-0.0617(3)	0.7652(3)	9.7(2)	1.0000

Table 1 (continued). Atomic coordinates, $B_{\text{iso}}/B_{\text{eq}}$ and occupancy

atom	x	y	z	B_{eq}	occ
O(18)	0.5292(4)	-0.0086(3)	0.8414(3)	6.1(1)	1.0000
O(19)	0.6881(5)	-0.0721(3)	0.8680(3)	7.2(1)	1.0000
O(20)	0.5371(4)	-0.1379(2)	0.8158(2)	4.61(10)	1.0000
O(21)	0.9170	0.3665	0.3164	12.9025	1.0000
O(22)	0.182(2)	0.389(1)	0.236(1)	13.7029	0.5000
C(85)	0.9220	0.4427	0.3208	10.3620	1.0000
C(86)	0.076(2)	0.353(2)	0.220(1)	10.3461	0.5000
H(1)	0.1634	0.3391	0.4702	3.8	1.0000
H(2)	0.1122	0.3787	0.4172	3.8	1.0000
H(3)	0.1293	0.2672	0.3471	5.3	1.0000
H(4)	0.2508	0.1956	0.2799	6.2	1.0000
H(5)	0.4486	0.2097	0.2937	5.1	1.0000
H(6)	0.5928	0.2913	0.4160	4.0	1.0000
H(7)	0.6103	0.2671	0.3463	4.0	1.0000
H(8)	0.5956	0.3504	0.3709	4.0	1.0000
H(9)	0.1047	0.4954	0.4292	3.7	1.0000
H(10)	0.1859	0.5482	0.4724	3.7	1.0000
H(11)	0.1232	0.5840	0.3521	4.3	1.0000
H(12)	0.2339	0.6190	0.2733	4.7	1.0000
H(13)	0.4212	0.5707	0.2609	4.4	1.0000
H(14)	0.5267	0.4262	0.3214	4.0	1.0000
H(15)	0.5691	0.4943	0.2919	4.0	1.0000
H(16)	0.5815	0.4939	0.3626	4.0	1.0000
H(17)	0.2106	0.5010	0.5533	3.3	1.0000
H(18)	0.1195	0.4379	0.5399	3.3	1.0000
H(19)	0.1590	0.3957	0.6414	3.8	1.0000
H(20)	0.2850	0.3320	0.7010	4.0	1.0000
H(21)	0.4612	0.2912	0.6593	3.7	1.0000
H(22)	0.5931	0.2847	0.5806	3.6	1.0000
H(23)	0.5395	0.2841	0.5148	3.6	1.0000

Table 1 (continued). Atomic coordinates, $B_{\text{iso}}/B_{\text{eq}}$ and occupancy

atom	x	y	z	B_{eq}	occ
H(24)	0.5995	0.3554	0.5479	3.6	1.0000
H(25)	0.2313	0.2029	0.6396	3.7	1.0000
H(26)	0.1325	0.1699	0.6741	3.7	1.0000
H(27)	0.3885	0.1557	0.6938	4.0	1.0000
H(28)	0.4868	0.0527	0.7233	4.4	1.0000
H(29)	0.4099	-0.0656	0.6928	4.4	1.0000
H(30)	0.1450	-0.1099	0.6449	4.9	1.0000
H(31)	0.2113	-0.1158	0.5839	4.9	1.0000
H(32)	0.2674	-0.1433	0.6418	4.9	1.0000
H(33)	0.1094	0.1911	0.5017	3.7	1.0000
H(34)	0.2010	0.2295	0.5482	3.7	1.0000
H(35)	0.3604	0.2138	0.4763	4.3	1.0000
H(36)	0.4863	0.1322	0.4217	5.0	1.0000
H(37)	0.4600	0.0046	0.4210	4.6	1.0000
H(38)	0.2277	-0.0842	0.4554	4.1	1.0000
H(39)	0.3596	-0.0955	0.4524	4.1	1.0000
H(40)	0.3020	-0.0789	0.5157	4.1	1.0000
H(41)	0.0084	0.2351	0.6165	3.6	1.0000
H(42)	-0.0413	0.1911	0.5560	3.6	1.0000
H(43)	-0.1710	0.2267	0.6736	4.5	1.0000
H(44)	-0.2900	0.1524	0.7231	4.7	1.0000
H(45)	-0.2628	0.0243	0.7111	4.4	1.0000
H(46)	-0.1550	-0.0807	0.6718	4.6	1.0000
H(47)	-0.1095	-0.0774	0.6062	4.6	1.0000
H(48)	-0.0257	-0.0649	0.6630	4.6	1.0000
H(49)	0.1287	0.4390	0.9067	3.8	1.0000
H(50)	0.1282	0.3559	0.9165	3.8	1.0000
H(51)	-0.0146	0.3582	0.9947	4.7	1.0000
H(52)	-0.0633	0.3985	1.0962	5.4	1.0000
H(53)	0.0459	0.4914	1.1543	5.3	1.0000

Table 1 (continued). Atomic coordinates, $B_{\text{iso}}/B_{\text{eq}}$ and occupancy

atom	x	y	z	B_{eq}	occ
H(54)	0.3053	0.5523	1.1280	5.3	1.0000
H(55)	0.2260	0.6088	1.1006	5.3	1.0000
H(56)	0.1949	0.5798	1.1618	5.3	1.0000
H(57)	0.2780	0.2898	0.9055	3.7	1.0000
H(58)	0.4024	0.3210	0.9053	3.7	1.0000
H(59)	0.3307	0.1978	0.9722	4.4	1.0000
H(60)	0.3769	0.1740	1.0731	4.9	1.0000
H(61)	0.4189	0.2744	1.1488	4.4	1.0000
H(62)	0.4364	0.4015	1.1791	4.4	1.0000
H(63)	0.4843	0.4474	1.1302	4.4	1.0000
H(64)	0.3542	0.4494	1.1441	4.4	1.0000
H(65)	0.3918	0.4147	0.8540	3.5	1.0000
H(66)	0.2654	0.4007	0.8308	3.5	1.0000
H(67)	0.2505	0.5081	0.7750	3.8	1.0000
H(68)	0.2392	0.6382	0.7801	4.2	1.0000
H(69)	0.2739	0.7107	0.8749	4.3	1.0000
H(70)	0.3961	0.6621	1.0019	4.7	1.0000
H(71)	0.3121	0.7208	0.9814	4.7	1.0000
H(72)	0.2655	0.6554	1.0129	4.7	1.0000
H(73)	0.3696	-0.0944	0.8906	3.6	1.0000
H(74)	0.3297	-0.1536	0.9308	3.6	1.0000
H(75)	0.3272	-0.1637	0.7920	4.1	1.0000
H(76)	0.1903	-0.2251	0.7219	4.8	1.0000
H(77)	0.0018	-0.2353	0.7531	4.9	1.0000
H(78)	-0.1260	-0.1376	0.8711	4.9	1.0000
H(79)	-0.1394	-0.2119	0.8276	4.9	1.0000
H(80)	-0.0939	-0.2119	0.8949	4.9	1.0000
H(81)	0.3877	-0.0839	1.0167	3.5	1.0000
H(82)	0.3100	-0.0211	1.0468	3.5	1.0000
H(83)	0.3610	-0.1525	1.1067	3.9	1.0000

Table 1 (continued). Atomic coordinates, $B_{\text{iso}}/B_{\text{eq}}$ and occupancy

atom	x	y	z	B_{eq}	occ
H(84)	0.2404	-0.2304	1.1537	4.1	1.0000
H(85)	0.0493	-0.2472	1.1180	3.7	1.0000
H(86)	-0.1008	-0.1441	1.0323	3.8	1.0000
H(87)	-0.0618	-0.2098	0.9851	3.8	1.0000
H(88)	-0.0995	-0.2240	1.0501	3.8	1.0000
H(89)	0.2972	0.0554	0.9813	3.6	1.0000
H(90)	0.3840	0.0186	0.9344	3.6	1.0000
H(91)	0.3627	0.1112	0.8630	4.0	1.0000
H(92)	0.2399	0.1636	0.7925	4.4	1.0000
H(93)	0.0511	0.1204	0.7780	4.5	1.0000
H(94)	-0.1023	0.0292	0.8687	4.2	1.0000
H(95)	-0.0977	0.0400	0.7996	4.2	1.0000
H(96)	-0.0580	-0.0342	0.8210	4.2	1.0000

$$B_{\text{eq}} = 8/3 \pi^2 (U_{11}(\text{aa}^*)^2 + U_{22}(\text{bb}^*)^2 + U_{33}(\text{cc}^*)^2 + 2U_{12}(\text{aa}^*\text{bb}^*)\cos \gamma + 2U_{13}(\text{aa}^*\text{cc}^*)\cos \beta + 2U_{23}(\text{bb}^*\text{cc}^*)\cos \alpha)$$

Table 2. Anisotropic Displacement Parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co(1)	0.0259(3)	0.0250(3)	0.0296(3)	-0.0017(2)	-0.0011(2)	0.0049(2)
Co(2)	0.0361(3)	0.0238(3)	0.0268(3)	-0.0037(2)	-0.0026(2)	0.0031(2)
Co(3)	0.0353(3)	0.0275(3)	0.0294(3)	-0.0010(2)	-0.0033(2)	0.0030(2)
Co(4)	0.0301(3)	0.0259(3)	0.0297(3)	-0.0021(2)	-0.0045(2)	0.0079(2)
O(1)	0.029(2)	0.026(1)	0.033(1)	-0.001(1)	0.000(1)	0.004(1)
O(2)	0.039(2)	0.026(1)	0.031(2)	-0.002(1)	-0.004(1)	0.005(1)
O(3)	0.039(2)	0.031(2)	0.032(2)	0.001(1)	-0.006(1)	0.000(1)
O(4)	0.030(2)	0.032(2)	0.031(1)	-0.002(1)	-0.006(1)	0.007(1)
N(1)	0.027(2)	0.030(2)	0.041(2)	-0.002(1)	-0.004(1)	0.008(2)
N(2)	0.038(2)	0.026(2)	0.032(2)	-0.002(1)	-0.004(2)	0.005(1)
N(3)	0.039(2)	0.029(2)	0.030(2)	-0.002(2)	-0.005(1)	0.004(1)

Table 2 (continued). Anisotropic Displacement Parameters

atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
N(4)	0.033(2)	0.025(2)	0.036(2)	-0.004(1)	-0.003(1)	0.007(1)
N(5)	0.043(2)	0.030(2)	0.028(2)	-0.006(2)	-0.003(2)	0.002(1)
N(6)	0.041(2)	0.033(2)	0.025(2)	-0.001(2)	-0.002(1)	0.005(1)
N(7)	0.038(2)	0.036(2)	0.028(2)	-0.004(2)	-0.005(1)	0.005(1)
N(8)	0.038(2)	0.036(2)	0.031(2)	0.000(2)	-0.001(2)	0.004(2)
N(9)	0.043(2)	0.026(2)	0.034(2)	0.001(2)	-0.005(2)	0.005(1)
N(10)	0.036(2)	0.042(2)	0.037(2)	0.001(2)	-0.005(2)	0.009(2)
N(11)	0.040(2)	0.036(2)	0.031(2)	-0.001(2)	-0.002(2)	0.009(2)
N(12)	0.036(2)	0.032(2)	0.037(2)	0.002(2)	-0.002(2)	0.006(2)
N(13)	0.029(2)	0.035(2)	0.036(2)	-0.005(1)	-0.004(1)	0.014(2)
N(14)	0.038(2)	0.026(2)	0.037(2)	-0.001(1)	-0.005(2)	0.006(1)
N(15)	0.035(2)	0.029(2)	0.030(2)	0.001(1)	-0.004(1)	0.011(1)
N(16)	0.041(2)	0.031(2)	0.029(2)	-0.001(2)	-0.001(2)	0.008(1)
C(1)	0.030(2)	0.036(2)	0.053(3)	-0.008(2)	-0.007(2)	0.004(2)
C(2)	0.040(3)	0.036(2)	0.037(2)	-0.007(2)	-0.009(2)	0.005(2)
C(3)	0.051(3)	0.058(3)	0.054(3)	-0.011(3)	-0.010(3)	-0.005(3)
C(4)	0.070(4)	0.064(4)	0.056(4)	-0.012(3)	-0.006(3)	-0.021(3)
C(5)	0.067(4)	0.045(3)	0.046(3)	-0.002(3)	0.002(3)	-0.008(2)
C(6)	0.045(3)	0.032(2)	0.035(2)	0.000(2)	0.000(2)	0.003(2)
C(7)	0.045(3)	0.039(3)	0.041(3)	0.008(2)	0.005(2)	0.000(2)
C(8)	0.031(2)	0.039(2)	0.048(3)	0.006(2)	-0.007(2)	0.008(2)
C(9)	0.035(2)	0.034(2)	0.037(2)	0.000(2)	-0.009(2)	0.003(2)
C(10)	0.047(3)	0.043(3)	0.045(3)	0.004(2)	-0.015(2)	0.011(2)
C(11)	0.067(4)	0.044(3)	0.040(3)	0.003(3)	-0.018(2)	0.012(2)
C(12)	0.065(4)	0.045(3)	0.028(2)	-0.007(2)	-0.005(2)	0.009(2)
C(13)	0.050(3)	0.031(2)	0.029(2)	-0.005(2)	-0.003(2)	0.004(2)
C(14)	0.050(3)	0.040(3)	0.038(2)	-0.004(2)	0.008(2)	0.007(2)
C(15)	0.026(2)	0.035(2)	0.043(2)	-0.004(2)	0.007(2)	0.004(2)
C(16)	0.035(2)	0.029(2)	0.037(2)	-0.008(2)	0.004(2)	0.003(2)
C(17)	0.046(3)	0.032(2)	0.043(3)	-0.007(2)	0.009(2)	0.005(2)

Table 2 (continued). Anisotropic Displacement Parameters

atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
C(18)	0.056(3)	0.034(2)	0.038(2)	-0.013(2)	0.006(2)	0.009(2)
C(19)	0.050(3)	0.029(2)	0.038(2)	-0.005(2)	-0.003(2)	0.011(2)
C(20)	0.039(3)	0.026(2)	0.038(2)	-0.007(2)	-0.005(2)	0.006(2)
C(21)	0.040(3)	0.029(2)	0.046(3)	0.004(2)	-0.002(2)	0.009(2)
C(22)	0.054(3)	0.029(2)	0.033(2)	-0.009(2)	-0.009(2)	0.001(2)
C(23)	0.039(3)	0.037(2)	0.029(2)	-0.007(2)	-0.002(2)	0.005(2)
C(24)	0.038(3)	0.049(3)	0.038(2)	-0.010(2)	-0.002(2)	0.001(2)
C(25)	0.035(3)	0.064(3)	0.038(3)	0.002(2)	-0.002(2)	-0.001(2)
C(26)	0.046(3)	0.058(3)	0.036(2)	0.009(2)	-0.002(2)	0.010(2)
C(27)	0.043(3)	0.047(3)	0.032(2)	0.002(2)	-0.003(2)	0.009(2)
C(28)	0.064(4)	0.036(3)	0.056(3)	0.004(2)	-0.016(3)	0.014(2)
C(29)	0.047(3)	0.028(2)	0.045(3)	-0.008(2)	-0.004(2)	0.011(2)
C(30)	0.040(3)	0.039(2)	0.031(2)	-0.007(2)	-0.005(2)	0.012(2)
C(31)	0.041(3)	0.045(3)	0.051(3)	-0.014(2)	-0.006(2)	0.018(2)
C(32)	0.039(3)	0.066(4)	0.057(3)	-0.009(3)	0.006(2)	0.025(3)
C(33)	0.040(3)	0.063(3)	0.043(3)	0.005(2)	0.007(2)	0.014(2)
C(34)	0.035(2)	0.049(3)	0.034(2)	-0.002(2)	-0.007(2)	0.007(2)
C(35)	0.042(3)	0.041(3)	0.046(3)	0.004(2)	-0.001(2)	0.000(2)
C(36)	0.047(3)	0.028(2)	0.039(2)	0.003(2)	-0.001(2)	0.001(2)
C(37)	0.046(3)	0.033(2)	0.031(2)	0.000(2)	-0.007(2)	-0.002(2)
C(38)	0.048(3)	0.048(3)	0.044(3)	0.006(2)	-0.001(2)	-0.005(2)
C(39)	0.041(3)	0.063(3)	0.043(3)	0.005(2)	0.002(2)	-0.006(2)
C(40)	0.036(3)	0.069(4)	0.035(2)	-0.007(2)	-0.002(2)	0.007(2)
C(41)	0.041(3)	0.048(3)	0.028(2)	-0.006(2)	-0.005(2)	0.008(2)
C(42)	0.055(3)	0.045(3)	0.049(3)	-0.009(2)	0.008(2)	0.017(2)
C(43)	0.043(3)	0.033(2)	0.043(3)	-0.008(2)	-0.011(2)	0.008(2)
C(44)	0.033(2)	0.035(2)	0.048(3)	0.002(2)	-0.004(2)	0.010(2)
C(45)	0.035(3)	0.049(3)	0.065(3)	0.000(2)	-0.002(2)	0.016(3)
C(46)	0.036(3)	0.074(4)	0.066(4)	0.005(3)	0.012(3)	0.020(3)
C(47)	0.046(3)	0.076(4)	0.047(3)	0.019(3)	0.010(2)	0.015(3)

Table 2 (continued). Anisotropic Displacement Parameters

atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
C(48)	0.043(3)	0.053(3)	0.042(3)	0.015(2)	0.000(2)	0.012(2)
C(49)	0.065(4)	0.064(4)	0.038(3)	0.013(3)	0.003(3)	-0.005(3)
C(50)	0.054(3)	0.025(2)	0.039(2)	0.002(2)	-0.009(2)	0.005(2)
C(51)	0.041(3)	0.034(2)	0.039(2)	0.000(2)	-0.009(2)	0.009(2)
C(52)	0.050(3)	0.037(3)	0.052(3)	-0.005(2)	-0.014(2)	0.010(2)
C(53)	0.059(4)	0.045(3)	0.057(3)	-0.007(2)	-0.011(3)	0.027(2)
C(54)	0.051(3)	0.048(3)	0.046(3)	-0.004(2)	-0.008(2)	0.025(2)
C(55)	0.040(3)	0.044(3)	0.037(2)	0.000(2)	-0.003(2)	0.010(2)
C(56)	0.052(3)	0.055(3)	0.033(2)	-0.002(2)	-0.002(2)	0.010(2)
C(57)	0.051(3)	0.030(2)	0.028(2)	0.003(2)	-0.007(2)	0.001(2)
C(58)	0.037(2)	0.031(2)	0.035(2)	-0.001(2)	-0.003(2)	0.007(2)
C(59)	0.046(3)	0.041(3)	0.033(2)	-0.001(2)	-0.003(2)	0.009(2)
C(60)	0.051(3)	0.042(3)	0.044(3)	-0.002(2)	-0.004(2)	0.017(2)
C(61)	0.056(3)	0.027(2)	0.052(3)	-0.001(2)	-0.007(2)	0.010(2)
C(62)	0.045(3)	0.029(2)	0.047(3)	0.002(2)	-0.004(2)	0.006(2)
C(63)	0.069(4)	0.028(2)	0.049(3)	0.008(2)	-0.008(3)	-0.001(2)
C(64)	0.034(2)	0.039(2)	0.044(3)	0.001(2)	0.001(2)	0.010(2)
C(65)	0.040(3)	0.025(2)	0.036(2)	0.001(2)	0.000(2)	0.011(2)
C(66)	0.051(3)	0.046(3)	0.035(2)	0.004(2)	0.003(2)	0.014(2)
C(67)	0.065(4)	0.051(3)	0.038(3)	0.007(3)	0.000(2)	0.005(2)
C(68)	0.052(3)	0.058(3)	0.043(3)	0.000(3)	-0.009(2)	0.003(2)
C(69)	0.042(3)	0.041(3)	0.040(2)	0.004(2)	-0.008(2)	0.005(2)
C(70)	0.041(3)	0.056(3)	0.052(3)	-0.002(2)	-0.005(2)	-0.011(3)
C(71)	0.032(2)	0.044(3)	0.036(2)	-0.003(2)	-0.008(2)	0.014(2)
C(72)	0.039(2)	0.032(2)	0.032(2)	0.003(2)	-0.007(2)	0.008(2)
C(73)	0.044(3)	0.042(3)	0.038(2)	0.003(2)	-0.011(2)	0.012(2)
C(74)	0.056(3)	0.040(3)	0.036(2)	0.005(2)	-0.006(2)	0.015(2)
C(75)	0.051(3)	0.031(2)	0.039(2)	0.002(2)	0.003(2)	0.014(2)
C(76)	0.044(3)	0.025(2)	0.037(2)	0.002(2)	-0.002(2)	0.008(2)
C(77)	0.042(3)	0.032(2)	0.049(3)	-0.003(2)	0.000(2)	0.016(2)

Table 2 (continued). Anisotropic Displacement Parameters

atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
C(78)	0.039(3)	0.035(2)	0.042(2)	-0.011(2)	-0.003(2)	0.011(2)
C(79)	0.040(3)	0.029(2)	0.037(2)	-0.001(2)	0.003(2)	0.009(2)
C(80)	0.050(3)	0.035(2)	0.044(3)	-0.003(2)	0.013(2)	0.012(2)
C(81)	0.066(4)	0.038(3)	0.041(3)	0.002(2)	0.014(2)	0.020(2)
C(82)	0.062(4)	0.049(3)	0.034(2)	0.011(3)	0.006(2)	0.019(2)
C(83)	0.046(3)	0.039(2)	0.027(2)	0.008(2)	0.001(2)	0.010(2)
C(84)	0.049(3)	0.052(3)	0.035(2)	0.002(2)	-0.012(2)	0.018(2)
Cl(1)	0.0415(7)	0.0366(6)	0.0785(9)	0.0029(5)	0.0011(6)	0.0121(6)
Cl(2)	0.0436(6)	0.0354(5)	0.0328(5)	0.0041(5)	-0.0020(4)	0.0050(4)
Cl(3)	0.0456(7)	0.0359(6)	0.0472(6)	0.0008(5)	0.0019(5)	0.0045(5)
Cl(4)	0.0386(6)	0.0356(5)	0.0365(5)	0.0012(4)	0.0035(4)	0.0074(4)
O(5)	0.149(6)	0.060(3)	0.095(4)	0.017(3)	-0.049(4)	0.018(3)
O(6)	0.056(3)	0.047(2)	0.087(3)	-0.008(2)	-0.010(2)	0.010(2)
O(7)	0.067(3)	0.078(3)	0.110(4)	-0.027(3)	0.031(3)	-0.026(3)
O(8)	0.048(3)	0.085(3)	0.088(3)	-0.017(2)	0.011(2)	0.016(3)
O(9)	0.114(4)	0.034(2)	0.083(3)	0.000(2)	-0.045(3)	-0.002(2)
O(10)	0.073(3)	0.074(3)	0.041(2)	-0.017(2)	-0.002(2)	0.000(2)
O(11)	0.082(4)	0.107(4)	0.098(4)	0.042(3)	0.050(3)	0.063(3)
O(12)	0.059(3)	0.049(2)	0.103(4)	0.011(2)	-0.016(2)	0.020(2)
O(13)	0.053(2)	0.060(2)	0.045(2)	0.011(2)	-0.001(2)	0.001(2)
O(14)	0.082(4)	0.148(6)	0.114(5)	0.063(4)	0.050(3)	0.078(4)
O(15)	0.045(3)	0.122(5)	0.172(6)	0.010(3)	-0.016(3)	-0.100(5)
O(16)	0.079(3)	0.071(3)	0.112(4)	-0.030(3)	-0.051(3)	0.057(3)
O(17)	0.207(8)	0.074(4)	0.088(4)	-0.043(4)	0.092(5)	-0.008(3)
O(18)	0.067(3)	0.060(3)	0.103(4)	0.027(2)	0.002(3)	0.004(3)
O(19)	0.083(4)	0.051(3)	0.136(5)	0.000(2)	-0.060(3)	0.007(3)
O(20)	0.059(3)	0.056(2)	0.059(2)	-0.018(2)	0.004(2)	0.000(2)

The general temperature factor expression:

$$\exp(-2\pi^2(a^2U_{11}h^2 + b^2U_{22}k^2 + c^2U_{33}l^2 + 2a*b*U_{12}hk + 2a*c*U_{13}hl + 2b*c*U_{23}kl))$$

Table 3. Bond Lengths(Å)

atom	atom	distance	atom	atom	distance
Co1	O1	1.974(3)	Co1	O1 ¹⁾	2.102(3)
Co1	N1	2.155(4)	Co1	N2	2.241(4)
Co1	N3	2.273(4)	Co1	N4	2.270(4)
Co2	O2	1.962(3)	Co2	O2 ²⁾	2.111(3)
Co2	N5	2.125(4)	Co2	N6	2.261(4)
Co2	N7	2.299(4)	Co2	N8	2.229(4)
Co3	O3	1.963(3)	Co3	O3 ³⁾	2.099(3)
Co3	N9	2.152(4)	Co3	N10	2.237(4)
Co3	N11	2.289(4)	Co3	N12	2.258(4)
Co4	O4	1.983(3)	Co4	O4 ⁴⁾	2.101(3)
Co4	N13	2.161(4)	Co4	N14	2.247(4)
Co4	N15	2.226(4)	Co4	N16	2.296(4)
N1	C1	1.492(6)	N1	C8	1.474(6)
N1	C15	1.477(6)	N2	C2	1.351(6)
N2	C6	1.356(6)	N3	C9	1.348(6)
N3	C13	1.360(6)	N4	C16	1.353(6)
N4	C20	1.360(6)	N5	C22	1.485(6)
N5	C29	1.473(6)	N5	C36	1.483(6)
N6	C23	1.341(6)	N6	C27	1.353(6)
N7	C30	1.354(6)	N7	C34	1.352(6)
N8	C37	1.351(6)	N8	C41	1.358(6)
N9	C43	1.471(7)	N9	C50	1.482(6)
N9	C57	1.480(6)	N10	C44	1.365(6)
N10	C48	1.335(7)	N11	C51	1.351(6)
N11	C55	1.345(6)	N12	C58	1.351(6)
N12	C62	1.350(6)	N13	C64	1.479(6)
N13	C71	1.482(6)	N13	C78	1.475(6)
N14	C65	1.343(6)	N14	C69	1.351(6)
N15	C72	1.354(6)	N15	C76	1.347(6)
N16	C79	1.352(6)	N16	C83	1.355(6)

Table 3 (continued). Bond Lengths(Å)

atom	atom	distance	atom	atom	distance
C1	C2	1.505(7)	C2	C3	1.385(7)
C3	C4	1.373(9)	C4	C5	1.370(9)
C5	C6	1.390(7)	C6	C7	1.501(7)
C8	C9	1.490(7)	C9	C10	1.386(7)
C10	C11	1.367(8)	C11	C12	1.398(9)
C12	C13	1.391(7)	C13	C14	1.495(8)
C15	C16	1.501(7)	C16	C17	1.387(7)
C17	C18	1.376(8)	C18	C19	1.390(8)
C19	C20	1.383(7)	C20	C21	1.492(7)
C22	C23	1.501(7)	C23	C24	1.380(7)
C24	C25	1.383(8)	C25	C26	1.369(8)
C26	C27	1.393(7)	C27	C28	1.492(8)
C29	C30	1.518(7)	C30	C31	1.380(7)
C31	C32	1.366(9)	C32	C33	1.376(8)
C33	C34	1.381(7)	C34	C35	1.498(7)
C36	C37	1.495(7)	C37	C38	1.403(7)
C38	C39	1.356(9)	C39	C40	1.375(9)
C40	C41	1.394(7)	C41	C42	1.504(8)
C43	C44	1.505(7)	C44	C45	1.380(7)
C45	C46	1.369(9)	C46	C47	1.372(10)
C47	C48	1.398(8)	C48	C49	1.494(9)
C50	C51	1.510(6)	C51	C52	1.379(7)
C52	C53	1.384(8)	C53	C54	1.381(8)
C54	C55	1.401(7)	C55	C56	1.477(7)
C57	C58	1.503(6)	C58	C59	1.378(6)
C59	C60	1.390(7)	C60	C61	1.371(8)
C61	C62	1.394(7)	C62	C63	1.506(7)
C64	C65	1.520(7)	C65	C66	1.381(7)
C66	C67	1.384(8)	C67	C68	1.367(9)
C68	C69	1.407(8)	C69	C70	1.506(8)

Table 3 (continued). Bond Lengths(Å)

atom	atom	distance	atom	atom	distance
C71	C72	1.500(7)	C72	C73	1.391(6)
C73	C74	1.373(8)	C74	C75	1.381(8)
C75	C76	1.394(7)	C76	C77	1.499(7)
C78	C79	1.508(7)	C79	C80	1.391(6)
C80	C81	1.393(8)	C81	C82	1.372(8)
C82	C83	1.394(7)	C83	C84	1.495(8)
Cl1	O5	1.420(5)	Cl1	O6	1.442(5)
Cl1	O7	1.408(5)	Cl1	O8	1.406(5)
Cl2	O9	1.428(4)	Cl2	O10	1.424(4)
Cl2	O11	1.416(5)	Cl2	O12	1.421(4)
Cl3	O13	1.436(4)	Cl3	O14	1.420(5)
Cl3	O15	1.397(5)	Cl3	O16	1.401(5)
Cl4	O17	1.391(5)	Cl4	O18	1.413(4)
Cl4	O19	1.414(5)	Cl4	O20	1.445(4)
O21	C85	1.38	O22	C86	1.40(3)

Symmetry operations

(1)	-X+1,-Y+1,-Z+1	(2)	-X,-Y,-Z+1
(3)	-X+1,-Y+1,-Z+2	(4)	-X,-Y,-Z+2

Table 4. Bond Angles(°)

atom	atom	atom	angle	atom	atom	atom	angle
O1	Co1	O1 ¹⁾	79.4(1)	O1	Co1	N1	169.4(1)
O1	Co1	N2	108.8(1)	O1	Co1	N3	106.2(1)
O1	Co1	N4	101.6(1)	O1 ¹⁾	Co1	N1	90.3(1)
O1 ¹⁾	Co1	N2	171.5(1)	O1 ¹⁾	Co1	N3	92.4(1)
O1 ¹⁾	Co1	N4	90.9(1)	N1	Co1	N2	81.6(1)
N1	Co1	N3	76.6(1)	N1	Co1	N4	75.7(1)
N2	Co1	N3	83.2(1)	N2	Co1	N4	89.6(1)
N3	Co1	N4	152.1(1)	O2	Co2	O2 ²⁾	79.6(1)

Table 3 (continued). Bond Lengths(Å)

atom	atom	distance	atom	atom	distance		
O2	Co2	N5	169.5(1)	O2	Co2	N6	109.4(1)
O2	Co2	N7	103.1(1)	O2	Co2	N8	103.0(1)
O2 ²⁾	Co2	N5	89.9(1)	O2 ²⁾	Co2	N6	169.4(1)
O2 ²⁾	Co2	N7	91.4(1)	O2 ²⁾	Co2	N8	92.0(1)
N5	Co2	N6	81.1(1)	N5	Co2	N7	77.1(1)
N5	Co2	N8	77.1(1)	N6	Co2	N7	81.2(1)
N6	Co2	N8	91.4(1)	N7	Co2	N8	153.9(1)
O3	Co3	O3 ³⁾	79.5(1)	O3	Co3	N9	170.5(1)
O3	Co3	N10	108.9(1)	O3	Co3	N11	103.4(1)
O3	Co3	N12	102.9(1)	O3 ³⁾	Co3	N9	91.1(1)
O3 ³⁾	Co3	N10	169.7(1)	O3 ³⁾	Co3	N11	91.6(1)
O3 ³⁾	Co3	N12	92.1(1)	N9	Co3	N10	80.5(2)
N9	Co3	N11	77.5(1)	N9	Co3	N12	76.3(1)
N10	Co3	N11	80.7(1)	N10	Co3	N12	91.8(1)
N11	Co3	N12	153.7(1)	O4	Co4	O4 ⁴⁾	80.0(1)
O4	Co4	N13	170.8(1)	O4	Co4	N14	108.1(1)
O4	Co4	N15	104.2(1)	O4	Co4	N16	102.6(1)
O4 ⁴⁾	Co4	N13	91.0(1)	O4 ⁴⁾	Co4	N14	170.9(1)
O4 ⁴⁾	Co4	N15	91.1(1)	O4 ⁴⁾	Co4	N16	92.2(1)
N13	Co4	N14	80.8(1)	N13	Co4	N15	77.3(1)
N13	Co4	N16	76.1(1)	N14	Co4	N15	90.9(1)
N14	Co4	N16	82.1(1)	N15	Co4	N16	153.2(1)
Co1	O1	Co1 ¹⁾	100.6(1)	Co2	O2	Co2 ²⁾	100.4(1)
Co3	O3	Co3 ³⁾	100.5(1)	Co4	O4	Co4 ⁴⁾	100.0(1)
Co1	N1	C1	109.0(3)	Co1	N1	C8	108.7(3)
Co1	N1	C15	106.9(3)	C1	N1	C8	112.7(4)
C1	N1	C15	109.9(4)	C8	N1	C15	109.5(4)
Co1	N2	C2	109.8(3)	Co1	N2	C6	131.0(3)
C2	N2	C6	118.0(4)	Co1	N3	C9	111.9(3)
Co1	N3	C13	129.7(3)	C9	N3	C13	118.0(4)

Table 3 (continued). Bond Lengths(Å)

atom	atom	distance	atom	atom	distance		
Co1	N4	C16	110.6(3)	Co1	N4	C20	130.7(3)
C16	N4	C20	117.7(4)	Co2	N5	C22	109.1(3)
Co2	N5	C29	109.1(3)	Co2	N5	C36	106.8(3)
C22	N5	C29	112.1(4)	C22	N5	C36	109.8(4)
C29	N5	C36	109.8(4)	Co2	N6	C23	108.8(3)
Co2	N6	C27	130.9(3)	C23	N6	C27	118.1(4)
Co2	N7	C30	111.1(3)	Co2	N7	C34	131.7(3)
C30	N7	C34	117.2(4)	Co2	N8	C37	110.7(3)
Co2	N8	C41	131.1(3)	C37	N8	C41	117.9(4)
Co3	N9	C43	109.4(3)	Co3	N9	C50	108.6(3)
Co3	N9	C57	106.0(3)	C43	N9	C50	112.0(4)
C43	N9	C57	110.3(4)	C50	N9	C57	110.4(4)
Co3	N10	C44	109.4(3)	Co3	N10	C48	128.4(4)
C44	N10	C48	118.5(5)	Co3	N11	C51	110.9(3)
Co3	N11	C55	130.5(3)	C51	N11	C55	118.6(4)
Co3	N12	C58	110.8(3)	Co3	N12	C62	131.2(3)
C58	N12	C62	117.9(4)	Co4	N13	C64	109.6(3)
Co4	N13	C71	107.8(3)	Co4	N13	C78	107.3(3)
C64	N13	C71	110.2(4)	C64	N13	C78	111.9(4)
C71	N13	C78	109.9(4)	Co4	N14	C65	109.3(3)
Co4	N14	C69	130.1(3)	C65	N14	C69	117.7(4)
Co4	N15	C72	111.9(3)	Co4	N15	C76	129.4(3)
C72	N15	C76	118.4(4)	Co4	N16	C79	111.2(3)
Co4	N16	C83	131.2(3)	C79	N16	C83	117.5(4)
N1	C1	C2	115.5(4)	N2	C2	C1	119.3(4)
N2	C2	C3	123.5(5)	C1	C2	C3	117.0(5)
C2	C3	C4	117.9(5)	C3	C4	C5	119.6(5)
C4	C5	C6	120.4(5)	N2	C6	C5	120.6(5)
N2	C6	C7	118.7(4)	C5	C6	C7	120.6(5)
N1	C8	C9	114.1(4)	N3	C9	C8	116.9(4)

Table 3 (continued). Bond Lengths(Å)

atom	atom	distance	atom	atom	distance		
N3	C9	C10	122.8(5)	C8	C9	C10	120.2(5)
C9	C10	C11	119.5(5)	C10	C11	C12	118.6(5)
C11	C12	C13	119.5(5)	N3	C13	C12	121.4(5)
N3	C13	C14	117.6(4)	C12	C13	C14	121.0(5)
N1	C15	C16	111.7(4)	N4	C16	C15	116.8(4)
N4	C16	C17	122.9(5)	C15	C16	C17	120.3(4)
C16	C17	C18	118.9(5)	C17	C18	C19	118.7(4)
C18	C19	C20	119.9(5)	N4	C20	C19	121.7(5)
N4	C20	C21	117.9(4)	C19	C20	C21	120.4(4)
N5	C22	C23	114.8(4)	N6	C23	C22	117.3(4)
N6	C23	C24	122.9(5)	C22	C23	C24	119.4(4)
C23	C24	C25	119.2(5)	C24	C25	C26	118.4(5)
C25	C26	C27	120.2(5)	N6	C27	C26	121.3(5)
N6	C27	C28	118.3(4)	C26	C27	C28	120.4(5)
N5	C29	C30	112.3(4)	N7	C30	C29	116.0(4)
N7	C30	C31	123.2(5)	C29	C30	C31	120.6(4)
C30	C31	C32	118.7(5)	C31	C32	C33	119.2(5)
C32	C33	C34	119.8(5)	N7	C34	C33	121.9(5)
N7	C34	C35	117.5(4)	C33	C34	C35	120.7(5)
N5	C36	C37	110.4(4)	N8	C37	C36	117.2(4)
N8	C37	C38	122.0(5)	C36	C37	C38	120.8(4)
C37	C38	C39	119.3(5)	C38	C39	C40	119.6(5)
C39	C40	C41	119.4(5)	N8	C41	C40	121.6(5)
N8	C41	C42	117.5(4)	C40	C41	C42	120.9(5)
N9	C43	C44	113.6(4)	N10	C44	C43	116.4(4)
N10	C44	C45	122.4(5)	C43	C44	C45	121.0(5)
C44	C45	C46	118.5(5)	C45	C46	C47	119.7(5)
C46	C47	C48	119.6(5)	N10	C48	C47	121.1(5)
N10	C48	C49	118.6(5)	C47	C48	C49	120.3(5)

N9	C50	C51	112.6(4)	N11	C51	C50	117.5(4)
N11	C51	C52	123.1(4)	C50	C51	C52	119.3(4)
C51	C52	C53	118.7(5)	C52	C53	C54	118.6(5)
C53	C54	C55	120.2(5)	N11	C55	C54	120.8(5)
N11	C55	C56	119.1(4)	C54	C55	C56	120.1(5)
N9	C57	C58	110.6(4)	N12	C58	C57	116.6(4)
N12	C58	C59	122.5(4)	C57	C58	C59	120.8(4)
C58	C59	C60	119.5(4)	C59	C60	C61	118.3(4)
C60	C61	C62	119.8(4)	N12	C62	C61	121.9(4)
N12	C62	C63	118.0(4)	C61	C62	C63	120.1(4)
N13	C64	C65	114.9(4)	N14	C65	C64	117.2(4)
N14	C65	C66	123.5(5)	C64	C65	C66	119.1(4)
C65	C66	C67	118.7(5)	C66	C67	C68	118.6(5)
C67	C68	C69	120.1(5)	N14	C69	C68	121.2(5)
N14	C69	C70	118.8(5)	C68	C69	C70	120.0(5)
N13	C71	C72	111.7(4)	N15	C72	C71	117.6(4)
N15	C72	C73	122.0(4)	C71	C72	C73	120.1(4)
C72	C73	C74	119.4(5)	C73	C74	C75	118.9(4)
C74	C75	C76	119.5(4)	N15	C76	C75	121.7(4)
N15	C76	C77	118.6(4)	C75	C76	C77	119.7(4)
N13	C78	C79	111.9(4)	N16	C79	C78	116.2(4)
N16	C79	C80	123.8(4)	C78	C79	C80	119.8(4)
C79	C80	C81	117.7(5)	C80	C81	C82	119.0(4)
C81	C82	C83	120.4(5)	N16	C83	C82	121.3(5)
N16	C83	C84	117.7(4)	C82	C83	C84	121.0(4)
O5	C11	O6	108.0(3)	O5	C11	O7	113.9(4)
O5	C11	O8	107.8(4)	O6	C11	O7	108.0(3)
O6	C11	O8	110.2(3)	O7	C11	O8	108.9(3)
O9	C12	O10	106.4(3)	O9	C12	O11	111.8(4)
O9	C12	O12	109.4(3)	O10	C12	O11	107.7(3)

Table 4(continued). Bond Angles($^{\circ}$)

atom	atom	atom	angle	atom	atom	atom	angle
O10	Cl2	O12	110.1(3)	O11	Cl2	O12	111.4(3)
O13	Cl3	O14	110.1(3)	O13	Cl3	O15	110.6(3)
O13	Cl3	O16	109.3(3)	O14	Cl3	O15	108.7(5)
O14	Cl3	O16	107.8(4)	O15	Cl3	O16	110.3(5)
O17	Cl4	O18	111.3(4)	O17	Cl4	O19	111.4(5)
O17	Cl4	O20	108.1(3)	O18	Cl4	O19	108.0(3)
O18	Cl4	O20	110.3(3)	O19	Cl4	O20	107.7(3)

Symmetry operations

(1)	-X+1,-Y+1,-Z+1	(2)	-X,-Y,-Z+1
(3)	-X+1,-Y+1,-Z+2	(4)	-X,-Y,-Z+2

Table 5. Non-bonded Contacts out to 3.60 Å

atom	atom	distance	atom	atom	distance
O1	O51)	3.496(8)	O3	O152)	3.327(6)
O4	O193)	3.403(6)	O5	O213)	2.931(7)
O5	C73)	3.285(9)	O5	C853)	3.427(7)
O5	C84)	3.441(8)	O5	C154)	3.566(7)
O6	C36	3.329(7)	O6	C1	3.338(7)
O6	C84)	3.371(7)	O6	C15	3.576(6)
O7	C285)	3.353(8)	O7	C1	3.386(7)
O7	O213)	3.441(7)	O7	C3	3.520(8)
O8	C213)	3.327(7)	O8	C285)	3.396(8)
O8	C36	3.570(7)	O9	C59	3.228(7)
O9	C476)	3.328(8)	O9	C57	3.335(7)
O9	C43	3.475(7)	O9	C58	3.514(7)
O10	C36	3.193(6)	O10	C17	3.250(7)
O10	C104)	3.365(7)	O10	C38	3.413(7)

O10	C18	3.536(7)	O11	C496)	3.193(7)
O11	C757)	3.276(6)	O11	C747)	3.468(7)
O11	C114)	3.545(8)	O12	O13	3.317(6)
O12	C81	3.340(7)	O12	C57	3.564(7)
O12	C82	3.579(7)	O13	C18	3.127(7)
O13	C57	3.231(6)	O13	C19	3.250(6)
O13	C50	3.376(6)	O13	C24	3.592(6)
O14	C391)	3.232(8)	O14	C19	3.400(8)
O14	C118)	3.407(9)	O14	C128)	3.440(8)
O14	C381)	3.592(7)	O15	C492)	3.255(9)
O15	C50	3.293(9)	O15	C749)	3.348(8)
O16	C739)	3.152(7)	O16	C749)	3.389(7)
O16	C24	3.494(7)	O16	C25	3.495(8)
O16	C80	3.499(7)	O17	C401)	3.270(8)
O17	C410)	3.424(9)	O17	C510)	3.550(8)
O18	C80	3.454(7)	O18	C78	3.499(7)
O18	C25	3.595(8)	O19	C701)	3.267(8)
O19	C719)	3.280(8)	O19	C539)	3.391(8)
O19	C841)	3.498(9)	O20	C549)	3.370(7)
O20	C539)	3.377(7)	O20	C66	3.385(7)
O20	C510)	3.389(7)	O20	C64	3.437(7)
O21	C861)	2.83(3)	O21	C6810)	3.340(6)
O21	C6710)	3.342(6)	O21	C608)	3.544(5)
O22	C3	3.48(2)	O22	C4711)	3.52(2)
C18	C22	3.568(7)	C24	C81	3.390(7)
C46	C8612)	3.56(3)	C47	C8612)	3.42(3)
C52	C77 ⁷⁾	3.477(8)	C68	C86 ⁵⁾	3.02(3)
C69	C86 ⁵⁾	3.48(3)	C70	C86 ⁵⁾	3.33(3)
C85	C86 ¹⁾	3.16(3)			

Symmetry operations

(1)X+1,Y,Z	(2) -X+1,-Y+1,-Z+2
(3)X-1,Y,Z	(4) -X,-Y+1,-Z+1
(5)-X,-Y,-Z+1	(6)-X,-Y+1,-Z+2
(7)-X,-Y,-Z+2	(8)-X+1,-Y+1,-Z+1
(9)-X+1,-Y,-Z+2	(10)-X+1,-Y,-Z+1
(11)X,Y,Z-1	(12)X,Y,Z+1

For complex 2a

A. Crystal Data

Empirical Formula	Co ₂ C ₄₂ H ₄₄ N ₈ O ₁₄ Cl ₂
Formula Weight	1073.63
Crystal Color, Habit	blue-violet, prism
Crystal Dimensions	0.30 X 0.20 X 0.10 mm
Crystal System	monoclinic
Lattice Type	Primitive
Indexing Images	3 oscillations at 9.0 minutes
Detector Position	120.00 mm
Lattice Parameters	a = 10.945(4) Å b = 18.626(5) Å c = 11.673(7) Å β = 110.57(3) ^o V = 222(8) Å ³
Space Group	P2 ₁ /c (#14)
Z value	2
D _{calc}	1.630 g/cm ³
F ₀₀₀	1104.00
μ(MoKα)	9.60 cm ⁻¹

B. Intensity Measurements

Diffractometer	Rigaku RAXIS-IV Imaging Plate
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Radiation	MoK α ($\lambda = 0.71070 \text{ \AA}$) graphite monochromated
Temperature	23.0 °C
Detector Aperture	300.0 mm x 300.0 mm
Data Images	25 exposures at 32.0 minutes
Oscillation Range	100.0°
Detector Position	120.00 mm
Detector Swing Angle	4.00°
Pixel Size	0.01 mm
$2\theta_{\text{max}}$	51.4°
No. of Reflections Measured	Total: 3237
Corrections	Lorentz-polarization

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma w (F_o - F_c)^2$
Least Squares Weights	$1/\sigma^2(F_o) = 4F_o^2/\sigma^2(F_o^2)$
p-factor	0.0920
Anomalous Dispersion	All non-hydrogen atoms
No. of Observations ($I > 3.00\sigma(I)$, $2\theta < 0.00^\circ$)	1886
No. Variables	307
Reflection/Parameter Ratio	6.14
Residuals: R; Rw	0.089 ; 0.124
Goodness of Fit Indicator	1.92
Max Shift/Error in Final Cycle	0.012
Maximum peak in Final Diff. Map	0.40 e ⁻ /Å ³
Minimum peak in Final Diff. Map	-0.67 e ⁻ /Å ³

Table 1. Atomic coordinates and $B_{\text{iso}}/B_{\text{eq}}$

atom	x	y	z	B_{eq}
Co(1)	0.8691(1)	-0.01414(8)	0.4565(1)	5.08(4)

Table 1 (continued). Atomic coordinates and $B_{\text{iso}}/B_{\text{eq}}$

atom	x	y	z	B_{eq}
O(1)	0.9812(6)	0.0575(4)	0.4417(6)	5.7(2)
O(2)	0.8819(8)	-0.0723(5)	0.3210(7)	7.1(2)
O(3)	0.869(1)	-0.1915(6)	0.265(1)	11.3(4)
N(1)	0.8214(8)	0.0319(5)	0.6009(7)	5.7(2)
N(2)	0.7753(8)	-0.0896(5)	0.4839(8)	5.5(2)
N(3)	0.7316(8)	0.0495(5)	0.3473(9)	5.8(2)
N(4)	0.9995(9)	-0.0830(6)	0.7913(8)	6.5(3)
C(1)	0.705(1)	-0.0081(7)	0.596(1)	7.1(4)
C(2)	0.713(1)	-0.0814(7)	0.565(1)	6.0(3)
C(3)	0.662(1)	-0.1415(9)	0.597(1)	7.7(4)
C(4)	0.673(1)	-0.2086(9)	0.543(2)	8.7(4)
C(5)	0.732(2)	-0.213(1)	0.457(2)	10.4(5)
C(6)	0.782(1)	-0.1523(8)	0.431(1)	6.9(3)
C(7)	0.854(1)	-0.140(1)	0.334(1)	8.8(4)
C(8)	0.794(1)	0.1070(6)	0.556(1)	6.4(3)
C(9)	0.721(1)	0.1069(7)	0.417(1)	6.1(3)
C(10)	0.647(1)	0.1631(7)	0.364(1)	8.2(4)
C(11)	0.584(2)	0.1611(9)	0.233(2)	9.8(5)
C(12)	0.592(1)	0.104(1)	0.157(1)	8.9(4)
C(13)	0.668(1)	0.0470(8)	0.217(1)	7.5(4)
C(14)	0.681(2)	-0.0161(9)	0.136(1)	9.9(4)
C(15)	0.899(1)	0.0349(6)	0.744(1)	6.4(3)
C(16)	0.923(1)	-0.0351(7)	0.819(1)	6.9(3)
C(17)	0.870(1)	-0.0509(10)	0.913(1)	8.6(4)
C(18)	0.903(2)	-0.113(1)	0.983(1)	9.5(5)
C(19)	0.981(2)	-0.1602(9)	0.958(2)	9.5(5)
C(20)	1.026(1)	-0.1451(8)	0.856(1)	8.2(4)
C(21)	1.108(2)	-0.1938(8)	0.824(2)	10.8(6)
Cl(1)	0.4188(4)	-0.1292(2)	0.2133(3)	8.0(1)
O(4)	0.466(2)	-0.0627(10)	0.251(3)	24.1(9)

Table 1 (continued). Atomic coordinates and $B_{\text{iso}}/B_{\text{eq}}$

atom	x	y	z	B_{eq}
O(5)	0.410(1)	-0.1608(9)	0.322(1)	16.0(6)
O(6)	0.4948(10)	-0.1710(6)	0.1616(10)	10.1(3)
O(7)	0.310(1)	-0.114(1)	0.124(1)	20.5(7)
H(1)	0.6954	-0.0059	0.6738	8.5
H(2)	0.6307	0.0131	0.5362	8.5
H(3)	0.6184	-0.1385	0.6547	9.3
H(4)	0.6401	-0.2510	0.5671	10.4
H(5)	0.7368	-0.2566	0.4180	12.5
H(6)	0.7425	0.1300	0.5959	7.6
H(7)	0.8743	0.1322	0.5739	7.6
H(8)	0.6372	0.2031	0.4102	9.8
H(9)	0.5329	0.2015	0.1944	11.8
H(10)	0.5481	0.1051	0.0708	10.7
H(11)	0.5972	-0.0368	0.0963	11.9
H(12)	0.7144	0.0011	0.0766	11.9
H(13)	0.7380	-0.0512	0.1857	11.9
H(14)	0.9821	0.0553	0.7557	7.7
H(15)	0.8518	0.0660	0.7783	7.7
H(16)	0.8101	-0.0181	0.9277	10.4
H(17)	0.8708	-0.1219	1.0472	11.4
H(18)	1.0075	-0.2028	1.0049	11.4
H(19)	1.1166	-0.2365	0.8710	13.0
H(20)	1.0708	-0.2049	0.7397	13.0
H(21)	1.1915	-0.1727	0.8411	13.0

$$B_{\text{eq}} = 8/3 \pi^2 (U_{11}(\text{aa}^*)^2 + U_{22}(\text{bb}^*)^2 + U_{33}(\text{cc}^*)^2 + 2U_{12}(\text{aa}^*\text{bb}^*)\cos \gamma + 2U_{13}(\text{aa}^*\text{cc}^*)\cos \beta + 2U_{23}(\text{bb}^*\text{cc}^*)\cos \alpha)$$

Table 2. Anisotropic Displacement Parameters

atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Co(1)	0.0508(9)	0.069(1)	0.079(1)	-0.0041(7)	0.0293(7)	0.0002(7)
O(1)	0.047(4)	0.073(5)	0.097(5)	-0.003(4)	0.025(3)	0.005(4)
O(2)	0.085(6)	0.092(6)	0.106(6)	-0.028(5)	0.052(4)	-0.030(5)
O(3)	0.15(1)	0.111(8)	0.19(1)	-0.018(7)	0.097(9)	-0.032(8)
N(1)	0.063(5)	0.082(7)	0.077(5)	-0.005(5)	0.030(4)	-0.003(5)
N(2)	0.056(5)	0.069(6)	0.085(5)	-0.005(4)	0.026(4)	-0.004(5)
N(3)	0.050(5)	0.083(7)	0.092(6)	-0.006(5)	0.028(5)	0.010(6)
N(4)	0.070(6)	0.092(7)	0.083(6)	-0.016(6)	0.022(5)	0.004(6)
C(1)	0.080(9)	0.097(10)	0.110(9)	-0.003(7)	0.054(7)	0.011(8)
C(2)	0.062(7)	0.077(9)	0.096(8)	-0.011(6)	0.036(6)	0.005(7)
C(3)	0.065(8)	0.11(1)	0.108(9)	-0.019(8)	0.024(7)	0.022(9)
C(4)	0.076(9)	0.09(1)	0.15(1)	-0.022(8)	0.014(9)	0.05(1)
C(5)	0.09(1)	0.12(1)	0.17(2)	-0.01(1)	0.02(1)	0.01(1)
C(6)	0.064(8)	0.076(9)	0.114(9)	-0.008(7)	0.022(7)	0.008(8)
C(7)	0.079(9)	0.15(1)	0.099(9)	0.012(10)	0.025(7)	-0.05(1)
C(8)	0.080(8)	0.070(8)	0.105(8)	0.004(6)	0.049(6)	-0.010(7)
C(9)	0.063(7)	0.079(8)	0.101(8)	0.002(6)	0.041(6)	0.000(7)
C(10)	0.072(8)	0.09(1)	0.14(1)	0.025(8)	0.036(8)	0.010(9)
C(11)	0.09(1)	0.09(1)	0.19(2)	0.004(9)	0.06(1)	0.04(1)
C(12)	0.085(10)	0.13(1)	0.12(1)	0.00(1)	0.028(8)	0.04(1)
C(13)	0.071(8)	0.11(1)	0.12(1)	-0.025(8)	0.050(8)	-0.011(9)
C(14)	0.11(1)	0.15(1)	0.103(9)	-0.02(1)	0.010(8)	0.014(10)
C(15)	0.085(8)	0.077(8)	0.088(7)	-0.004(6)	0.037(6)	-0.013(6)
C(16)	0.080(8)	0.092(9)	0.092(8)	0.004(7)	0.036(7)	0.009(7)
C(17)	0.11(1)	0.14(1)	0.097(8)	-0.016(10)	0.050(8)	-0.003(10)
C(18)	0.12(1)	0.13(1)	0.12(1)	0.00(1)	0.051(9)	0.04(1)
C(19)	0.13(1)	0.10(1)	0.14(1)	-0.02(1)	0.06(1)	0.02(1)
C(20)	0.084(9)	0.10(1)	0.13(1)	-0.001(8)	0.041(8)	0.030(10)
C(21)	0.12(1)	0.09(1)	0.22(2)	0.004(10)	0.08(1)	0.04(1)

Cl(1)	0.087(2)	0.109(3)	0.118(3)	0.021(2)	0.050(2)	0.009(2)
O(4)	0.21(2)	0.17(1)	0.63(4)	-0.07(1)	0.27(2)	-0.20(2)
O(5)	0.19(1)	0.27(2)	0.20(1)	0.10(1)	0.13(1)	0.09(1)
O(6)	0.118(8)	0.127(8)	0.169(8)	0.041(7)	0.089(7)	0.013(7)
O(7)	0.14(1)	0.44(3)	0.16(1)	0.15(2)	0.011(9)	-0.01(1)

The general temperature factor expression:

$$\exp(-2\pi^2(a^2U_{11}h^2 + b^2U_{22}k^2 + c^2U_{33}l^2 + 2a*b*U_{12}hk + 2a*c*U_{13}hl + 2b*c*U_{23}kl))$$

Table 3. Bond Lengths(Å)

atom	atom	distance	atom	atom	distance
Co1	Co11)	2.734(3)	Co1	O1	1.861(7)
Co1	O11)	1.839(7)	Co1	O2	1.962(8)
Co1	N1	2.114(9)	Co1	N2	1.833(9)
Co1	N3	1.986(9)	O2	C7	1.32(2)
O3	C7	1.30(2)	N1	C1	1.46(1)
N1	C8	1.49(1)	N1	C15	1.59(1)
N2	C2	1.35(1)	N2	C6	1.33(2)
N3	C9	1.38(1)	N3	C13	1.43(2)
N4	C16	1.33(1)	N4	C20	1.36(2)
C1	C2	1.43(2)	C2	C3	1.37(2)
C3	C4	1.43(2)	C4	C5	1.37(2)
C5	C6	1.33(2)	C6	C7	1.61(2)
C8	C9	1.54(2)	C9	C10	1.33(2)
C10	C11	1.44(2)	C11	C12	1.40(2)
C12	C13	1.39(2)	C13	C14	1.54(2)
C15	C16	1.54(2)	C16	C17	1.45(2)
C17	C18	1.39(2)	C18	C19	1.33(2)
C19	C20	1.47(2)	C20	C21	1.41(2)
Cl1	O4	1.35(1)	Cl1	O5	1.44(1)
Cl1	O6	1.420(9)	Cl1	O7	1.31(1)

Symmetry operations (1) $-X+2,-Y,-Z+1$

Table 4. Bond Angles(⁰)

atom	atom	atom	angle	atom	atom	atom	angle
Co11)	Co1	O1	42.1(2)	Co11)	Co1	O11)	42.7(2)
Co11)	Co1	O2	92.5(2)	Co11)	Co1	N1	98.4(2)
Co11)	Co1	N2	131.4(3)	Co11)	Co1	N3	125.6(3)
O1	Co1	O11)	84.8(3)	O1	Co1	O2	94.9(3)
O1	Co1	N1	98.0(3)	O1	Co1	N2	173.4(3)
O1	Co1	N3	83.6(3)	O11)	Co1	O2	88.8(4)
O11)	Co1	N1	94.4(3)	O11)	Co1	N2	88.7(3)
O11)	Co1	N3	168.2(3)	O2	Co1	N1	167.0(3)
O2	Co1	N2	85.5(4)	O2	Co1	N3	93.7(4)
N1	Co1	N2	82.0(4)	N1	Co1	N3	85.8(4)
N2	Co1	N3	103.0(4)	Co1	O1	Co11)	95.2(3)
Co1	O2	C7	110.3(8)	Co1	N1	C1	102.7(7)
Co1	N1	C8	100.2(6)	Co1	N1	C15	131.6(7)
C1	N1	C8	113.7(9)	C1	N1	C15	101.3(8)
C8	N1	C15	107.6(8)	Co1	N2	C2	119.1(8)
Co1	N2	C6	117.7(8)	C2	N2	C6	122(1)
Co1	N3	C9	106.7(7)	Co1	N3	C13	129.5(9)
C9	N3	C13	122(1)	C16	N4	C20	117(1)
N1	C1	C2	111(1)	N2	C2	C1	112(1)
N2	C2	C3	117(1)	C1	C2	C3	130(1)
C2	C3	C4	119(1)	C3	C4	C5	120(1)
C4	C5	C6	117(1)	N2	C6	C5	122(1)
N2	C6	C7	108(1)	C5	C6	C7	128(1)
O2	C7	O3	123(1)	O2	C7	C6	114(1)
O3	C7	C6	122(1)	N1	C8	C9	109.5(9)
N3	C9	C8	120(1)	N3	C9	C10	119(1)
C8	C9	C10	120(1)	C9	C10	C11	117(1)

C10	C11	C12	125(1)	C11	C12	C13	115(1)
N3	C13	C12	119(1)	N3	C13	C14	124(1)
C12	C13	C14	116(1)	N1	C15	C16	119.1(9)
N4	C16	C15	115(1)	N4	C16	C17	120(1)
C15	C16	C17	124(1)	C16	C17	C18	121(1)
C17	C18	C19	118(1)	C18	C19	C20	118(1)
N4	C20	C19	123(1)	N4	C20	C21	115(1)
C19	C20	C21	120(1)				
O4	C11	O5	102(1)	O4	C11	O6	115.3(8)
O4	C11	O7	101(1)	O5	C11	O6	112.6(7)
O5	C11	O7	117(1)	O6	C11	O7	106.3(8)

Symmetry operations (1) $-X+2,-Y,-Z+1$

Table 5. Non-bonded Contacts out to 3.60 Å

atom	atom	distance	atom	atom	distance
O3	C211)	3.26(2)	O3	C41)	3.30(2)
O3	C201)	3.47(2)	O3	C191)	3.50(2)
O4	C13	3.14(2)	O4	C14	3.21(3)
O4	C12)	3.28(2)	O4	N3	3.44(2)
O4	N2	3.56(3)	O5	C82)	3.20(2)
O5	C4	3.25(2)	O5	C113)	3.38(2)
O5	C3	3.44(2)	O5	C5	3.46(2)
O6	C103)	3.43(2)	O6	C41)	3.56(2)
O6	C113)	3.58(2)	O7	C152)	3.50(2)
O7	C194)	3.54(3)	O7	C204)	3.60(2)
O7	C172)	3.60(3)	C3	C102)	3.59(2)
C15	C185)	3.48(2)	C16	C175)	3.54(2)
C17	C175)	3.43(3)			

Symmetry operations

(1) $X,-Y-1/2,Z-1/2$

(2) $-X+1,-Y,-Z+1$

- (3) $-X+1, Y-1/2, -Z+1/2$
 (5) $-X+2, -Y, -Z+2$

- (4) $X-1, Y, Z-1$

For complex 2b

A. Crystal Data

Empirical Formula	$H_{64}C_{46}N_8O_{20}Cl_2Co_2$
Formula Weight	1237.83
Crystal Color, Habit	Colorless, Prism
Crystal Dimensions	0.07 X 0.07 X 0.05mm
Crystal System	triclinic
Lattice Type	Primitive
Lattice Parameters	$a = 11.249(1) \text{ \AA}$ $b = 11.2127(8) \text{ \AA}$ $c = 12.030(3) \text{ \AA}$ $\alpha = 68.693(4)^\circ$ $\beta = 84.087(4)^\circ$ $\gamma = 70.387(2)^\circ$ $V = 1331.3(3) \text{ \AA}^3$
Space Group	$P\bar{1}$ (No. 2)
Z value	1
D_{calc}	1.544 g/cm^3
F000	644.00
$\mu(\text{MoK}\alpha)$	8.08 cm^{-1}

B. Intensity Measurements

Diffractometer	Quantum CCD/Rigaku AFC7
Radiation	MoK α ($\lambda = 0.71069 \text{ \AA}$) graphite monochromated
Temperature	$-150.0 \text{ }^\circ\text{C}$
Voltage, Current	50 kV, 200 mA
Detector Aperture	70 mm x 70 mm

Data Images	1440 exposures @30.0 seconds
ω Oscillation Range ($\chi=45.0$, $\phi=0.0$)	-80.0 - 100.0 ^o
($\chi=45.0$, $\phi=90.0$)	-80.0 - 100.0 ^o
Detector Position	35.98 mm
Detector Swing Angle	10.00 ^o
$2\theta_{\max}$	55.0 ^o
No. of Reflections Measured	Total: 13665
	Unique: 5751 ($R_{\text{int}} = 0.039$)
Corrections	Lorentz-polarization

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SHELXS-86)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma w (Fo - Fc)^2$
Least Squares Weights	$1/\sigma^2(Fo) = 4Fo^2/\sigma^2(Fo^2)$
p-factor	0.0570
Anomalous Dispersion	All non-hydrogen atoms
No. of Observations ($I > 3.00\sigma(I)$, $2\theta < 54.97^{\circ}$)	3498
No. Variables	352
Reflection/Parameter Ratio	9.94
Residuals: R; Rw	0.048 ; 0.063
Goodness of Fit Indicator	1.17
Max Shift/Error in Final Cycle	0.001
Maximum peak in Final Diff. Map	0.60 e ⁻ / \approx^3
Minimum peak in Final Diff. Map	-0.35 e ⁻ / \approx^3

Table 1. Atomic coordinates and $B_{\text{iso}}/B_{\text{eq}}$

atom	x	y	z	B_{eq}
Co(1)	0.53392(6)	0.12184(6)	0.93529(5)	1.94(1)
O(1)	0.4065(3)	0.0668(3)	1.0378(3)	2.10(6)
O(2)	0.6348(3)	0.1032(3)	1.0627(3)	2.62(6)
O(3)	0.8213(4)	0.1133(4)	1.1037(4)	3.85(9)

Table 1 (continued). Atomic coordinates and $B_{\text{iso}}/B_{\text{eq}}$

atom	x	y	z	B_{eq}
N(1)	0.4672(4)	0.1792(4)	0.7640(3)	2.44(8)
N(2)	0.6827(3)	0.1344(3)	0.8495(3)	2.21(7)
N(3)	0.4416(3)	0.3139(3)	0.9153(3)	2.11(7)
N(4)	0.2068(4)	0.2201(4)	0.8822(4)	3.02(9)
C(1)	0.5778(5)	0.1132(5)	0.7003(4)	2.80(10)
C(2)	0.6930(5)	0.1239(4)	0.7409(4)	2.72(9)
C(3)	0.8080(5)	0.1174(5)	0.6831(5)	3.3(1)
C(4)	0.9086(5)	0.1168(5)	0.7404(6)	3.9(1)
C(5)	0.8968(5)	0.1192(5)	0.8547(5)	3.4(1)
C(6)	0.7802(4)	0.1283(4)	0.9069(4)	2.64(9)
C(7)	0.7471(5)	0.1169(5)	1.0340(5)	3.0(1)
C(8)	0.4486(5)	0.3290(4)	0.7104(4)	2.61(9)
C(9)	0.4027(4)	0.3937(4)	0.8014(4)	2.34(8)
C(10)	0.3285(5)	0.5272(5)	0.7691(5)	3.1(1)
C(11)	0.2935(5)	0.5848(5)	0.8570(5)	3.7(1)
C(12)	0.3293(5)	0.5051(5)	0.9723(5)	3.4(1)
C(13)	0.4028(4)	0.3686(4)	1.0032(4)	2.63(9)
C(14)	0.4312(5)	0.2870(5)	1.1303(4)	3.1(1)
C(15)	0.3544(5)	0.1531(5)	0.7343(4)	3.0(1)
C(16)	0.2304(5)	0.2374(5)	0.7650(4)	3.0(1)
C(17)	0.1408(6)	0.3266(6)	0.6759(5)	4.1(1)
C(18)	0.0259(6)	0.4021(7)	0.7071(7)	5.1(2)
C(19)	0.0048(6)	0.3847(6)	0.8273(7)	4.7(1)
C(20)	0.0964(5)	0.2945(5)	0.9120(5)	3.5(1)
C(21)	0.0768(6)	0.2711(6)	1.0420(6)	4.5(1)
Cl(1)	0.6743(1)	0.5338(1)	0.6252(1)	2.96(2)
O(4)	0.6791(4)	0.4449(4)	0.7467(3)	3.67(8)
O(5)	0.5451(4)	0.6065(5)	0.5868(4)	5.0(1)
O(6)	0.7343(4)	0.6314(4)	0.6167(4)	4.8(1)
O(7)	0.7347(4)	0.4580(4)	0.5503(3)	4.51(9)

Table 1 (continued). Atomic coordinates and $B_{\text{iso}}/B_{\text{eq}}$

atom	x	y	z	B_{eq}
C(22)	0.091(1)	0.1758(9)	0.4138(9)	8.0(3)
C(23)	-0.024(1)	0.256(1)	0.364(1)	10.5(3)
O(8)	0.0824(5)	0.0574(5)	0.5109(4)	6.1(1)
O(9)	0.4921(6)	0.1042(5)	0.4003(5)	6.7(1)
O(10)	0.7306(6)	0.0885(7)	0.3339(5)	7.5(2)
H(1)	0.3390	0.1103	0.9935	3.2
H(2)	0.5669	0.1637	0.6097	3.2
H(3)	0.5893	0.0151	0.7190	3.2
H(4)	0.8141	0.1114	0.6075	3.2
H(5)	0.9967	0.1191	0.7111	3.2
H(6)	0.9727	0.1375	0.8904	3.2
H(7)	0.5390	0.3412	0.6782	3.2
H(8)	0.3944	0.3670	0.6395	3.2
H(9)	0.2993	0.5879	0.6816	3.2
H(10)	0.2341	0.6769	0.8521	3.2
H(11)	0.3231	0.5217	1.0453	3.2
H(12)	0.3806	0.3255	1.1771	3.2
H(13)	0.4257	0.2007	1.1488	3.2
H(14)	0.5119	0.2661	1.1596	3.2
H(15)	0.3636	0.0552	0.7811	3.2
H(16)	0.3583	0.1718	0.6419	3.2
H(17)	0.1650	0.3154	0.5801	3.2
H(18)	-0.0571	0.4670	0.6476	3.2
H(19)	-0.0797	0.4426	0.8598	3.2
H(20)	0.0077	0.3571	1.0591	3.2
H(21)	0.0610	0.1892	1.0835	3.2
H(22)	0.1161	0.2971	1.0535	3.2

$$B_{\text{eq}} = 8/3 \pi^2 (U_{11}(\text{aa}^*)^2 + U_{22}(\text{bb}^*)^2 + U_{33}(\text{cc}^*)^2 + 2U_{12}(\text{aa}^*\text{bb}^*)\cos \gamma + 2U_{13}(\text{aa}^*\text{cc}^*)\cos \beta + 2U_{23}(\text{bb}^*\text{cc}^*)\cos \alpha)$$

Table 2. Anisotropic Displacement Parameters

atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Co(1)	0.0239(3)	0.0249(3)	0.0270(3)	-0.0100(2)	0.0034(2)	-0.0104(2)
O(1)	0.023(1)	0.026(1)	0.031(2)	-0.009(1)	0.004(1)	-0.010(1)
O(2)	0.033(2)	0.034(2)	0.035(2)	-0.011(1)	-0.001(1)	-0.014(1)
O(3)	0.038(2)	0.052(2)	0.062(2)	-0.014(2)	-0.008(2)	-0.025(2)
N(1)	0.033(2)	0.033(2)	0.032(2)	-0.014(2)	0.001(2)	-0.013(2)
N(2)	0.030(2)	0.022(2)	0.034(2)	-0.011(1)	0.006(2)	-0.010(1)
N(3)	0.025(2)	0.026(2)	0.033(2)	-0.012(1)	0.006(1)	-0.012(1)
N(4)	0.032(2)	0.037(2)	0.048(2)	-0.013(2)	-0.001(2)	-0.016(2)
C(1)	0.044(3)	0.033(2)	0.030(2)	-0.011(2)	0.005(2)	-0.015(2)
C(2)	0.036(3)	0.031(2)	0.037(2)	-0.012(2)	0.009(2)	-0.014(2)
C(3)	0.042(3)	0.043(3)	0.039(3)	-0.014(2)	0.018(2)	-0.016(2)
C(4)	0.033(3)	0.041(3)	0.065(4)	-0.014(2)	0.020(3)	-0.011(2)
C(5)	0.032(3)	0.031(2)	0.061(3)	-0.012(2)	0.009(2)	-0.012(2)
C(6)	0.029(2)	0.026(2)	0.047(3)	-0.010(2)	0.001(2)	-0.013(2)
C(7)	0.031(2)	0.030(2)	0.051(3)	-0.004(2)	-0.005(2)	-0.017(2)
C(8)	0.037(3)	0.030(2)	0.028(2)	-0.011(2)	-0.001(2)	-0.005(2)
C(9)	0.026(2)	0.027(2)	0.035(2)	-0.011(2)	0.000(2)	-0.007(2)
C(10)	0.033(3)	0.034(2)	0.048(3)	-0.011(2)	0.004(2)	-0.012(2)
C(11)	0.041(3)	0.035(2)	0.062(3)	-0.010(2)	0.008(3)	-0.017(2)
C(12)	0.041(3)	0.041(3)	0.054(3)	-0.014(2)	0.011(2)	-0.026(2)
C(13)	0.036(2)	0.032(2)	0.039(2)	-0.018(2)	0.008(2)	-0.016(2)
C(14)	0.041(3)	0.035(2)	0.041(3)	-0.006(2)	0.002(2)	-0.020(2)
C(15)	0.041(3)	0.041(3)	0.036(2)	-0.019(2)	-0.003(2)	-0.014(2)
C(16)	0.037(3)	0.042(3)	0.039(3)	-0.022(2)	-0.004(2)	-0.009(2)
C(17)	0.044(3)	0.055(3)	0.052(3)	-0.025(3)	-0.010(3)	-0.002(3)
C(18)	0.042(3)	0.061(4)	0.076(5)	-0.022(3)	-0.013(3)	0.000(3)
C(19)	0.035(3)	0.045(3)	0.087(5)	-0.015(2)	0.002(3)	-0.009(3)
C(20)	0.030(2)	0.038(3)	0.063(3)	-0.013(2)	0.002(2)	-0.015(2)
C(21)	0.047(3)	0.052(3)	0.078(4)	-0.021(3)	0.020(3)	-0.032(3)

Cl(1)	0.0425(7)	0.0334(6)	0.0367(6)	-0.0163(5)	0.0030(5)	-0.0093(5)
O(4)	0.062(2)	0.038(2)	0.035(2)	-0.019(2)	-0.003(2)	-0.004(1)
O(5)	0.043(2)	0.073(3)	0.054(2)	-0.004(2)	-0.004(2)	-0.010(2)
O(6)	0.072(3)	0.053(2)	0.074(3)	-0.040(2)	0.021(2)	-0.025(2)
O(7)	0.074(3)	0.044(2)	0.044(2)	-0.004(2)	0.005(2)	-0.020(2)
O(8)	0.084(4)	0.077(3)	0.060(3)	-0.034(3)	0.011(2)	-0.008(2)
C(22)	0.132(8)	0.074(5)	0.098(6)	-0.065(6)	-0.024(6)	0.006(5)
C(23)	0.130(10)	0.074(6)	0.15(1)	-0.037(6)	-0.047(8)	0.023(6)
O(9)	0.126(5)	0.050(3)	0.067(3)	-0.013(3)	-0.007(3)	-0.017(2)
O(10)	0.119(5)	0.113(5)	0.064(3)	-0.059(4)	-0.009(3)	-0.020(3)

The general temperature factor expression:

$$\exp(-2\pi^2(a^2U_{11}h^2 + b^2U_{22}k^2 + c^2U_{33}l^2 + 2a*b*U_{12}hk + 2a*c*U_{13}hl + 2b*c*U_{23}kl))$$

Table 3. Bond Lengths(≈)

atom	atom	distance	atom	atom	distance
Co1	O1	1.906(3)	Co1	O11)	1.903(3)
Co1	O2	1.910(3)	Co1	N1	2.063(4)
Co1	N2	1.892(4)	Co1	N3	1.987(3)
O2	C7	1.319(6)	O3	C7	1.223(6)
N1	C1	1.510(6)	N1	C8	1.512(5)
N1	C15	1.497(6)	N2	C2	1.343(6)
N2	C6	1.326(6)	N3	C9	1.356(6)
N3	C13	1.372(6)	N4	C16	1.361(7)
N4	C20	1.340(7)			
C1	C2	1.487(7)	C2	C3	1.397(6)
C3	C4	1.382(9)	C4	C5	1.378(9)
C5	C6	1.383(6)	C6	C7	1.505(7)
C8	C9	1.483(7)	C9	C10	1.376(6)
C10	C11	1.389(8)	C11	C12	1.363(8)
C12	C13	1.402(7)	C13	C14	1.471(7)
C15	C16	1.497(7)	C16	C17	1.389(7)

C17	C18	1.387(10)	C18	C19	1.39(1)
C19	C20	1.374(8)	C20	C21	1.495(9)
Cl1	O4	1.432(3)	Cl1	O5	1.435(4)
Cl1	O6	1.437(4)	Cl1	O7	1.427(4)
O8	C22	1.439(9)	C22	C23	1.35(1)

Symmetry operations (1)-X+1,-Y,-Z+2

Table 4. Bond Angles(^o)

atom	atom	atom	angle	atom	atom	atom	angle
O1	Co1	O11)	79.8(1)	O1	Co1	O2	94.1(1)
O1	Co1	N1	105.6(1)	O1	Co1	N2	166.9(1)
O1	Co1	N3	90.5(1)	O11)	Co1	O2	93.4(1)
O11)	Co1	N1	95.3(1)	O11)	Co1	N2	88.0(1)
O11)	Co1	N3	169.6(1)	O2	Co1	N1	159.6(1)
O2	Co1	N2	81.7(2)	O2	Co1	N3	91.2(1)
N1	Co1	N2	80.2(2)	N1	Co1	N3	83.5(2)
N2	Co1	N3	101.9(1)	Co1	O1	Co11)	100.2(1)
Co1	O2	C7	116.2(3)	Co1	N1	C1	104.8(3)
Co1	N1	C8	104.5(3)	Co1	N1	C15	124.1(3)
C1	N1	C8	105.6(3)	C1	N1	C15	107.0(4)
C8	N1	C15	109.4(4)	Co1	N2	C2	118.3(3)
Co1	N2	C6	118.3(3)	C2	N2	C6	122.2(4)
Co1	N3	C9	113.9(3)	Co1	N3	C13	127.6(3)
C9	N3	C13	118.2(4)	C16	N4	C20	119.2(5)
N1	C1	C2	107.4(4)	N2	C2	C1	113.5(4)
N2	C2	C3	118.5(5)	C1	C2	C3	127.9(5)
C2	C3	C4	119.4(5)	C3	C4	C5	120.4(4)
C4	C5	C6	117.8(5)	N2	C6	C5	121.4(5)
N2	C6	C7	110.4(4)	C5	C6	C7	127.8(5)
O2	C7	O3	124.6(5)	O2	C7	C6	113.0(4)
O3	C7	C6	122.2(5)	N1	C8	C9	110.6(3)

N3	C9	C8	115.5(4)	N3	C9	C10	123.5(4)
C8	C9	C10	120.9(4)	C9	C10	C11	118.6(5)
C10	C11	C12	118.6(5)	C11	C12	C13	121.7(5)
N3	C13	C12	119.4(4)	N3	C13	C14	122.1(4)
C12	C13	C14	118.5(4)	N1	C15	C16	114.7(4)
N4	C16	C15	118.1(4)	N4	C16	C17	121.6(5)
C15	C16	C17	120.3(5)	C16	C17	C18	119.1(6)
C17	C18	C19	118.4(6)	C18	C19	C20	120.2(6)
N4	C20	C19	121.5(6)	N4	C20	C21	116.5(5)
C19	C20	C21	121.9(5)				
O4	C11	O5	109.5(2)	O4	C11	O6	109.6(3)
O4	C11	O7	110.1(2)	O5	C11	O6	107.5(3)
O5	C11	O7	109.5(3)	O6	C11	O7	110.5(3)
O8	C22	C23	111.2(9)				

Symmetry operations (1) $-X+1,-Y,-Z+2$

Table 5. Non-bonded Contacts out to 3.60 \approx

atom	atom	distance	atom	atom	distance
O2	O101)	3.471(6)	O3	O101)	2.800(7)
O3	C52)	3.307(6)	O3	C113)	3.385(7)
O3	C42)	3.436(7)	O4	C6	3.222(6)
O4	N2	3.231(5)	O4	C9	3.306(6)
O4	C8	3.392(6)	O4	C5	3.497(6)
O4	N3	3.572(5)	O4	C2	3.575(6)
O5	O94)	3.188(7)	O5	C10	3.236(6)
O5	C84)	3.379(6)	O5	C8	3.412(6)
O5	C9	3.487(6)	O6	O94)	3.149(7)
O6	C224)	3.288(9)	O6	C185)	3.405(8)
O6	C174)	3.579(8)	O7	C3	3.397(6)
O7	C174)	3.451(7)	O7	C84)	3.519(6)

O8	O106)	2.621(8)	O8	O87)	2.67(1)
O8	C48)	3.352(8)	O8	C36)	3.452(8)
O8	C237)	3.54(1)	O8	C38)	3.545(7)
O8	C227)	3.575(10)	O9	O96)	2.642(10)
O9	O10	2.685(9)	O9	C149)	3.147(7)
O9	C16)	3.414(7)	O10	C114)	3.481(8)
O10	C79)	3.495(8)	O10	C156)	3.527(8)
O10	C226)	3.57(1)	C5	C195)	3.476(8)
C10	C2310)	3.60(1)			

Symmetry operations

(1)X,Y,Z+1	(2) -X+2,-Y,-Z+2
(3)-X+1,-Y+1,-Z+2	(4) -X+1,-Y+1,-Z+1
(5)X+1,Y,Z	(6) -X+1,-Y,-Z+1
(7)-X,-Y,-Z+1	(8) X-1,Y,Z
(9)X,Y,Z-1	(10)-X,-Y+1,-Z+1

For complex 3

A. Crystal Data

Empirical Formula	$C_{43}H_{50}N_8O_{12}Cl_2Co_2$
Formula Weight	1059.69
Crystal Color, Habit	pale-brown, chunk
Crystal Dimensions	0.25 X 0.15 X 0.05 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 10.3443(8) Å b = 19.216(2) Å c = 23.330(1) Å $\beta = 94.187(8)^\circ$ V = 4625.2(6) Å ³
Space Group	P2 ₁ /c (#14)

Z value	4
D_{calc}	1.522 g/cm ³
F_{000}	2192.00
$\mu(\text{MoK}\alpha)$	9.04 cm ⁻¹

B. Intensity Measurements

Diffractometer	Rigaku RAXIS-IV Imaging Plate
Radiation	MoK α ($\lambda = 0.71070 \text{ \AA}$) graphite monochromated
Temperature	23.0 °C
Detector Aperture	300.0 mm x 300.0 mm
Data Images	45 exposures at 18.0 minutes
Oscillation Range	90.0°
Detector Position	120.00 mm
Detector Swing Angle	2.00°
Pixel Size	0.01 mm
$2\theta_{\text{max}}$	51.3°
No. of Reflections Measured	Total: 4385
Corrections	Lorentz-polarization

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	$\sum w (F_o - F_c)^2$
Least Squares Weights	$1/\sigma^2(F_o) = 4F_o^2/\sigma^2(F_o^2)$
p-factor	0.0960
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I > 3.00\sigma(I)$)	2523
No. Variables	575
Reflection/Parameter Ratio	4.39
Residuals: R; Rw	0.070 ; 0.095
Goodness of Fit Indicator	1.61

Max Shift/Error in Final Cycle	0.027
Maximum peak in Final Diff. Map	0.64 e ⁻ /Å ³
Minimum peak in Final Diff. Map	-0.57 e ⁻ /Å ³

Table 1. Atomic coordinates, B_{iso}/B_{eq} and occupancy

atom	x	y	z	B _{eq}	occ
Co(1)	0.7624(2)	0.3808(1)	-0.07665(8)	4.74(5)	1.0000
Co(2)	0.8280(2)	0.21320(10)	0.05531(9)	4.68(5)	1.0000
O(1)	0.8999(9)	0.3817(5)	-0.0152(4)	5.4(3)	1.0000
O(2)	0.7815(8)	0.2874(5)	-0.0132(4)	4.7(2)	1.0000
O(3)	0.9400(9)	0.2978(5)	0.0508(4)	5.3(3)	1.0000
N(1)	0.616(1)	0.3513(7)	-0.1366(6)	5.1(4)	1.0000
N(2)	0.759(1)	0.4698(6)	-0.1299(5)	4.9(3)	1.0000
N(3)	0.854(1)	0.3085(6)	-0.1335(5)	4.7(3)	1.0000
N(4)	0.599(1)	0.4027(7)	-0.0271(7)	6.3(4)	1.0000
N(5)	0.684(1)	0.1385(6)	0.0423(5)	4.5(3)	1.0000
N(6)	0.880(1)	0.1503(6)	0.1268(5)	4.8(3)	1.0000
N(7)	0.904(1)	0.1383(7)	-0.0059(6)	5.8(4)	1.0000
N(8)	0.678(1)	0.2548(7)	0.1113(6)	5.4(4)	1.0000
C(1)	0.630(2)	0.389(1)	-0.1891(10)	13.0(9)	1.0000
C(2)	0.677(1)	0.4645(9)	-0.1744(8)	6.6(5)	1.0000
C(3)	0.649(1)	0.519(1)	-0.2119(7)	6.7(5)	1.0000
C(4)	0.719(2)	0.5801(9)	-0.2044(8)	6.2(5)	1.0000
C(5)	0.803(2)	0.5826(9)	-0.1608(7)	6.4(5)	1.0000
C(6)	0.823(2)	0.5286(8)	-0.1244(7)	6.0(5)	1.0000
C(7)	0.921(3)	0.531(1)	-0.0755(9)	15.1(9)	1.0000
C(8)	0.638(2)	0.276(1)	-0.1464(10)	10.1(7)	1.0000
C(9)	0.771(2)	0.261(1)	-0.1533(7)	5.8(5)	1.0000
C(10)	0.799(2)	0.199(1)	-0.1748(8)	7.3(6)	1.0000
C(11)	0.922(4)	0.180(1)	-0.1765(9)	9.5(8)	1.0000
C(12)	1.010(2)	0.227(2)	-0.158(1)	9.7(9)	1.0000
C(13)	0.977(2)	0.292(1)	-0.1362(8)	7.1(6)	1.0000

Table 1 (continued). Atomic coordinates, $B_{\text{iso}}/B_{\text{eq}}$ and occupancy

atom	x	y	z	B_{eq}	occ
C(14)	1.068(2)	0.345(1)	-0.113(1)	12.2(8)	1.0000
C(15)	0.496(2)	0.361(1)	-0.1160(9)	12.0(8)	1.0000
C(16)	0.501(2)	0.3643(9)	-0.0490(8)	6.2(5)	1.0000
C(17)	0.402(2)	0.342(1)	-0.016(1)	8.0(7)	1.0000
C(18)	0.405(3)	0.365(2)	0.041(1)	9.2(9)	1.0000
C(19)	0.498(4)	0.406(2)	0.0602(10)	9.8(9)	1.0000
C(20)	0.601(2)	0.424(1)	0.028(1)	7.9(7)	1.0000
C(21)	0.700(3)	0.471(1)	0.0511(10)	12.0(9)	1.0000
C(22)	0.708(1)	0.0810(8)	0.0834(7)	5.8(4)	1.0000
C(23)	0.801(1)	0.0960(8)	0.1322(7)	4.7(4)	1.0000
C(24)	0.808(2)	0.0552(9)	0.1804(8)	7.4(6)	1.0000
C(25)	0.897(2)	0.068(1)	0.2236(8)	8.1(6)	1.0000
C(26)	0.977(2)	0.122(1)	0.2166(8)	6.6(5)	1.0000
C(27)	0.970(1)	0.1606(8)	0.1692(7)	4.9(4)	1.0000
C(28)	1.065(2)	0.2178(9)	0.1627(8)	7.4(5)	1.0000
C(29)	0.689(2)	0.1160(9)	-0.0180(8)	6.2(5)	1.0000
C(30)	0.816(2)	0.098(1)	-0.0337(8)	6.1(5)	1.0000
C(31)	0.844(3)	0.046(1)	-0.0694(9)	8.5(7)	1.0000
C(32)	0.971(3)	0.038(1)	-0.083(1)	10.0(9)	1.0000
C(33)	1.058(2)	0.077(2)	-0.056(1)	9.5(9)	1.0000
C(34)	1.025(2)	0.1284(10)	-0.0166(9)	6.8(6)	1.0000
C(35)	1.126(2)	0.173(1)	0.010(1)	10.1(7)	1.0000
C(36)	0.567(2)	0.1721(9)	0.0523(8)	6.4(5)	1.0000
C(37)	0.571(2)	0.2155(9)	0.1056(8)	5.8(5)	1.0000
C(38)	0.478(2)	0.220(1)	0.143(1)	7.7(6)	1.0000
C(39)	0.492(2)	0.266(1)	0.1870(9)	8.2(7)	1.0000
C(40)	0.594(2)	0.308(1)	0.1950(9)	7.7(6)	1.0000
C(41)	0.685(2)	0.298(1)	0.1550(10)	6.0(5)	1.0000
C(42)	0.798(2)	0.339(1)	0.1653(8)	8.3(6)	1.0000
C(43)	0.875(1)	0.3259(9)	0.0076(7)	4.5(4)	1.0000

Table 1 (continued). Atomic coordinates, $B_{\text{iso}}/B_{\text{eq}}$ and occupancy

atom	x	y	z	B_{eq}	occ
Cl(1)	0.3805(4)	0.1446(3)	-0.1333(3)	7.9(1)	1.0000
Cl(2)	0.7345(6)	-0.0238(4)	-0.2594(4)	12.0(2)	1.0000
O(4)	0.281(2)	0.105(1)	-0.1470(8)	14.4(5)	1.0000
O(5)	0.489(2)	0.1280(9)	-0.1541(8)	12.8(5)	1.0000
O(6)	0.384(1)	0.1858(9)	-0.0867(7)	11.6(4)	1.0000
O(7)	0.341(2)	0.202(1)	-0.179(1)	8.2(6)	0.5000
O(8)	0.380(4)	0.083(3)	-0.086(2)	17(1)	0.5000
O(9)	0.634(2)	0.006(1)	-0.296(1)	8.9(6)	0.5000
O(10)	0.662(4)	0.036(2)	-0.239(2)	15(1)	0.5000
O(11)	0.799(3)	0.012(2)	-0.214(1)	13.3(8)	0.6000
O(12)	0.865(5)	0.004(3)	-0.269(2)	9(1)	0.3000
O(13)	0.820(4)	-0.037(2)	-0.308(2)	17(1)	0.6000
O(14)	0.701(3)	-0.100(2)	-0.256(1)	9.3(7)	0.5000
O(15)	0.681(2)	-0.063(1)	-0.209(1)	16.7(7)	1.0000
O(16)	0.437(2)	0.029(1)	0.1318(9)	17.3(7)	1.0000
H(1)	0.6895	0.3654	-0.2110	15.6050	1.0000
H(2)	0.5521	0.3905	-0.2105	15.6050	1.0000
H(3)	0.5851	0.5153	-0.2416	8.0323	1.0000
H(4)	0.7064	0.6185	-0.2298	7.4041	1.0000
H(5)	0.8519	0.6237	-0.1549	7.7122	1.0000
H(6)	0.8826	0.5247	-0.0404	18.1102	1.0000
H(7)	0.9809	0.4959	-0.0802	18.1102	1.0000
H(8)	0.9609	0.5756	-0.0752	18.1102	1.0000
H(9)	0.6114	0.2503	-0.1145	12.1328	1.0000
H(10)	0.5907	0.2616	-0.1801	12.1328	1.0000
H(11)	0.7348	0.1678	-0.1886	8.7876	1.0000
H(12)	0.9450	0.1355	-0.1902	11.4236	1.0000
H(13)	1.0956	0.2159	-0.1598	11.6459	1.0000
H(14)	1.1510	0.3291	-0.1168	14.6819	1.0000
H(15)	1.0564	0.3878	-0.1336	14.6819	1.0000

Table 1 (continued). Atomic coordinates, B_{iso}/B_{eq} and occupancy

atom	x	y	z	B_{eq}	occ
H(16)	1.0559	0.3534	-0.0736	14.6819	1.0000
H(17)	0.4620	0.4035	-0.1310	14.3580	1.0000
H(18)	0.4439	0.3234	-0.1287	14.3580	1.0000
H(19)	0.3366	0.3132	-0.0315	9.6179	1.0000
H(20)	0.3412	0.3518	0.0651	10.9908	1.0000
H(21)	0.4962	0.4236	0.0980	11.8024	1.0000
H(22)	0.7793	0.4494	0.0483	14.4323	1.0000
H(23)	0.6980	0.5134	0.0297	14.4323	1.0000
H(24)	0.6877	0.4810	0.0902	14.4323	1.0000
H(25)	0.6315	0.0690	0.0989	6.9550	1.0000
H(26)	0.7385	0.0423	0.0629	6.9550	1.0000
H(27)	0.7510	0.0179	0.1839	8.8810	1.0000
H(28)	0.9032	0.0394	0.2572	9.6698	1.0000
H(29)	1.0396	0.1325	0.2461	7.8842	1.0000
H(30)	1.1462	0.1981	0.1637	8.9114	1.0000
H(31)	1.0481	0.2409	0.1271	8.9114	1.0000
H(32)	1.0602	0.2503	0.1931	8.9114	1.0000
H(33)	0.6370	0.0762	-0.0238	7.4224	1.0000
H(34)	0.6582	0.1528	-0.0421	7.4224	1.0000
H(35)	0.7807	0.0161	-0.0852	10.2270	1.0000
H(36)	0.9922	0.0044	-0.1111	11.9682	1.0000
H(37)	1.1437	0.0704	-0.0635	11.4492	1.0000
H(38)	1.1268	0.1686	0.0508	12.1002	1.0000
H(39)	1.2045	0.1574	-0.0023	12.1002	1.0000
H(40)	1.1127	0.2198	-0.0006	12.1002	1.0000
H(41)	0.5442	0.2012	0.0205	7.6726	1.0000
H(42)	0.5050	0.1370	0.0555	7.6726	1.0000
H(43)	0.4051	0.1919	0.1384	9.2129	1.0000
H(44)	0.4281	0.2691	0.2134	9.7898	1.0000
H(45)	0.6032	0.3420	0.2249	9.2963	1.0000

H(46)	0.8676	0.3084	0.1721	9.9394	1.0000
H(47)	0.8112	0.3669	0.1327	9.9394	1.0000
H(48)	0.7905	0.3679	0.1978	9.9394	1.0000

$$B_{eq} = 8/3 \pi^2 (U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos \gamma + 2U_{13}(aa^*cc^*)\cos \beta + 2U_{23}(bb^*cc^*)\cos \alpha)$$

Table 2. Anisotropic Displacement Parameters

atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Co(1)	0.071(1)	0.057(1)	0.050(1)	-0.007(1)	-0.012(1)	0.008(1)
Co(2)	0.062(1)	0.050(1)	0.065(1)	-0.0005(10)	-0.005(1)	0.011(1)
O(1)	0.078(7)	0.056(7)	0.066(7)	-0.018(5)	-0.027(5)	0.024(6)
O(2)	0.058(6)	0.056(6)	0.061(6)	0.000(5)	-0.013(5)	0.006(5)
O(3)	0.073(6)	0.061(7)	0.063(7)	-0.017(5)	-0.014(6)	0.005(6)
N(1)	0.049(7)	0.067(10)	0.08(1)	-0.006(6)	-0.003(7)	0.012(8)
N(2)	0.080(8)	0.058(9)	0.046(8)	-0.013(7)	-0.007(7)	0.014(7)
N(3)	0.045(8)	0.082(10)	0.052(8)	-0.005(7)	-0.005(6)	0.002(7)
N(4)	0.12(1)	0.057(9)	0.06(1)	0.010(8)	0.001(9)	-0.008(8)
N(5)	0.057(8)	0.054(8)	0.059(9)	-0.009(6)	0.004(6)	0.001(7)
N(6)	0.068(8)	0.051(8)	0.061(9)	0.002(7)	-0.008(7)	0.011(7)
N(7)	0.060(9)	0.07(1)	0.09(1)	0.019(8)	0.021(9)	0.015(8)
N(8)	0.09(1)	0.047(8)	0.06(1)	0.022(8)	0.005(8)	0.000(8)
C(1)	0.14(2)	0.21(3)	0.13(2)	-0.08(2)	-0.08(2)	0.12(2)
C(2)	0.07(1)	0.09(1)	0.09(1)	-0.029(10)	-0.008(10)	0.06(1)
C(3)	0.07(1)	0.10(2)	0.08(1)	0.02(1)	0.007(9)	0.03(1)
C(4)	0.11(1)	0.04(1)	0.08(1)	0.02(1)	0.02(1)	0.027(10)
C(5)	0.13(1)	0.06(1)	0.06(1)	-0.02(1)	-0.02(1)	0.007(10)
C(6)	0.13(1)	0.04(1)	0.06(1)	-0.021(10)	-0.003(10)	0.014(9)
C(7)	0.30(3)	0.13(2)	0.12(2)	-0.13(2)	-0.14(2)	0.06(2)
C(8)	0.08(1)	0.12(2)	0.17(2)	0.00(1)	-0.04(1)	-0.06(2)
C(9)	0.07(1)	0.08(1)	0.07(1)	0.01(1)	-0.003(9)	-0.02(1)

C(10)	0.10(2)	0.10(2)	0.08(1)	0.02(1)	0.02(1)	-0.01(1)
C(11)	0.18(3)	0.10(2)	0.08(2)	0.04(2)	0.00(2)	0.00(1)
C(12)	0.10(2)	0.18(3)	0.10(2)	0.07(2)	0.01(1)	0.02(2)
C(13)	0.07(1)	0.13(2)	0.07(1)	0.02(1)	-0.01(1)	0.02(1)
C(14)	0.06(1)	0.25(3)	0.15(2)	-0.05(2)	0.00(1)	-0.02(2)
C(15)	0.08(1)	0.27(3)	0.11(2)	-0.06(2)	0.02(1)	-0.11(2)
C(16)	0.08(1)	0.07(1)	0.09(1)	0.01(1)	0.04(1)	0.00(1)
C(17)	0.09(2)	0.09(2)	0.13(2)	0.02(1)	0.03(2)	0.02(2)
C(18)	0.12(2)	0.13(2)	0.11(2)	0.06(2)	0.05(2)	0.05(2)
C(19)	0.17(3)	0.14(2)	0.07(2)	0.09(2)	0.03(2)	0.00(2)
C(20)	0.12(2)	0.10(2)	0.08(2)	0.08(1)	0.02(2)	0.03(2)
C(21)	0.20(3)	0.13(2)	0.11(2)	0.04(2)	-0.06(2)	-0.05(2)
C(22)	0.07(1)	0.07(1)	0.08(1)	-0.019(9)	-0.011(9)	-0.01(1)
C(23)	0.068(10)	0.043(10)	0.07(1)	-0.004(8)	0.027(9)	0.004(9)
C(24)	0.13(2)	0.08(1)	0.07(1)	-0.01(1)	0.03(1)	0.03(1)
C(25)	0.13(2)	0.12(2)	0.05(1)	0.01(1)	-0.02(1)	0.04(1)
C(26)	0.08(1)	0.09(1)	0.08(1)	-0.01(1)	0.008(10)	0.02(1)
C(27)	0.07(1)	0.05(1)	0.07(1)	-0.003(8)	0.007(9)	0.022(9)
C(28)	0.08(1)	0.09(1)	0.10(1)	0.00(1)	-0.03(1)	0.04(1)
C(29)	0.09(1)	0.07(1)	0.08(1)	-0.004(10)	0.01(1)	0.00(1)
C(30)	0.10(1)	0.08(1)	0.06(1)	-0.01(1)	0.01(1)	0.01(1)
C(31)	0.19(2)	0.07(1)	0.07(1)	0.01(2)	0.04(1)	0.00(1)
C(32)	0.17(3)	0.10(2)	0.12(2)	0.04(2)	0.09(2)	0.02(2)
C(33)	0.12(2)	0.11(2)	0.14(3)	0.04(2)	0.05(2)	0.06(2)
C(34)	0.12(2)	0.05(1)	0.09(2)	0.01(1)	0.03(1)	0.01(1)
C(35)	0.09(1)	0.13(2)	0.18(2)	0.00(1)	0.06(1)	0.00(2)
C(36)	0.09(1)	0.08(1)	0.08(1)	0.00(1)	0.02(1)	0.00(1)
C(37)	0.06(1)	0.07(1)	0.09(2)	0.01(1)	0.02(1)	0.02(1)
C(38)	0.07(1)	0.11(2)	0.11(2)	0.01(1)	0.02(1)	-0.01(2)
C(39)	0.13(2)	0.11(2)	0.08(2)	0.05(2)	0.04(1)	0.01(1)
C(40)	0.10(2)	0.11(2)	0.08(2)	0.01(1)	-0.02(1)	0.00(1)

C(41)	0.06(1)	0.08(1)	0.09(2)	-0.01(1)	0.01(1)	0.00(1)
C(42)	0.15(2)	0.09(1)	0.08(1)	0.04(1)	0.01(1)	0.00(1)
C(43)	0.07(1)	0.05(1)	0.05(1)	-0.005(9)	-0.007(8)	0.004(9)
Cl(1)	0.079(3)	0.100(4)	0.123(4)	-0.025(3)	0.017(3)	-0.041(4)
Cl(2)	0.114(5)	0.151(7)	0.189(8)	0.019(4)	-0.011(5)	0.001(6)

The general temperature factor expression:

$$\exp(-2\pi^2(a^2U_{11}h^2 + b^2U_{22}k^2 + c^2U_{33}l^2 + 2a*b*U_{12}hk + 2a*c*U_{13}hl + 2b*c*U_{23}kl))$$

Table 3. Bond Lengths(Å)

atom	atom	distance	atom	atom	distance
Co1	O1	1.944(8)	Co1	N1	2.06(1)
Co1	N2	2.11(1)	Co1	N3	2.18(1)
Co1	N4	2.16(2)	Co2	O2	2.170(9)
Co2	O3	2.004(9)	Co2	N5	2.07(1)
Co2	N6	2.10(1)	Co2	N7	2.21(1)
Co2	N8	2.25(1)	O1	C43	1.23(2)
O2	C43	1.29(2)	O3	C43	1.29(2)
N1	C1	1.43(2)	N1	C8	1.49(2)
N1	C15	1.38(2)	N2	C2	1.30(2)
N2	C6	1.31(2)	N3	C9	1.31(2)
N3	C13	1.32(2)	N4	C16	1.33(2)
N4	C20	1.34(2)	N5	C22	1.47(2)
N5	C29	1.47(2)	N5	C36	1.41(2)
N6	C23	1.34(2)	N6	C27	1.32(2)
N7	C30	1.33(2)	N7	C34	1.30(2)
N8	C37	1.33(2)	N8	C41	1.31(2)
C1	C2	1.57(3)	C2	C3	1.38(2)
C3	C4	1.38(2)	C4	C5	1.29(2)
C5	C6	1.35(2)	C6	C7	1.47(2)
C8	C9	1.42(2)	C9	C10	1.35(2)
C10	C11	1.32(3)	C11	C12	1.34(3)

C12	C13	1.40(3)	C13	C14	1.47(3)
C15	C16	1.56(3)	C16	C17	1.39(3)
C17	C18	1.39(3)	C18	C19	1.30(3)
C19	C20	1.39(3)	C20	C21	1.45(3)
C22	C23	1.46(2)	C23	C24	1.37(2)
C24	C25	1.34(2)	C25	C26	1.36(2)
C26	C27	1.33(2)	C27	C28	1.49(2)
C29	C30	1.43(2)	C30	C31	1.34(2)
C31	C32	1.38(3)	C32	C33	1.31(3)
C33	C34	1.41(3)	C34	C35	1.46(3)
C36	C37	1.50(2)	C37	C38	1.35(2)
C38	C39	1.35(3)	C39	C40	1.34(3)
C40	C41	1.38(3)	C41	C42	1.42(2)
Cl1	O4	1.30(2)	Cl1	O5	1.30(2)
Cl1	O6	1.34(2)	Cl1	O7	1.56(3)
Cl1	O8	1.63(5)	Cl2	O9	1.42(3)
Cl2	O10	1.47(4)	Cl2	O11	1.39(3)
Cl2	O12	1.48(5)	Cl2	O13	1.51(4)
Cl2	O14	1.50(3)	Cl2	O15	1.53(2)

Table 4. Bond Angles(°)

atom	atom	atom	angle	atom	atom	atom	angle
O1	Co1	N1	164.4(5)	O1	Co1	N2	113.9(4)
O1	Co1	N3	97.2(4)	O1	Co1	N4	99.3(5)
N1	Co1	N2	81.0(5)	N1	Co1	N3	75.1(5)
N1	Co1	N4	81.6(6)	N2	Co1	N3	98.5(5)
N2	Co1	N4	100.2(5)	N3	Co1	N4	147.3(5)
O2	Co2	O3	61.7(3)	O2	Co2	N5	103.2(4)
O2	Co2	N6	174.0(4)	O2	Co2	N7	91.3(4)
O2	Co2	N8	94.0(4)	O3	Co2	N5	164.9(4)
O3	Co2	N6	113.2(4)	O3	Co2	N7	105.0(5)

O3	Co2	N8	99.8(5)	N5	Co2	N6	81.8(5)
N5	Co2	N7	75.0(5)	N5	Co2	N8	79.2(5)
N6	Co2	N7	93.1(4)	N6	Co2	N8	83.8(4)
N7	Co2	N8	154.2(6)	Co1	O1	C43	98.5(8)
Co2	O2	C43	88.8(9)	Co2	O3	C43	96.4(9)
Co1	N1	C1	109.1(10)	Co1	N1	C8	105.1(9)
Co1	N1	C15	111(1)	C1	N1	C8	109(1)
C1	N1	C15	112(1)	C8	N1	C15	109(1)
Co1	N2	C2	112(1)	Co1	N2	C6	130.9(10)
C2	N2	C6	116(1)	Co1	N3	C9	110(1)
Co1	N3	C13	130(1)	C9	N3	C13	115(1)
Co1	N4	C16	107(1)	Co1	N4	C20	128(1)
C16	N4	C20	119(1)	Co2	N5	C22	109.8(8)
Co2	N5	C29	105.7(9)	Co2	N5	C36	106.1(10)
C22	N5	C29	112(1)	C22	N5	C36	109(1)
C29	N5	C36	112(1)	Co2	N6	C23	113.5(10)
Co2	N6	C27	129(1)	C23	N6	C27	116(1)
Co2	N7	C30	115(1)	Co2	N7	C34	127(1)
C30	N7	C34	117(1)	Co2	N8	C37	110(1)
Co2	N8	C41	132(1)	C37	N8	C41	115(1)
N1	C1	C2	109(1)	N2	C2	C1	114(1)
N2	C2	C3	122(1)	C1	C2	C3	121(1)
C2	C3	C4	118(1)	C3	C4	C5	116(1)
C4	C5	C6	121(1)	N2	C6	C5	123(1)
N2	C6	C7	114(1)	C5	C6	C7	121(1)
N1	C8	C9	111(1)	N3	C9	C8	116(1)
N3	C9	C10	126(1)	C8	C9	C10	117(1)
C9	C10	C11	119(1)	C10	C11	C12	116(2)
C11	C12	C13	123(2)	N3	C13	C12	119(1)
N3	C13	C14	114(2)	C12	C13	C14	126(2)
N1	C15	C16	112(1)	N4	C16	C15	111(1)

N4	C16	C17	121(1)	C15	C16	C17	124(2)
C16	C17	C18	117(2)	C17	C18	C19	119(2)
C18	C19	C20	122(2)	N4	C20	C19	119(2)
N4	C20	C21	120(2)	C19	C20	C21	120(2)
N5	C22	C23	115(1)	N6	C23	C22	116(1)
N6	C23	C24	121(1)	C22	C23	C24	121(1)
C23	C24	C25	120(1)	C24	C25	C26	116(1)
C25	C26	C27	122(1)	N6	C27	C26	122(1)
N6	C27	C28	117(1)	C26	C27	C28	119(1)
N5	C29	C30	114(1)	N7	C30	C29	110(1)
N7	C30	C31	124(1)	C29	C30	C31	125(2)
C30	C31	C32	119(2)	C31	C32	C33	117(2)
C32	C33	C34	121(2)	N7	C34	C33	120(1)
N7	C34	C35	120(2)	C33	C34	C35	118(2)
N5	C36	C37	114(1)	N8	C37	C36	111(1)
N8	C37	C38	121(1)	C36	C37	C38	126(1)
C37	C38	C39	119(1)	C38	C39	C40	122(2)
C39	C40	C41	112(1)	N8	C41	C40	127(1)
N8	C41	C42	118(2)	C40	C41	C42	113(2)
O1	C43	O2	120(1)	O1	C43	O3	126(1)
O2	C43	O3	112(1)				

Table 5. Non-bonded Contacts out to 3.60 Å

atom	atom	distance	ADC	atom	atom	distance	ADC
C12	O16	3.58(2)	65503	O1	C7	3.18(2)	76503
O4	C33	3.29(3)	45501	O4	C24	3.29(3)	65503
O4	C4	3.50(3)	64402	O5	C8	3.23(3)	1
O5	C10	3.55(3)	1	O6	C17	3.43(3)	1
O6	C8	3.52(3)	1	O7	C8	3.42(3)	1
O7	C12	3.53(3)	45501	O14	C1	3.58(3)	64402
O8	C22	3.28(5)	65503	O8	C33	3.45(5)	45501

O8	C29	3.52(5)	1	O9	C3	2.96(3)	64402
O9	C2	3.33(3)	64402	O9	C1	3.54(4)	64402
O9	C42	3.58(3)	55404	O9	C40	3.59(4)	55404
O10	C3	3.35(4)	64402	O10	C40	3.41(5)	55404
O11	C31	3.44(4)	1	O11	C32	3.46(5)	1
O11	C26	3.47(4)	75503	O11	C25	3.52(4)	75503
O11	C11	3.56(4)	1	O12	C25	2.94(5)	75503
O12	C26	3.12(5)	75503	O12	C42	3.44(5)	55404
O13	C14	3.18(5)	74402	O13	C26	3.31(4)	75503
O13	C25	3.46(4)	75503	O14	C26	3.41(3)	75503
O14	C15	3.58(4)	64402	O14	O16	3.58(4)	65503
O16	C22	3.25(3)	1	O16	C31	3.47(3)	65503
C2	C25	3.47(3)	55404	C3	C24	3.42(3)	55404
C3	C25	3.49(3)	55404	C10	C40	3.58(3)	55404

Symmetry Operators:

(1)X,	Y,	Z	(2)-X,	1/2+Y,	1/2-Z
(3)-X,	-Y,	-Z	(4)X,	1/2-Y,	1/2+Z

Korean Abstract

다리 리간드인 chromate, molybdate, oxalate, terephthalate를 이용해서 Ni(II) 및 Cu(II) 거대고리 리간드를 기본으로 한 일련의 새로운 일차 선형 분자들을 합성, 연구하였다. Dicyanamide를 이용한 Ni(II) 거대고리 착화합물 역시 합성, 연구 하였으며 단결정 X-ray 회절법을 이용한 구조 분석 결과 단분자 형태임을 알 수 있었다. 이러한 모든 화합물들은 분자간상호작용을 이용하여 자기조립 및 분자인지 과정에 의해 합성이 되었고, 이들을 통하여 초분자 화학에 대해 보다 많은 이해가 가능하였다. 특히, 대부분의 이러한 화합물들에서 물 분자의 존재가 초분자적 배열에 필수적인 역할을 함을 알 수 있었다.

생체내에서 산소를 활성화 할 수 있는 non-heme 촉매들의 반응 과정을 이해하기 위해서 모방 분자가 합성되었고 그것의 활성화된 화합물들 역시 분리하여 분석적, 분광적, 구조학적으로 조화를 이룬 연구를 진행하였다. 이러한 연구 결과를 통하여 전이금속의 역할은 분자인지라고 할 수 있는 배위권 속에서의 산소와 기질의 만남에서부터 산화된 생성물을 발생시키는 화학적 변환 과정에 이르기까지 매우 광범위 함을 알 수 있었다.

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