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Thesis for the Degree of Master of Science

Studies of Zinc(II) and Cadmium(II) Cyclam Complexes

by

Chungsik Jang

Department of Chemistry

The Graduate School

Pukyong National University

August 2012

Studies of Zinc(II) and Cadmium(II) Cyclam Complexes
아연과 카드뮴의 사이클람 착물에 관한 연구

Advisor : Prof. Ju Chang Kim

by
Chungsik Jang

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

Master of Science

in Department of Chemistry, The Graduate School
Pukyong National University

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Studies of Zinc(II) and Cadmium(II) Cyclam Complexes

A dissertation

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Chungsik Jang

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August 24, 2012

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Studies of Zinc(II) and Cadmium(II) Cyclam Complexes

Chungsik Jang

Department of Chemistry, The Graduate School,
Pukyong National University

Abstract

Four new zinc(II) and cadmium(II) complexes with the composition $[\mathrm{Zn}(\mathbf{L})(2,6\text{-ndc})]_n$ (**1**), $\{[\mathrm{Zn}(\mathbf{L})(\mathrm{H_2O})_2](2,6\text{-nds})\}_n$ (**2**), $\{[\mathrm{Cd_2}(\mathbf{L})_2(\mathrm{WO_4})_2]\cdot 9\mathrm{H_2O}\}_n$ (**3**) and $\{[\mathrm{Cd_2}(\mathbf{L})_2(\mathrm{MoO_4})_2]9\mathrm{H_2O}\}_n$ (**4**), where **L** = 1,4,8,11-tetraazacyclotetradecane, 2,6-ndc = 2,6-naphthalenedicarboxylate, 2,6-nds = 2,6-naphthalenedisulfonate, have been synthesized and structurally characterized by a combination of microanalytical, spectroscopic, and X-ray diffraction methods. The complex **1** shows a one-dimensional coordination polymer in which each zinc ion is bridged by an ndc anion. The complex **2** shows a two-dimensional hydrogen bonded supramolecular structure in which each mononuclear unit is connected by intermolecular hydrogen bonds between the molecules. Two cadmium complexes, **3** and **4** show 2D sheet structures, respectively, in which each dimeric unit is connected by intermolecular hydrogen bonds between molecules.

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Chapter I

Introduction

General introduction

The chemistry of coordination polymers is rapidly growing area in inorganic chemistry. Coordination polymer is an inorganic-organic hybrid compound. The coordination polymers are formed as one dimensional chain, two dimensional sheet or three dimensional networks, which are constructed by covalent bonds between connectors and linkers. The connectors are defined as metal ion building blocks and decide final coordination polymer structures. The linkers connect each connector [1].

The terminology "*Supramolecule*" was first introduced by K.L. Wolf at 1937 [2]. Supramolecules are usually constructed by intermolecular interactions such as hydrogen bonds [3], C-H$\cdots\pi$ interactions [4], $\pi\cdots\pi$ interactions [5] and so on, in addition to metal-ligand coordination bonds. The applications of supramolecules are being applied in various fields [6-9].

In the assembly of metallosupramolecular networks, utilization of metallomacrocycles as a metal building block offers some advantages over free

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metal ions. Free ions have many binding sites for bind to organic ligands, and thus the extending direction of the networks cannot be easily controlled. However, metallomacrocycles in square-planar geometry have only two vacant sites at the axial positions, thereby acting as linear linkers for the organic ligands. Therefore, the utilization of macrocyclic complexes simplifies the design of the one dimensional chain structure [10].

Macrocyclic complexes are thermodynamically more stable and selective than metal ion binders [11]. Cyclam is one of the most commonly studied and used marcrocyclic ligand for inorganic chemists [12]. In most cyclam complexes, central metal ions bind with four nitrogen atoms of the cyclam. The metal ion sits on the center of square-planar geometry [13]. Therefore, cyclam complexes act as a good "connector" for the construction of coordination polymers or supramolecules with bridging ligands.

In this thesis, the syntheses and properties of two new zinc(II) cyclam complexes and two new cadmium(II) cyclam complexes have been described. Overall this thesis is composed of two chapters. In the Chapter I, it is described the synthesis and properties of new zinc(II) cyclam complexes containing zinc(II) cyclam and bridging aromatic ligands. In the Chapter II, it is described about synthesis and properties of two new cadmium complexes containing cadmium(II) cyclam and bridging tetraoxometalate ligands.

Chapter II

Molecular interactions between zinc(II) cyclam and bridging ligands

Abstract

Two new zinc cyclam of the composition $[Zn(\mathbf{L})(2,6\text{-ndc})]_n$ (**1**), $\{[Zn(\mathbf{L})(H_2O)_2](2,6\text{-nds})\}_n$ (**2**), (**L** = cyclam (1,4,8,11-tetraazacyclotetradecane), 2,6-ndc = 2,6-natphthalenedicarboxylate, 2,6-nds = 2,6-naphthalenedisulfonate) have been prepared and structurally characterized by a combination of microanalytical, spectroscopic, and X-ray diffraction methods. The complex **1** exhibits one dimensional polymeric chain with zinc(II) cyclam and bridging carboxylate ligands. The complex **2** shows a two dimensional hydrogen bonded supramolecular structure in which each mononuclear unit is connected by intermolecular hydrogen bonds between the molecules.

Introduction

In recent years, the chemistry of coordination polymer has been growing rapidly. Coordination polymers are constructed by covalent bonds between connectors and linkers. There are three types of coordination polymers exist, which are one dimensional chain, two dimensional sheets, and three dimensional networks. Generally, the structure of coordination polymer depends on the connector's chemical environments, such as the number of binding sites, oxidation state, etc. The multidentate ligands usually act as linkers, and bridge each connector [1].

Supramolecules which are formed with coordination polymers have been first defined by Jean-Marie Lehn [14]. The supramolecules are constructed by the intermolecular interactions such as hydrogen bonds [3], C-H···π interactions [4], π···π interactions [5], and so on. They have great potentials to be applied in many fields, such as catalysis [7], gas storage [9], ion exchange [15], and medicine [16].

Metallomacrocyclic compounds are kinetically and theromodynamically stable [11]. Cyclam is one of the most commonly studied and used macrocyclic ligands [12]. The $[Zn(\mathbf{L})]\cdot(ClO_4)_2$ which is taking advantage of the afore-mentioned characteristics, were reacted to various aromatic organic ligands. Herein, the details of synthesis, structures, and properties of new zinc complex **1** and **2** are described.

Experimental

Materials and methods

All chemicals used in this work were of reagent grade and were used without further purification. Distilled water was used for all procedures. Infrared spectra were measured as Nujol mulls between KBr plates using a Perkin-Elmer Spectrum 2000 FT-IR spectrophotometer over the range 4000 and 400 cm^{-1}. Elemental analyses were performed by the Korea Research Institute of Chemical Technology, Taejon, Korea.

Caution! The perchlorate salts are potentially explosive and should be handled in small quantities.

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*Synthesis of [Zn(**L**)]·2ClO$_4$*

The precursor complex [Zn(**L**)]·2ClO$_4$ was prepared according to the literature procedures previously reported [17].

*Synthesis of [Zn(**L**)(2,6-ndc)]$_n$ (**1**)*

To a solution of [Zn(**L**)]·2ClO$_4$ (46 mg, 0.1 mmol) in DMF (10 mL) were added dropwise an aqueous solution (10 mL) of 2,6-naphthalene dicarboxlic acid disodium salt (29 mg, 0.01 mmol), which was allowed to stand in an open beaker at ambient temperature. After two weeks, colorless crystals of **1** were obtained. Suitable crystals of **1** for X-ray diffraction studies and subsequent spectroscopic measurements were manually collected under the microscope. Anal. Calcd. for $C_{22}H_{30}N_4O_4Zn$: C, 55.00%; H, 6.25%; N, 11.67%; O, 13.33%. Found C, 54.16%; H, 6.25%; N, 11.63%; O, 13.55%. IR (Nujol, cm^{-1}) 3418 (OH), 3276 (NH), 1608, 1579 (COO).

Synthesis of $\{[Zn(\mathbf{L})(H_2O)_2](2,6\text{-nds})\}_n$ *(2)*

To a solution of $[Zn(\mathbf{L})]\cdot 2ClO_4$ (232 mg, 0.5 mmol) in DMF (10 mL) were added dropwise an aqueous solution (10 mL) of 2,6-naphthalenedisulfonic acid disodium salt (166 mg, 0.5 mmol), which was allowed to stand in an open beaker at ambient temperature. After two weeks, colorless crystals of **2** were obtained. Suitable crystals of **2** for X-ray diffraction studies and subsequent spectroscopic measurements were manually collected under the microscope. Anal. Calcd. for $C_{20}H_{30}N_4O_8S_2Zn$: C, 40.85%; H, 5.83%; N, 9.53%; S, 10.91%. Found. C, 40.67%; H, 5.84%; N, 9.54%; S, 12.21%. IR (Nujol, cm^{-1}) 3361 (OH), 3244 (NH), 1086, 1027 (SO_4).

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X-ray crystallography

X-ray data were collected on a Nonius Kappa CCD diffractometer, using graphite monochromated Mo Kα (λ=7.1073 Å). A combination of 1° and ω (with κ offsets) scans were used to collect sufficient data. The data frames were integrated and scaled using the Denzo-SMN package [18]. The structures were solved and refined using the SHELXTL\PC V6.1 package [19]. Refinement was performed by full-matrix least squares on F^2, using all data (negative intensities included). Hydrogen atoms were included in calculated positions.

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Results and Discussion

A summary of crystallographic data of X-ray crystallography for **1** and **2** are given in Table 1.1. The structure of complex **1** exhibits a one dimensional coordination polymer with basic Zn(**L**)(2,6-ndc) unit (Figure 1.1). The **L** adopts trans-III (*S*,*S*,*R*,*R*) configuration in the solid state. The coordination environment around the central zinc(II) ion shows a slightly distorted octahedron. The zinc(II) ion sits on an inversion center. The selected bond distances and angles are listed in Table 1.2. The four Zn-N bonds show two different distances, 2.087(2) and 2.100(2) Å. The 2.2268(17) Å of Zn-O distance is even longer than that observed in similar complexes ($\{\mathrm{Zn}(\mathbf{L})(\mathrm{tp})(\mathrm{H_2O})\}_n$; 2.1559(12) Å [20], $[\mathrm{Zn}(\mathbf{L})(\mathrm{phthalate})]_n(\mathrm{CH_3OH})_{2n}$; 2.220(2) and 2.190(2) Å [17]). As shown in Figure 1.2, the structure of **1** is composed of zinc(II) cyclams and bridging ndc ligands. The complex **1** has hydrogen bonds between uncoordinated oxygen atom of bridging ndc and N-H groups of cyclam (Table 1.3). Each one dimensional coordination polymer which is parallel arranged created two dimensional sheets. They packed like a plywood array structure (Figure 1.3).

Table 1.1. Crystal data and structure refinement parameters for $[Zn(\mathbf{L})(2,6\text{-ndc})]_n$ (**1**) and $\{[Zn(\mathbf{L})(H_2O)_2](2,6\text{-nds})\}_n$ (**2**).

	1	**2**
Empirical formula	$C_{22}H_{30}N_4O_4Zn$	$C_{20}H_{34}N_4O_8S_2Zn$
Formula weight	479.87	588.00
Temperature(K)	150(1)	150(1)
Wavelength(Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a(Å)	8.9199(5)	8.3647(5)
b(Å)	10.3623(5)	8.7680(4)
c(Å)	12.1317(6)	8.7968(5)
α(°)		73.878(3)
β(°)	109.405(3)	82.219(3)
γ(°)		77.310(4)
V(Å^3)	1057.64(9)	602.75(6)
Z	2	1
D_{calcd}(Mg/m^3)	1.507	1.620
Absorption coefficient (mm^{-1})	1.199	1.247
F(000)	504	308
Crystal size(mm)	0.18 x 0.15 x 0.14	0.24 x 0.10 x 0.10
θ range for data collection(°)	2.65 to 27.47	2.98 to 27.43
Index ranges	$-11 \leq h \leq 11$ $-12 \leq k \leq 13$ $-15 \leq l \leq 15$	$-10 \leq h \leq 10$ $-10 \leq k \leq 11$ $-9 \leq l \leq 11$
Reflections collected	5775	6446
Independent reflections	2396 [R(int) = 0.0368]	2688 [R (int) = 0.0479]
Completeness to θ	98.9% (θ = 27.47°)	98.0% (θ = 27.43°)
Absorption correction	Semi-empirical from equiv.	Semi-empirical from equiv.
Max. and min. transmission	0.848 and 0.809	0.890 and 0.788
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	2396/0/142	2688/0/160
Goodness-of-fit on F^2	1.067	1.080
Final R indices [I>2σ (I)]	$R_1 = 0.0445$, $wR_2 = 0.1033$	$R_1 = 0.0455$, $wR_2 = 0.1054$
R indices (all data)	$R_1 = 0.0729$, $wR_2 = 0.1194$	$R_1 = 0.0728$, $wR_2 = 0.1221$
Largest diff. peak and hole	0.500 and -0.702 e. Å^{-3}	0.794 and -0.648 e. Å^{-3}

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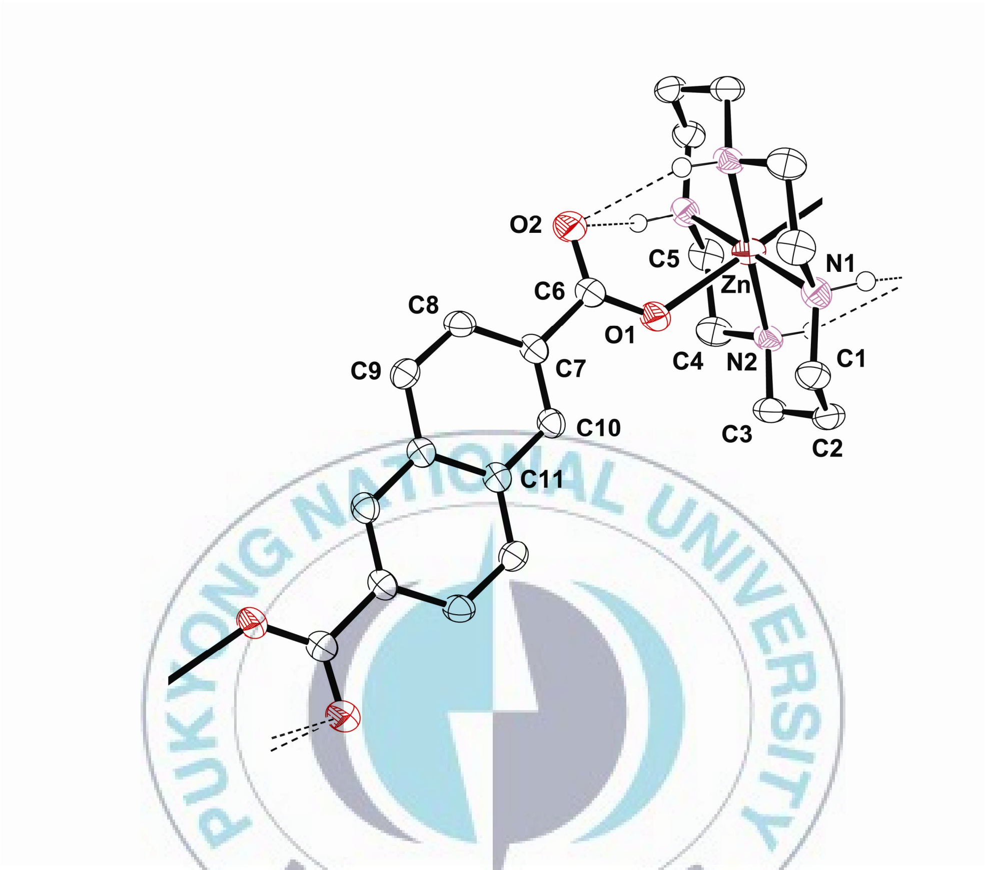

Figure 1.1. Molecular structure of [Zn(**L**)(2,6-ndc)]$_n$ (**1**) with atom labeling scheme. Hydrogen atoms other than those participating in hydrogen bonds are omitted for clarity.

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Table 1.2. Selected bond distances (Å) and angles (°) for $[Zn(\mathbf{L})(2,6\text{-ndc})]_n$ (**1**).

Zn1-N1	2.087(2)	Zn1-N2	2.100(2)
Zn1-O1	2.22268(17)		
N1-Zn1-N2	94.17(9)	N1-Zn1-N2#1	85.83(9)
N1-Zn1-O1#1	92.75(7)	N1#1-Zn1-O1#1	87.25(7)
N2-Zn1-O1#1	92.19(8)	N2#1-Zn1-O1#1	87.81(8)

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

Table 1.3. Hydrogen bonds for $[Zn(\mathbf{L})(2,6\text{-ndc})]_n$ (**1**) (Å and °).

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
N1-H1...O2#1	0.93	2.37	3.099(3)	135.3
N2-H2...O2#1	0.93	2.62	3.281(3)	128.1

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

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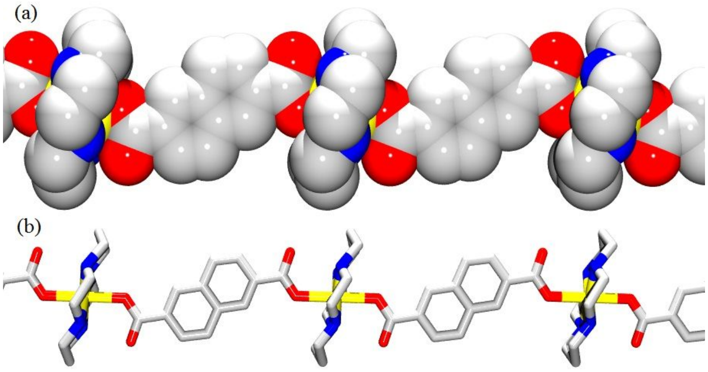

Figure 1.2. Space filling diagram (a) and one dimensional coordination polymer chain (b) of [Zn(**L**)(2,6-ndc)]$_n$ (**1**). Hydrogen atoms other than those participating in hydrogen bonds are omitted for clarity.

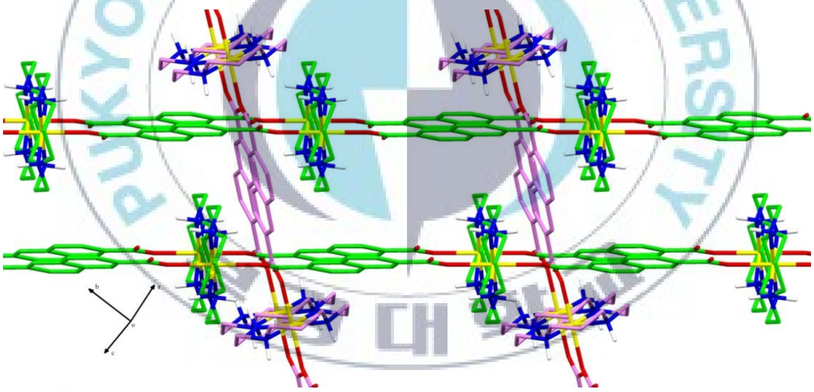

Figure 1.3. View of three dimensional structure of [Zn(**L**)(2,6-ndc)]$_n$ (**1**). Vertical chains and horizontal chains packed likes plywood array. Hydrogen atoms other than those participating in hydrogen bonds are omitted for clarity.

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The crystal structure of complex **2**, as illustrated in Figure 1.4, consists of $[Zn(cyclam)(H_2O)_2]^{2+}$ cations and uncoordinated nds counter anions. The zinc ion sits on an inversion center. It has four Zn-N bonds and two Zn-O bonds. The selected bond distances and angles of 2 are listed in Table 1.4. The bond distances of Zn-N are 2.105(3) and 2.109(3) Å. The 2.257(2) Å of Zn-O (aqua ligand) distance is similar to the values of observed in related complexes ($[Zn(\mathbf{L})(H_2O)_2](fumarate)\cdot 4H_2O$; 2.2539(13) Å [19], $[Zn(\mathbf{L})(H_2O)_2](acetate)\cdot 4H_2O$; 2.2719(14) Å [17]). The oxygen atoms of nds counter anions are hydrogen bonded to diaqua Zn(**L**) cations (Table 1.5). As shown in Figure 1.4, the hydrogen bonds between N-H groups of the cyclam and oxygen atoms of nds anions, supporting the hydrogen bond between aqua ligand and nds anions. Through these hydrogen bonds, the complex **2** extends its structure to two dimensional supramolecule (Figure 1.5).

The infrared spectrum of **1** shows specific absorption bands, which are 1608, 1579 (νCOO), 3276 (νNH), and 3418 cm^{-1} (νOH). The carboxylate groups were came from bridging ndc ligands. The band of 3276 is assignable to the N-H stretching of cyclam. In addition, the broad band of 3418 cm^{-1} is origin from O-H stretching of the solvent molecules (Figure 1.6(a)). The solid state infrared spectrum of **2** shows absorptions at 1086, 1027 cm^{-1} (νSO_3) originated from sulfate groups of the nds anions. The absorption band at 3244 cm^{-1} is observed, which is absorbed by N-H groups of cyclams. In addition, the band of 3361 cm^{-1} (νOH) is observed, indicating the presence of the aqua ligands (Figure 1.6 (b)).

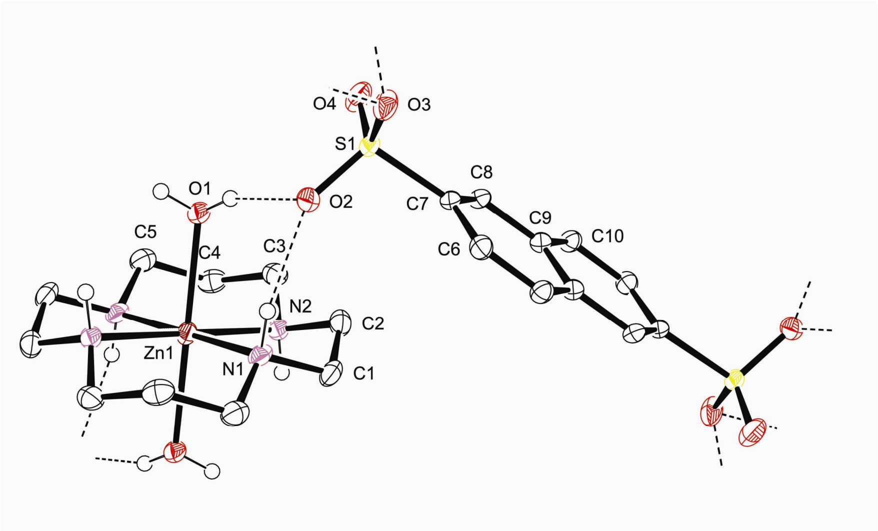

Figure 1.4. Molecular structure of {[Zn(**L**)(H_2O)$_2$](2,6-nds)}$_n$ (**2**) with atom labeling scheme. Hydrogen atoms other than those participating in hydrogen bonds are omitted for clarity.

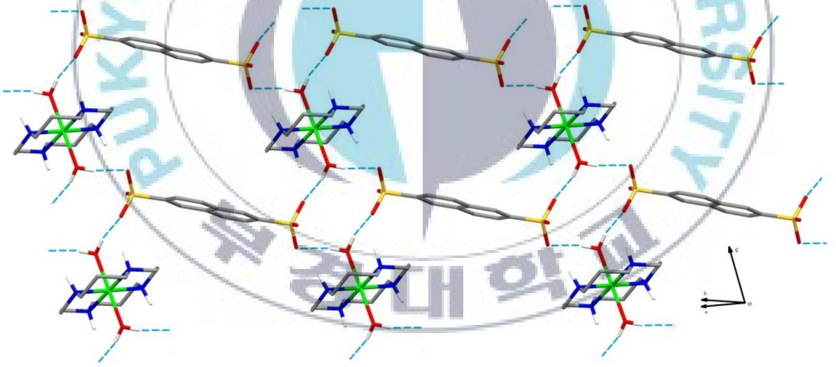

Figure 1.5. View of two dimensional structure of {[Zn(**L**)(H_2O)$_2$](2,6-nds)}$_n$ (**2**). Hydrogen atoms other than those participating in hydrogen bonds are omitted for clarity.

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Table 1.4. Selected bond distances (Å) and angles (°) for {[Zn(**L**)(H_2O)$_2$](2,6-nds)}$_n$ (**2**).

Zn1-N1	2.105(3)	Zn1-N2	2.109(3)
Zn1-O1	2.257(2)		
N1-Zn1-N2	85.47(10)	N1-Zn1-N2#1	94.53(10)
N1-Zn1-O1	90.94(9)	N1-Zn1-O1#1	89.06(9)
N2-Zn1-O1	90.58(9)	N2-Zn1-O1#1	89.42(9)

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

Table 1.5. Hydrogen bonds for {[Zn(**L**)(H_2O)$_2$](2,6-nds)}$_n$ (**2**) (Å and °).

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
N1-H1...O2	0.93	2.13	3.006(3)	157.1
N2-H2...O3#3	0.93	2.33	3.156(4)	148.3
O1-H1O...O2	0.84	2.00	2.801(3)	160.4
O1-H2O...O3#4	0.84	1.96	2.784(3)	165.2

Symmetry transformations used to generate equivalent atoms:

#3 x, y, z+1 #4 –x+1, -y+1, -z

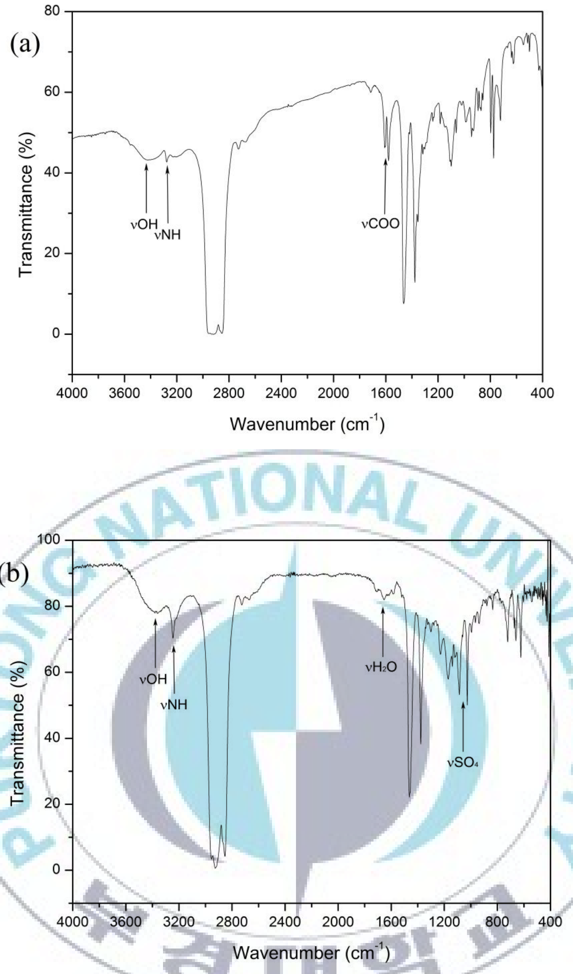

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Figure 1.6. Infrared spectra of (a) [Zn(**L**)(2,6-ndc)]$_n$ (**1**) and (b) {[Zn(**L**)(H_2O)$_2$](2,6-nds)}$_n$ (**2**) [Nujol Mull].

Conclusion

Two new zinc(II) cyclam complexes were prepared and structurally characterized. The complex **1** shows strong coordination behavior between the zinc(II) cyclam and carboxylate ligand. Also **1** has hydrogen bond interactions toward the N-H groups of cyclam and oxygen atoms of bridging ndc ligands. The one dimensional coordination polymers of **1** create two dimensional sheets and three dimensional plywood array structure. The complex **2** has two aqua ligands at axial sites. The nds anions are hydrogen bonded to aqua ligands of $[\mathrm{Zn}(\mathbf{L})(\mathrm{H_2O})_2]^{2+}$ units. The extended structure of complex **2** is constructed by hydrogen bond between aqua ligands of cyclams and oxygen atoms of nds anions. The interactions between zinc(II) cyclams and aromatic organic bridging ligands were able to be understood through this research.

Chapter III

Synthesis and properties of cadmium(II) macrocyclic complexes

Abstract

Two new complexes, $\{[Cd_2(\mathbf{L})_2(MoO_4)_2]\cdot 9H_2O\}_n$ (**3**) and $\{[Cd_2(\mathbf{L})_2(WO_4)_2]\cdot 9H_2O\}_n$ (**4**) have been successfully synthesized and characterized by a combination of microanalytical, thermal, spectroscopic, and X-ray diffraction methods. The complexes **3** and **4** show two dimensional sheet structures, respectively, in which each dimeric unit connected by intermolecular hydrogen bonds between the molecules. It may provide better knowledge for the improved design of receptor-targeted cyclam complexes in anti-HIV agents that the interaction between cadmium(II) macrocycles and bridging ligands.

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Introduction

Cyclams and bicyclam are very interesting materials. Because they have highly potent and selective anti-HIV activity by specifically blocking the co-receptor CXCR4 [21-23]. Cyclam itself is known to exhibit significant anti-HIV activity as well. It has been suggested that the carboxylate groups of aspartate residues Asp 171 and Asp 262 of CXCR4 play key roles in the recognition of cyclams [24]. Therefore, the understanding of interactions between oxygen terminals and cyclam complexes is crucial in design and development of more effective anti-HIV agents.

Recently, several cadmium(II) cyclam complexes such as $[Cd_2(\mathbf{L})_2(oxalate)](ClO_4)$ [25], $[Cd_3(\mathbf{L})_3(CO_3)](ClO_4)_4{\cdot}3H_2O$ [26], and $[Cd(Bz\text{-}cyclam)](NO_3)PF_6{\cdot}0.75H_2O$ [27] etc. have been prepared and structurally characterized. However, the structurally characterized cadmium(II) cyclam complexes are still rare.

In this context, it is interesting to try to synthesized new two cadmium cyclam complexes of $\{[Cd_2(\mathbf{L})_2(MoO_4)_2]{\cdot}9H_2O\}_n$ (**3**) and $\{[Cd_2(\mathbf{L})_2(WO_4)_2]{\cdot}9H_2O\}_n$ (**4**) were investigated. The details of the synthesis, structures and properties of the complexes **3** and **4** are described in this chapter.

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Experimental

Materials and methods

All chemicals used in this work were of reagent grade and were used without further purification. Distilled water was used for all procedures. Infrared spectra were measured as Nujol mulls between KBr plates using a Perkin-Elmer Spectrum 2000 FT-IR spectrophotometer over the range 4000 and 400 cm^{-1}. Elemental analyses were performed by the Korea Research Institute of Chemical Technology, Taejon, Korea.

Caution! The perchlorate salts are potentially explosive and should be handled in small quantities.

Synthesis of $[Cd(\mathbf{L})]\cdot 2ClO_4$

The precursor complex $[Cd(\mathbf{L})]\cdot 2ClO_4$ was prepared according to the literature procedures previously reported [26].

Synthesis of $\{[Cd_2(\mathbf{L})_2(MoO_4)_2]\cdot 9H_2O\}_n$ *(**3**)*

To a solution of $[Cd(\mathbf{L})]\cdot 2ClO_4$ (126 mg, 0.2 mmol) in DMF (5 mL) were added dropwise an aqueous solution (10 mL) of potassium molybdate (60 mg, 0.2

mmol), which was allowed to stand in an open beaker at ambient temperature. After six hours, colorless crystals of **3** were obtained. Suitable crystals of **3** for X-ray diffraction studies and subsequent spectroscopic measurements were manually collected under the microscope. Anal. Calcd. for $C_{20}H_{66}N_8O_{17}Cd_2Mo_2$: C, 21.69%; H, 6.01%; N, 10.12%. Found. C, 21.56%; H, 5.87%; N, 10.09%. IR (Nujol, cm^{-1}) 3341 (OH), 3214 (NH), 1668 (H_2O), 846, 827, 814, 802 (MoO_4).

Synthesis of $\{[Cd_2(\mathbf{L})_2(WO_4)_2]\cdot 9H_2O\}_n$ *(4)*

To a solution of $[Cd(\mathbf{L})]\cdot 2ClO_4$ (126 mg, 0.2 mmol) in DMF (5 mL) were added dropwise an aqueous solution (5 mL) of potassium tungstate (100 mg, 0.2 mmol), which was allowed to stand in an open beaker at ambient temperature. After six hours, colorless crystals of **4** were obtained. Suitable crystals of **4** for X-ray diffraction studies and subsequent spectroscopic measurements were manually collected under the microscope. Anal. Calcd. for $C_{20}H_{66}N_8O_{17}Cd_2W_2$: C, 18.72%; H, 5.18%; N, 8.73%. Found. C, 19.91%; H, 4.63%; N, 9.25%. IR (Nujol, cm^{-1}) 3392 (OH), 3216 (NH), 1668 (H_2O), 847, 829, 814, 805 (WO_4).

X-ray crystallography

X-ray data were collected on a Nonius Kappa CCD diffractometer, using

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graphite monochromated Mo Kα (λ=7.1073 Å). A combination of 1° and ω (with κ offsets) scans were used to collect sufficient data. The data frames were integrated and scaled using the Denzo-SMN package [18]. The structures were solved and refined using the SHELXTL\PC V6.1 package [19]. Refinement was performed by full-matrix least squares on F^2, using all data (negative intensities included). Hydrogen atoms were included in calculated positions. Crystal data and refinement details for **3** and **4** are listed in Table 2.1.

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Table 2.1. Crystal data and structure refinement parameters for $\{[Cd_2(\mathbf{L})_2(MoO_4)_2]\cdot 9H_2O\}_n$ (**3**) and $\{[Cd_2(\mathbf{L})_2(WO_4)_2]\cdot 9H_2O\}_n$ (**4**).

	3	**4**
Empirical formula	$C_{20}H_{66}Cd_2Mo_2N_8O_{17}$	$C_{20}H_{66}Cd_2N_8O_{17}W_2$
Formula weight	1107.49	1283.31
Temperature(K)	150(1)	150(1)
Wavelength(Å)	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12$	$P2_12_12$
a(Å)	14.124(3)	14.142(3)
b(Å)	15.682(3)	15.712(3)
c(Å)	8.9220(18)	8.9256(18)
V(Å^3)	1976.1(7)	1983.3(7)
Z	2	2
D_{calcd}(Mg/m^3)	1.861	2.149
Absorption coefficient (mm^{-1})	1.755	6.912
F(000)	1116	1244
Crystal size(mm)	0.20 x 0.14 x 0.12	0.16 x 0.15 x 0.10
θ range for data collection(°)	2.60 to 27.51	2.59 to 27.50
Index ranges	$-17 \leq h \leq 18$	$-18 \leq h \leq 18$
	$-20 \leq k \leq 20$	$-20 \leq k \leq 20$
	$-11 \leq l \leq 11$	$-11 \leq l \leq 11$
Reflections collected	14581	17540
Independent reflections	4434 [R(int) = 0.0523]	4487 [R (int) = 0.0856]
Completeness to θ	98.9% (θ = 27.47°)	98.0% (θ = 27.43°)
Absorption correction	Semi-empirical from equiv.	Semi-empirical from equiv.
Max. and min. transmission	0.816 and 0.722	0.506 and 0.334
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	4434/0/222	4487/0/222
Goodness-of-fit on F^2	1.119	1.101
Final R indices [I>2σ (I)]	$R_1 = 0.0422$, $wR_2 = 0.0906$	$R_1 = 0.0436$, $wR_2 = 0.0886$
R indices (all data)	$R_1 = 0.0610$, $wR_2 = 0.1032$	$R_1 = 0.0561$, $wR_2 = 0.0951$
Largest diff. peak and hole	1.700 and -1.405 e. Å^{-3}	1.688 and -1.815 e. Å^{-3}

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Results and Discussion

The structure of dimeric unit is illustrated in Figure 2.1. It consists of two cadmium macrocyclic binuclear cations and molybdate anions. Each cyclam have *cis*-V (*S*,*S*,*S*,*S*) conformations. The central cadmium metal ions connected to four nitrogen atoms of cyclam and two oxygen atoms of each molybdate anion. In anti-HIV system of metallocyclam, possible configuration of the ring that is bound to two carboxylate residues would be *cis*-V conformation suggested by P. J. Sadler and co-workers, where the one of oxygen atoms of Asp 262 should be the one coordinating the metal ion and Glu 288 the one interacting through hydrogen bonds to the opposite site of the metallocyclam plane [28]. The complex **3** has similar systems to anti-HIV systems of metallocyclam. The selected bond distance and angles of complex **3** are listed at Table 2.2. The bond distances of Cd-N are 2.312(6), 2.344(5), 2.337(5) and 2.325(6) Å, respectively. The bond distances of Cd-O are 2.310(4) and 2.271(4) Å. The Cd-N and Cd-O distances of complex **3** are similar to the values reported for related cadmium(II) complexes ($[Cd_2(\mathbf{L})_2(oxalate)](ClO_4)_2$; Cd-N = 2.340(5), 2.348(7), 2.333(5) and 2.328(6) Å, Cd-O = 2.292(4) 2.312(4) Å [25], $[Cd_3(\mathbf{L})_3(CO_3)](ClO_4)_4 \cdot 3H_2O$; Cd-N = 2.323(12), 2.270(12), 2.289(12), and 2.311(12) Å, Cd-O = 2.373(7), 2.412(7) Å [26]). As is observed in complex **3** has hydrogen bonds between N-H groups of the macrocycles and oxygen atoms of tungstate anion, creating the two dimensional

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extended structure (Table 2.3, Figure 2.2).

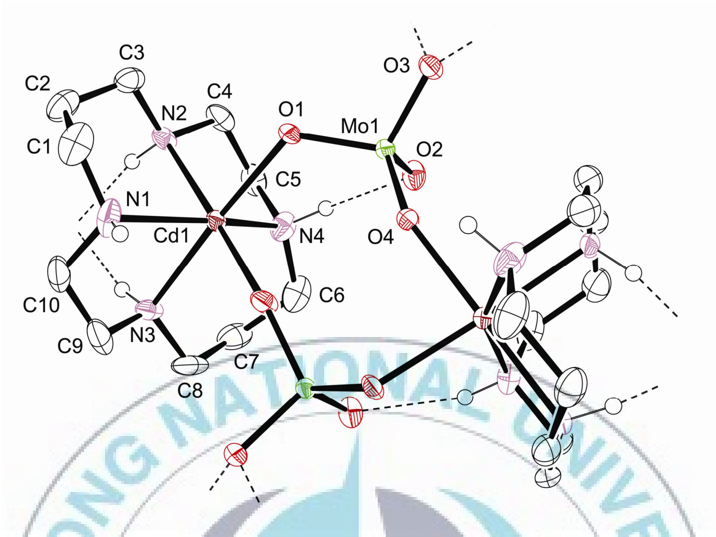

Figure 2.1. Molecular structure of $\{[Cd_2(\mathbf{L})_2(MoO_4)_2]\cdot 9H_2O\}_n$ (**3**) with atom labeling scheme. Hydrogen atoms other than those participating in hydrogen bonds are omitted for clarity.

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Table 2.2. Selected bond distances (Å) and angles (°) for $\{[Cd_2(\mathbf{L})_2(MoO_4)_2]\cdot 9H_2O\}_n$ (**3**).

Cd1-N1	2.312(6)	Cd1-N2	2.344(5)
Cd1-N3	2.337(5)	Cd1-N4	2.325(6)
Cd1-O1	2.310(4)	Cd1-O4#1	2.271(4)
Mo1-O1	1.773(4)	Mo1-O4	1.748(4)
N1-Cd1-N2	87.6(2)	N1-Cd1-N3	77.3(3)
N1-Cd1-N4	157.1(2)	N2-Cd1-N3	90.60(18)
N2-Cd1-N4	76.8(2)	N3-Cd1-N4	86.1(2)
N1-Cd1-O1	104.2(2)	N1-Cd1-O4#1	88.8(2)
N2-Cd1-O1	92.38(17)	N2-Cd1-O4#	175.95(19)
N3-Cd1-O1	176.72(18)	N3-Cd1-O4#1	90.40(17)
N4-Cd1-O1	93.23(19)	N4-Cd1-O4#1	107.2(2)
O1-Cd1-O4#1	86.73(16)	O1-Mo1-O4	111.6(2)
Mo1-O1-Cd1	120.3(2)	Mo1-O4-Cd1#1	150.2(3)

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

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Table 2.3. Hydrogen bonds for $\{[Cd_2(\mathbf{L})_2(MoO_4)_2]\cdot 9H_2O\}_n$ (**3**) (Å and °).

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
N2-H2C...O3#2	0.93	2.07	2.992(7)	169.5
N3-H3C...O3#2	0.93	2.15	3.063(7)	168.2
N4-H4C...O2	0.93	2.15	3.036(8)	158.3

Symmetry transformations used to generate equivalent atoms:
#2 –x+3/2, -y-1/2, -z+1

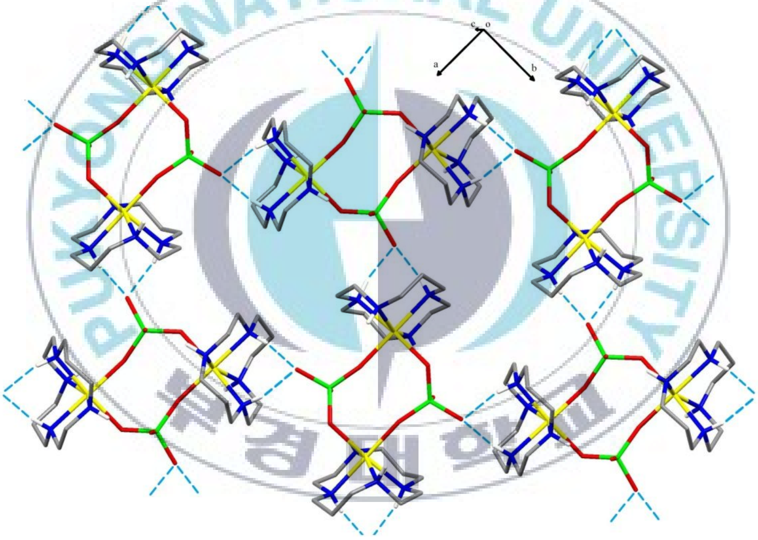

Figure 2.2. View of two dimensional sheet by hydrogen bond between each molecule of $\{[Cd_2(\mathbf{L})_2(MoO_4)_2]\cdot 9H_2O\}_n$ (**3**). Hydrogen atoms other than those participating in hydrogen bonds are omitted for clarity.

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The structure of **4** is similar to that of complex **3**. Figure 2.3 shows the structure of dimeric unit of **4** as determined by single crystal X-ray diffraction method. The cyclam skeleton of **4** has *cis*-V (*R*,*R*,*R*,*R*) conformation which is enantiomeric relationship with that of complex **3**. The central cadmium ion is connected to four nitrogen atoms of cyclam and two oxygen atoms of each tungstate anion. The N-H groups of cyclams are interacted with oxygen atoms of neighboring tungstate. The cadmium cyclam of complex 4 has similar systems to anti-HIV systems of metallocyclam [28]. Selected bond distance and angles of complex **4** are listed at Table 2.4. The bond distances of Cd-N are 2.315(10), 2.322(8), 2.352(9) and 2.330(10) Å, respectively. And bond distances of Cd-O are 2.312 (7) and 2.260 (6) Å. These bond distances are similar to reported for related cadmium complexes. complexes ($[Cd_2(\mathbf{L})_2(ox)](ClO_4)_2$; Cd-N = 2.340(5), 2.348(7), 2.333(5) and 2.328(6) Å, Cd-O = 2.292(4) 2.312(4) Å [25], $[Cd_3(\mathbf{L})_3(CO_3)](ClO_4)_4{\cdot}3H_2O$; Cd-N = 2.323(12), 2.270(12), 2.289(12) and 2.311(12) Å, Cd-O = 2.373(7), 2.412(7) Å [26]). The structure of **4** exhibits two dimensional sheets which is constructed by hydrogen bond between each dimeric molecules (Figure 2.4, Table 2.5).

The Infrared spectrum of complex **3** displays characteristic bands of molybdate (MoO_4) at 846, 827, 814 and 802 cm^{-1}. The band of 3214 cm^{-1} is

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assigned to the N-H groups of cyclams. In addition, two strong broad bands at 3342 (νOH) and 1668 cm^{-1} (νH_2O) are originated from lattice water molecules (Figure 2.5 (a)). The infrared spectrum of complex **4** shows specific bands at 847, 829, 814 and 805 cm^{-1} due to the tungstate (WO_4) ligands. The absorption band at 3216 cm^{-1} is observed, which is absorbed by N-H groups of cyclams. The lattice water molecules absorb infrared at 3392 (νOH) and 1668 cm^{-1} (νH_2O) (Figure 2.5 (b)).

TGA curves for complex **3** shows a first weight loss of 14.54% (calculated 14.64%) over ~54 - 280 °C, corresponding to the loss of nine lattice water molecules. On further heating, gradual weight loss accompanies due to the loss of cyclams. Finally, TGA curves shows residue (observed 51.04%, calculated 49.18%) in 700°C. The residue consists of CdO and MoO_3 metal oxides. (Figure 2.6 (a)). The curves of complex 4 shows first weight loss of 12.63% (calculated 12.63%) over ~74 – 235°C, corresponding the loss of nine lattice water molecules. On further heating, gradual weight loss was observed in 235 – 630°C range with loss of cyclams. Finally, the CdO and WO_3 residue (observed 54.82%, calculated 56.14%) was remaining above 630°C (Figure 2.6 (b)).

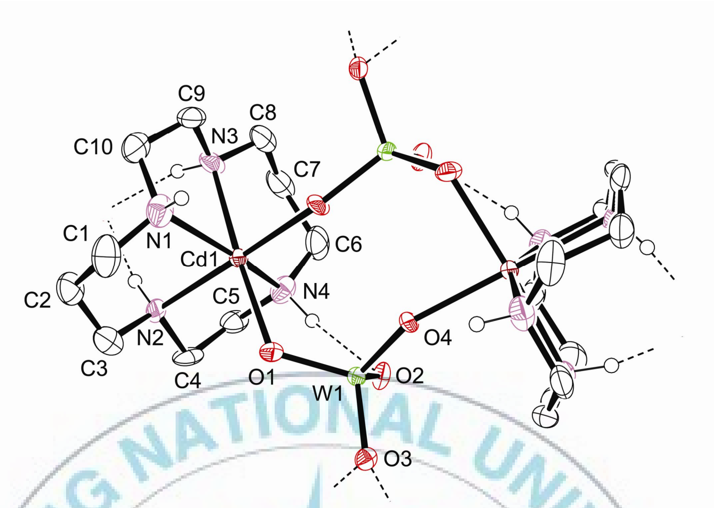

Figure 2.3. Molecular structure of $\{[Cd_2(\mathbf{L})_2(WO_4)_2]\cdot 9H_2O\}_n$ (**4**) with atom labeling scheme. Hydrogen atoms other than those participating in hydrogen bonds are omitted for clarity.

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Table 2.4. Selected bond distances (Å) and angles (°) for $[Cd_2(\mathbf{L})_2(WO_4)_2]\cdot 9H_2O\}_n$ (**4**).

Cd1-N1	2.315(10)	Cd1-N2	2.322(8)
Cd1-N3	2.352(9)	Cd1-N4	2.330(10)
Cd1-O1	2.312(7)	Cd1-O4#1	2.260(6)
W1-O1	1.795(7)	W1-O4	1.763(6)
N1-Cd1-N2	88.2(3)	N1-Cd1-N3	77.4(4)
N1-Cd1-N4	157.2(3)	N2-Cd1-N3	90.6(3)
N2-Cd1-N4	76.1(3)	N3-Cd1-N4	86.2(4)
N1-Cd1-O1	103.6(3)	N1-Cd1-O4#1	88.6(3)
N2-Cd1-O1	92.7(3)	N2-Cd1-O4#1	176.3(3)
N3-Cd1-O1	176.6(3)	N3-Cd1-O4#1	90.7(3)
N4-Cd1-O1	93.8(3)	N4-Cd1-O4#1	107.5(3)
O1-Cd1-O4#1	86.1(3)	O1-W1-O4	111.6(3)
W1-O1-Cd1	120.0	W1-O4-Cd1#1	149.7(4)

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

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Table 2.5. Hydrogen bonds for $\{[Cd_2(\mathbf{L})_2(WO_4)_2]\cdot 9H_2O\}_n$ (**4**) (Å and °).

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
N2-H2C...O3#2	0.93	2.06	2.983(10)	170.4
N3-H3C...O3#2	0.93	2.15	3.064(10)	167.2
N4-H4C...O2	0.93	2.21	3.086(12)	157.8

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

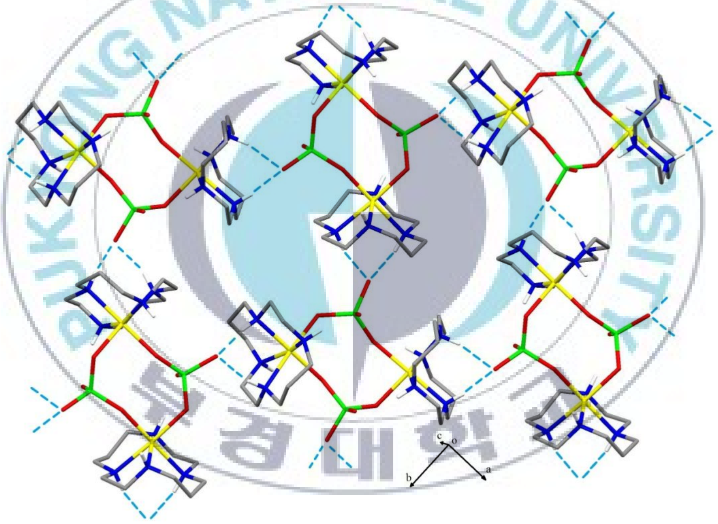

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Figure 2.4. View of two dimensional sheet by hydrogen bond between each molecule of $\{[Cd_2(\mathbf{L})_2(MoO_4)_2]\cdot 9H_2O\}_n$ (**4**). Hydrogen atoms other than those participating in hydrogen bonds are omitted for clarity.

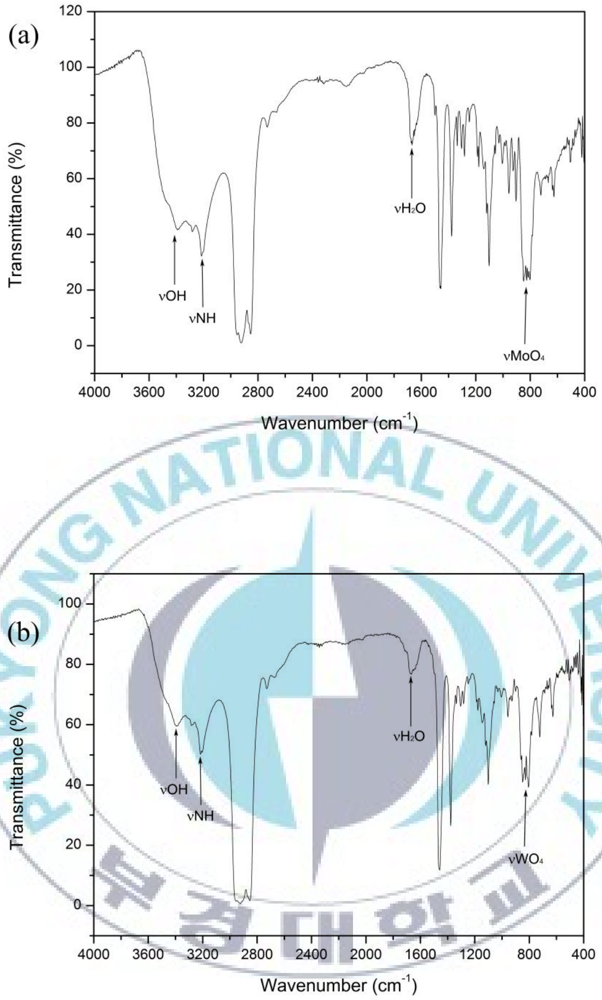

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Figure 2.5. Infrared spectra of (a) $\{[Cd_2(\mathbf{L})_2(MoO_4)_2]\cdot 9H_2O\}_n$ (**3**) and (b) $\{[Cd_2(\mathbf{L})_2(WO_4)_2]\cdot 9H_2O\}_n$ (**4**) [Nujol Mull].

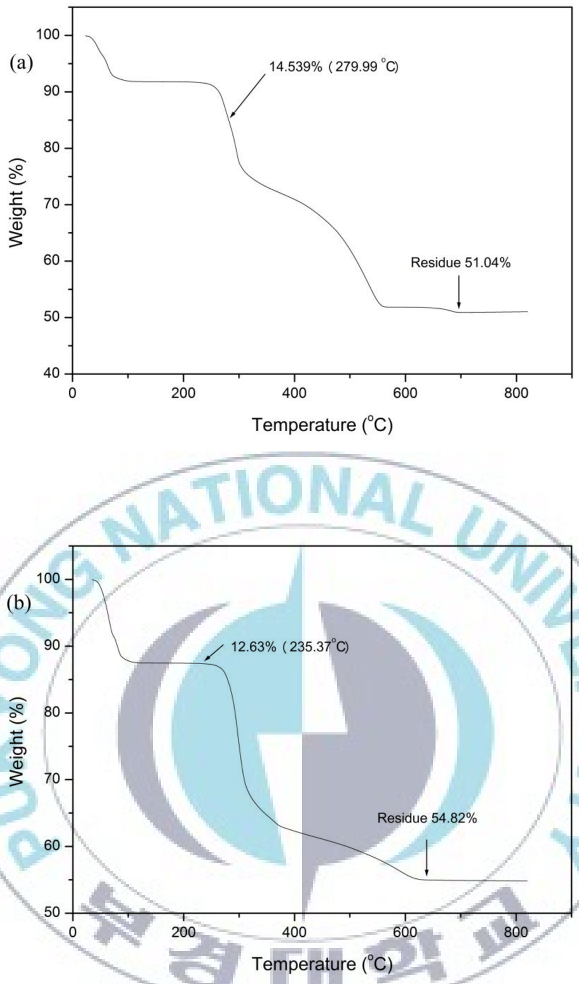

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Figure 2.6. Thermogravimetric analyses of (a) $\{[Cd_2(\mathbf{L})_2(MoO_4)_2]\cdot 9H_2O\}_n$ (**3**) and (b) $\{[Cd_2(\mathbf{L})_2(WO_4)_2]\cdot 9H_2O\}_n$ (**4**).

Conclusion

Two new cadmium cyclam complexes were prepared and fully characterized. The complexes dimmers were observed in the complex **3** and **4**. Each dimer extended to two dimensional sheets by hydrogen bonds. Two complexes have *cis*-V configurations in the macrocyclic skeleton. It may provide better knowledge for the improved design of receptor-targeted cyclam complexes in anti-HIV agents that the interaction between cadmium(II) macrocycles and bridging ligands.

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References

[1] Kitagawa, S.; Kitaura, R.; Noro, S.-I. *Angew. Chem. Int. Ed.* **2004**, *43*, 2334.

[2] Wolf, K. L.; Frahm, H.; Harms, H. *Z. Phys. Chem.* **1937**, *B36*, 237.

[3] Lewiński, J.; Zachara, J.; Justyniak, I.; Dranka, M. *Coord. Chem. Rev.* **2005**, *249*, 1185.

[4] Han, S.; Kim, T.; Lough, A. J.; Kim, J. C. *Inorg. Chim. Acta*, **2011**, *370*, 170.

[5] Roesky, H. W.; Andruh, M. *Coord. Chem. Rev.* **2003**, *236*, 91.

[6] Bauer, C. A.; Timofeeva, T. V.; Settersten, T. B.; Patterson, B.D.; Liu, V. H.; Simmons, B. A.; Allendorf, M. D. *J. Am. Chem. Soc.* **2007**, *129*, 7136.

[7] Wu, C.-D.; Hu, A.; Zhang, L.; Lin W. *J. Am. Chem. Soc.* **2005**, *127*, 8940.

[8] Min, K. S.; Suh, M. P. *Inorg. Chem.* **2001**, *7*, 303.

[9] Choi, H. J.; Suh, M. P. *Inorg. Chem.* **1999**, *38*, 6309.

[10] Suh, M. P.; Cheon, Y. E.; Lee, E. Y. *Coord. Chem. Rev.* **2008**, *252*, 1007.

[11] Lindoy, L. F. *The Chemistry of Macrocyclic Ligand Complexes*, Cambridge University Press, Cambridge, UK, 1989.

[12] Donnelly, M. A.; Zimmer, M. *Inorg. Chem.* **1999**, *38*, 1650.

[13] Cabbiness, D. K.; Margerum, D. W. *J. Am. Chem. Soc.* **1969**, *91*, 6540.

[14] Lehn, J.-M. *Supramolecular Chemistry : Concepts and Perspectives*; VCH Publishers, Weinheim, Germany, 1995.

[15] Min, K. S.; Suh, M. P. *J. Am. Chem. Soc.* **2000**, *122*, 6834.

[16] Bertrand, N.; Gauthier, M. A.; Bouvet, C.; Moreau, P.; Petitjean, A.; Leroux, J.-C.; Leblond, J. *Jounal of controlled release*, **2011**, *155*, 200.

[17] Liang, X.; Weishäupl, M.; Parkinson, J. A.; Parsons, S.; Mcgregor, P. A.; Sadler, P. J. *Chem. Eur. J.* **2003**, *9*, 4709.

[18] Otwinowski, Z. Minor, W. *Methods in Enzymology*. **1997**. *276*. 1783.

[19] Sheldrick, G.M. SHELXTL\PC V6.1, Brucker Analytical X-ray Systems, Madison, WI, USA, 2001.

[20] Jo, H. J.; Lough, A. J.; Kim, J. C. *Inorg. Chim. Acta*, **2005**, *358*, 1274.

[21] Liang, X.; Sadler, P. J. *Chem. Soc. Rev.* **2004**, *33*, 246.

[22] Paisey, S. J.; Sadler, P. J. *Chem. Commun.* **2004**, 306.

[23] Gerlach, L. O.; Jakobsen, J. S.; Jensen, K. P.; Rosenkilde, M. R.; Skerlj, R. T.; Ryde, U.; Bridger, G. J.; Schwartz, T. W. *Biochemistry* **2003**, *42*, 710.

[24] Gerlach, L. O.; Skerlj, R. T.; Bridger, G. J.; Schwarts, T. W. *J. Biol. Chem.* **2001**, *276*, 14153.

[25] Kwag, J. S.; Jeong, M. H.; Lough, A. J.; Kim, J. C. *Bull. Korean Chem. Soc.* **2010**, *31*, 2069.

[26] Liang, X.; Parkinson, J. A.; Parsons, S.; Weishäupl, M.; Sadler, P. J. *Inorg. Chem.* **2002**, *41*, 4539.

[27] Dong, Y.; Lindoy, L. F.; Turner, P.; Wei, G. *Dalton Trans.* **2004**, 1264.

[28] Liang, X.; Parkinson, J. A.; Weishäupl, M.; Gould, R. O.; Paisey, S. J.; Park, H. –S.; Hunter, T. M.; Blindauer, C. A.; Parsons, S.; Sadler, P. J. *J. Am. Chem. Soc.* **2002**, *124*, 9105.

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Korean Abstract

아연과 카드뮴의 사이클람 착물에 관한 연구

장 충 식

부경대학교 대학원 화학과

요약

$[Zn(\mathbf{L})(2,6\text{-ndc})]_n$ (**1**), $\{[Zn(\mathbf{L})(H_2O)_2](2,6\text{-nds})\}_n$ (**2**), $\{[Cd_2(\mathbf{L})_2(WO_4)_2]\cdot 9H_2O\}_n$ (**3**) and $\{[Cd_2(\mathbf{L})_2(MoO_4)_2]9H_2O\}_n$ (**4**), where **L** = 1,4,8,11-tetraazacyclotetradecane, 2,6-ndc = 2,6-naphthalenedicarboxylate, 2,6-nds = 2,6-naphthalenedisulfonate의 구성을 가지는 새로운 네 가지의 아연(II)과 카드뮴(II) 화합물이 합성되었으며, 분광학적, 결정학적인 방법들의 조합을 통하여 구조적인 특성을 분석하였다. 1번 착물의 경우 아연이온과 다리리간드인 ndc간의 공유결합을 통하여 1차원 배위고분자가 나타난다. 2번 착물은 이차원의 초분자구조를 발견할 수 있는데, 이는 아연사이클람의 단분자 반복체와 다리리간드간의 수소결합을 통해서 생성된다. 두 카드뮴 착물인 3, 4번 착물의 경우 각각, 다이머형태의 반복유닛간 수소결합을 통해 생성된 2차원 시트구조를 발견할 수 있다.

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