Investigation of Molecular Interactions in the Carboxylato Zn(II) and Cd(II) Macrocyclic Complexes

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Coordination polymers on the basis of the assembly of metal ion “connectors” and multidentate ligand “linkers” have been of great interest due to their intriguing architectures and versatile applications.^{1–9} Metallotetraazamacrocycles bearing equatorial amines coordinated to the central metal ions and axial sites opened for incoming “linkers” are good “connectors” as building blocks for the construction of coordination polymers.^{10–15} Among multidentate ligands, polycarboxylates have been widely used as “linkers” due to their versatile coordination modes toward metal ions.^{16–19} An fdc (fdc = 1,1'-ferrocenedicarboxylate ion) ligand as a kind of polycarboxylates has attracted attention not only in the field of coordination chemistry but also in the field of organometallic chemistry.^{20–23} During our efforts to explore the molecular interactions between metallomacrocycles and polycarboxylate ligands in zinc(II) and cadmium(II) tetraazamacrocycles containing bridging polycarboxylate ligands, we successfully synthesized and structurally characterized two 1D zinc(II) coordination polymers **1** and **2**, where each ferrocenyl of bridging fdc ligands adopts different conformation, and a macrocyclic cadmium(II) dimer **3**. Thus, two Cp (Cp = cyclopentadienyl) rings of fdc ligands in **1** are mutually staggered, whereas they are eclipsed in **2**. The cadmium(II) cyclams with folded macrocycles are bridged by an oxalate ligand in **3**. In this report we describe the details of the synthesis and structures of **1–3**.

Experimental Section

Materials, methods and apparatus. All chemicals used in the synthesis were of reagent grade and 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. UV-vis spectra were measured on a Cary 1C spectrophotometer within the range 200 – 800 nm. Elemental and thermal analyses were performed by the Korea Research Institute of Chemical Technology, Daejeon, Korea. The free ligands **L1** and **L2** were synthesized by literature procedures.²⁴ The precursor complex $\text{Zn}(\text{L1})(\text{NO}_3)_2$ or $\text{Zn}(\text{L2})(\text{NO}_3)_2$ was prepared by refluxing ligand **L1** or **L2** (336 mg, 1.0 mmole) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (300 mg, 1.01 mmole) in stirring methanol for a day, filtering the white powder, washing with methanol, and finally drying in air. Yield > 95%. The starting $\text{Cd}(\text{cyclam})(\text{ClO}_4)_2$ complex was prepared by reported methods.²⁵

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

Synthesis of 1: Compound **1** was prepared by adding an aqueous solution of sodium fdc (32 mg, 0.1 mmole) to a DMF solution of $\text{Zn}(\text{L1})(\text{NO}_3)_2$ (53 mg, 0.1 mmole). Slow evaporation of the solution provided orange single crystals of **1**. Suitable crystals **1** for X-ray diffraction studies and other measurements were manually collected under a microscope. Yield > 90%. Anal. Calcd. for $\text{C}_{32}\text{H}_{54}\text{FeN}_4\text{O}_7\text{Zn}$ (**1**): C, 52.79%; H, 7.48%; N, 7.70%. Found C, 52.72%; H, 7.29%; N, 7.70%.

Synthesis of 2: Compound **2** was prepared by a same method described for **1** using $\text{Zn}(\text{L2})(\text{NO}_3)_2$ instead of $\text{Zn}(\text{L1})(\text{NO}_3)_2$. Yield > 90%. Anal. Calcd. for $\text{C}_{32}\text{H}_{52}\text{FeN}_4\text{O}_6\text{Zn}$ (**2**): C, 54.13%; H, 7.38%; N, 7.89%. Found C, 54.03%; H, 7.26%; N, 7.87%.

Synthesis of 3: To an aqueous solution of $\text{Cd}(\text{cyclam})(\text{ClO}_4)_2$ (511 mg, 1.0 mmole) was added an aqueous solution of $\text{K}_2\text{oxalate} \cdot \text{H}_2\text{O}$ (92 mg, 0.5 mmole). The mixture was allowed in an open beaker at room temperature. Colorless plates of **3** were obtained in a week. Suitable crystals of **3** for X-ray diffraction studies and other measurements were manually collected under a microscope. Yield > 90%. Anal. Calcd. for $\text{C}_{22}\text{H}_{48}\text{N}_8\text{Cd}_2\text{Cl}_2\text{O}_{12}$: C, 28.93%; H, 5.26%; N, 12.28%; O, 21.04%. Found C, 29.20%; H, 5.24%; N, 12.20%; O, 21.22%.

X-ray crystallography. A summary of selected crystallographic data and structure refinement for **1–3** is given in Table 1. X-ray data were collected on a Nonius Kappa CCD diffractometer, using graphite monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). A combination of $1^\circ \phi$ and ω (with κ offsets) scans were used to collect sufficient data. The data frames were integrated and scaled using the Denzo-SMN package.²⁶ The structure was solved and refined using the SHELXTL/PC V6.1 package.²⁷

Table 1. Crystal data and structure refinement for **1-3**

	1	2	3
Empirical formula	C ₃₂ H ₅₄ FeN ₄ O ₇ Zn	C ₃₂ H ₅₂ FeN ₄ O ₆ Zn	C ₂₂ H ₄₈ N ₈ Cd ₂ Cl ₂ O ₁₂
Formula weight	728.01	710.00	912.38
Temperature (K)	150(1)	150(1)	150(2)
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>C</i> 2/c	<i>P</i> $\bar{1}$
Unit cell dimensions	a = 9.9439(3) Å b = 12.2581(3) Å c = 15.7746(5) Å α = 111.4410(16) $^\circ$ β = 90.2750(16) $^\circ$ γ = 111.2840(18) $^\circ$	a = 17.5564(5) Å b = 10.2621(3) Å c = 18.3590(5) Å β = 102.2230(16) $^\circ$	a = 8.1346(3) Å b = 12.0765(4) Å c = 17.2460(9) Å α = 85.184(3) $^\circ$ β = 84.483(2) $^\circ$ γ = 85.437(2) $^\circ$
Volume	1646.59(8) Å ³	3232.68(16) Å ³	1676.03(12) Å ³
Z	2	4	2
Density (calcd)	1.468 Mg/m ³	1.459 Mg/m ³	1.808 Mg/m ³
Absorption coefficient	1.222 mm ⁻¹	1.240 mm ⁻¹	1.497 mm ⁻¹
Independent reflections	7481 [R(int) = 0.0425]	3408 [R(int) = 0.0660]	7601 [R(int) = 0.0534]
Goodness-of-fit on <i>F</i> ²	1.036	1.059	1.058
Final R indices [I > 2 σ (I)]	<i>R</i> _I = 0.0425, <i>wR</i> ₂ = 0.1007	<i>R</i> _I = 0.0469, <i>wR</i> ₂ = 0.1115	<i>R</i> _I = 0.0558, <i>wR</i> ₂ = 0.1302
R indices (all data)	<i>R</i> _I = 0.0655, <i>wR</i> ₂ = 0.1135	<i>R</i> _I = 0.0706, <i>wR</i> ₂ = 0.1303	<i>R</i> _I = 0.0933, <i>wR</i> ₂ = 0.1533

Figure 1. Molecular structure of **1** with atom-labeling scheme (top) and two Cp rings showing staggered (bottom). Hydrogen atoms other than those participating in hydrogen bonding and on the Cp rings are omitted for clarity. Selected bond distances (Å) and angles ($^\circ$): Zn1-N1, 2.1008(19); Zn1-N2, 2.110(2); Zn2-N3, 2.150(2); Zn2-N4, 2.082(2); Zn1-O1, 2.2107(16); Zn2-O3, 2.2042(17); N1-Zn1-N2, 84.41(8); N1-Zn1-N2#1, 95.59(8); N1-Zn1-O1#1, 88.36(7); N2-Zn1-O1#1, 89.16(7); N1-Zn1-O1, 91.64(7); N2-Zn1-O1, 90.84(7). Symmetry transformations used to generate equivalent atoms: #1 -x, -y+1, -z.

Refinement was performed by full-matrix least squares on *F*² using all data (negative intensities included). Hydrogen atoms were included in calculated positions.

Results and Discussion

The different ferrocenyl conformations of bridging fdc ligands

in **1** and **2** can be induced by the introduction of macrocycles **L1** and **L2**. The macrocycles **L1** and **L2** are diastereomerically related each other in which the macrocycle **L1** contains two *cis*-fused cyclohexane rings on a cyclam and the macrocycle **L2** contains two *trans*-fused cyclohexane rings on a cyclam.²⁴

The solid state structures of **1** and **2** were determined by X-ray diffraction methods. An ORTEP drawing of the complex **1** is shown in Figure 1. The structure of **1** exhibits a 1D coordination polymer with the basic unit of [Zn(**L1**)(fdc)] which is composed of two independent macrocycles and bridging fdc ligands. Each zinc atom sits on an inversion center and two Cp rings of fdc ligands are staggered. The staggered conformation of two Cp rings in **1** is induced by the introduction of macrocycle **L1** which has larger steric hindrance compared to that of the macrocycle **L2** as well as hydrogen bonds between fdc ligands and three lattice water molecules. In 2D sheets, these hydrogen bonds pull the neighboring 1D polymeric chain closer, resulting in a larger steric hindrance between the Cp rings of 1D interchains. The average Fe-C bond distance of Cp is 2.052 Å and the Fe-Cp (centroid) distance is 1.656 Å in a staggered ferrocenyl moiety. These are comparative to those reported for related ferrocene compounds.^{28,29} The rotational angle between the two Cp rings in **1** is close to 46.7 $^\circ$ (measured by C(11)-Cp (centroid)-Cp (centroid)-C(8)). Another pertinent structural feature found in **1** is that each 1D chain is linked together *via* hydrogen bonds. Water molecules mediate in connecting each 1D chain (Figure 2, Table 2). Through these hydrogen bonding interactions, the complex **1** extends its structure to form a 2D supramolecule. The complex **2** containing the macrocycle **L2** exhibits a 1D coordination polymer with a basic [Zn(**L2**)(fdc)] unit (Figure 3). Similarly to **1**, each zinc atom sits on an inversion center. However, in the complex **2**, two Cp rings of bridging fdc ligands are an eclipsed conformation (Figure 3). The complex **2** with **L2** which has a smaller steric hindrance compared

Table 2. Hydrogen bonds for **1** (Å and °)

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N2-H2...O2#1	0.93	2.08	2.967(3)	159.4
N4-H4...O4	0.93	2.12	2.967(3)	150.9
O1W-H1WA...O2	0.84	1.96	2.804(3)	179.4
O1W-H1WB...O4	0.84	1.96	2.800(2)	179.4
O2W-H2WA...O1W	0.84	2.06	2.879(3)	163.3
O2W-H2WB...O1W#3	0.84	2.16	2.990(3)	167.6
O3W-H3WA...O2	0.84	2.07	2.907(3)	179.6
O3W-H3WB...O2W	0.84	2.10	2.936(3)	179.6

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

Table 3. Hydrogen bonds for **2** (Å and °)

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N2-H2...O2#2	0.93	2.13	2.957(3)	146.9
O1W-H3WA...O2	0.78	2.08	2.823(3)	158.7
O1W-H3WB...O2#3	0.85	2.07	2.861(3)	154.0

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

Figure 2. Extended molecular structure of **1** illustrating a 1D coordination polymer (top) and 2D supramolecule (bottom).

to that of the macrocycle **L1** exhibits symmetric hydrogen bonds with two water molecules. In 2D sheets, the ferrocenyl groups in one polymeric chain reside far apart from another ferrocenyl groups of neighboring polymeric chain due to these symmetric hydrogen bonds, resulting in a smaller steric hindrance between the Cp rings of 1D interchains (Figure 4). Under these circumstances, the complex **2** favorably adopts the eclipsed conformation of two Cp rings of bridging fdc ligands. The complex **2** shows the average Fe-C of Cp distance of 2.045 Å and Fe-Cp (centroid) distance of 1.647 Å. These are also similar to those found in the complex **1** and other related ferrocene complexes.^{28,29} The rotational angle between the two Cp rings in **1** is close to 7.2° (measured by C(6)-Cp (centroid)-Cp (centroid)-C(3)#1; symmetry code: #1 -x+1,y,-z+3/2). Water molecules in **2** interact with each other as well as carboxylates of Cp rings

Figure 3. Molecular structure of **2** with atom-labeling scheme (top) and two Cp rings showing eclipsed (bottom). Hydrogen atoms other than those participating in hydrogen bonding and on the Cp rings are omitted for clarity. Selected bond distances (Å) and angles (°): Zn(1)-N(1), 2.129(2); Zn(1)-N(2), 2.083(2); Zn(1)-O(1), 2.204(2); N1-Zn1-N2, 95.35(9); N1-Zn1-N2#2, 84.65(9); N1-Zn1-O1#2, 85.39(9); N2-Zn1-O1#2, 94.33(9); N1-Zn1-O1, 94.61(9); N2-Zn1-O1, 85.67(9). Symmetry transformations used to generate equivalent atoms: #2 -x+1,-y+1,-z+1. **Figure 4.** Extended molecular structure of **2** illustrating a 1D coordination polymer (top) and 2D supramolecule (bottom).

to form a 2D supramolecule (Figure 4, Table 3). The results in **1** and **2** are in contrast to the previous reports that two Cp rings of a ferrocene nearly adopt an eclipsed conformation (D_{5h}) in the gas phase,^{30,31} meanwhile, staggered Cp rings of a ferrocene (D_{5d}) are in single crystals.^{31,32}

The structure for **3** contains two independent centrosymmetric dimers. One of these along with the anions is shown in Figure 5. The basic structure of **3** exhibits a macrocyclic cadmium(II) dimer, where each cyclam is folded in a *cis*-I (*R,S,R,S*) fashion and an oxalate ligand acts as a bridge in a bis-biden-