Studies of new Ni(II), Cu(II) and Zn(II) macrocyclic complexes with polycarboxylate anions

다카복실산 음이온을 포함한 새로운 니켈, 구리 및 아연 거대고리 착화합물에 관한 연구

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Studies of new Ni(II), Cu(II), and Zn(II) macrocyclic complexes with polycarboxylate anions

A Dissertation

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Abstract

Eight new Ni(II), Cu(II), and Zn(II) macrocyclic complexes of the composition $\{[\mathrm{Cu}(\mathbf{L1})(\mathrm{fumarato})]\cdot 6\mathrm{H_2O}\}_n$, $[\mathrm{Cu}(\mathbf{L1})(\mathrm{H_2bta^{2-}})]$, $\{[\mathrm{Ni}(\mathbf{L2})(\mathrm{H_2bta^{2-}})]\cdot 2\mathrm{H_2O}\}_n$, $\{[\mathrm{Cu}(\mathbf{L2})(\mathrm{H_2bta^{2-}})]\cdot \mathrm{H_2O}\}_n$, $\{[\mathrm{Zn}(\mathbf{L2})(\mathrm{tp^{2-}})]\cdot \mathrm{H_2O}\}_n$, $\{[\mathrm{Zn}(\mathbf{L2})(\mathrm{H_2bta^{2-}})]\cdot 2\mathrm{H_2O}\}_n$, $[\mathrm{Zn_2}(\mathbf{L2})_2(\mathrm{ox^{2-}})]\cdot 2\mathrm{ClO_4}\cdot 2\mathrm{DMF}$, and $[\mathrm{Zn}(\mathbf{L2})(\mathrm{H_2btc^-})_2]\cdot 2\mathrm{DMF}$, where **L1**=3,14-dimethyl-2,6,13,17-tetraazatricyclo[14.4.0$^{1.18}$.0$^{7.12}$]docosane, **L2** = 1,4,8,11-tetraazacyclotetradecane, $\mathrm{tp^{2-}}$ = terephthalic acid dianion, $\mathrm{H_2bta^{2-}}$ = 1,2,4,5-benzenetetracarboxylic acid dianion, $\mathrm{ox^{2-}}$ = oxalic acid dianion, $\mathrm{H_2btc^-}$ = 1,3,5-benzenetricarboxylic acid anion, have been synthesized and structually characterized by a combination of analytical, spectroscopic, and crystallographic methods. Some complexes show one-dimensional coordination polymers in which each metal ion is bridged by the polycarboxylate anion. In all complexes, various types of hydrogen bonding interactions and the pre-organization of N-H directionality play an important role in reinforcing the metal-ligand ligations as well as in determining the shapes of the carboxylate anions.

General Introduction

Supramolecular chemistry has been the fields of rapid growth in recent years. The application of supramolecular concepts such as self-assembly and molecular recognition offers an approach to crystal engineering that is based upon the design of infinite networks. Self-assembly of more than one molecular component is particularly attractive since it can be accomplished in one-pot reactions with existing molecular components and allows for facile fine-tuning of structural and functional features [1].

Macrocyclic complexes have been understood important building blocks of ligand-bridged complexes that possess various dimensional structures. Saturated macrocyclic polyamines exhibit interesting properties beyond those anticipated from mere assemblies of linear polyamines [3]. The significance of macrocyclic ligands and their metal complexes is obvious as they relate to naturally occurring macrocylic molecules such as heme groups, which are the active site of hemoglobin and myoglobin, vitamin B12, and chlorophyll. The iron porphyrin of the heme and the chlorophyll contain 16-membered rings, while the vitamin B12 contains a 15-membered ring. Thus synthetic macrocyclic complexes have been used as model systems for these natural products.

Besides, in recent years many interests have been focused on the design and synthesis of low dimensional coordination polymers constructed by the reaction of metal ions with multifunctional ligands such as polycarboxylates. Low dimensional coordination polymers, generally including one-dimensional (1D) and two-dimensional (2D) structures, have intriguing structural features and unique electroconductive, nonlinear optical, and magnetic properties different from those of three-dimensional (3D) coordination polymers [4].

The bridging ligand is one of the important factors that influence the structures of the coordination polymers. Multidentate polycarboxylate anions are well-known versatile ligands able to chelate and bridge metal ions leading to the formation of polynuclear systems. And they can act not only as hydrogen bond donors but also acceptors due to the existence of protonated and/or deprotonated carboxyl groups [4]. In particular, polyaza macrocyclic complexes with multi-connecting ligands have been proved to be good building blocks for the construction of coordination polymers and multi-dimensional supramolecular networks.

On the basis of the aforementioned points, we have attempted to construct low dimensional transition metal complexes with tetraaza macrocyclic ligands and polycarboxylate ligands. In this thesis, we report the syntheses and properties of new macrocyclic Ni(II), Cu(II), and Zn(II) carboxylato complexes where each metallomacrocycle is bridged by polycarboxylates such as fumarate, terephthalate, 1,2,4,5-benzentetracarboxylate, 1,3,5-benzentricarboxylate, and oxalate. In all complexes, various types of hydrogen bonding interactions and the pre-organization of N-H directionality play an important role in reinforcing the metal-ligand ligations as well as in determining the shapes of the carboxylate anions. The details of the structures for the new complexes are determined by analytical, spectroscopic, and X-ray diffraction methods.

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CHAPTER I

Syntheses and X-ray crystal structures of 14-membered tetraaza macrocyclic copper(II) complexes with polycarboxylate ligands

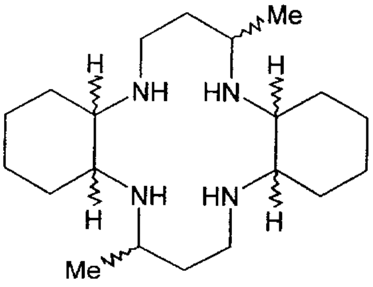
Abstract

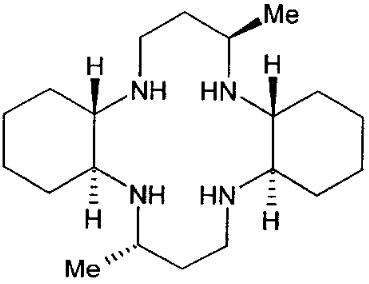
The fumarate-bridged 1D copper(II) coordination polymer, $\{[Cu(\mathbf{L1})(O_2CCH{=}CHCO_2)]\cdot 6H_2O\}_n$ (**1**) (**L1**=3,14-dimethyl-2,6,13,17-tetraazatricyclo[14.4.0$^{1.18}$.0$^{7.12}$]docosane) and the 1,2,4,5-benzenetetracarboxylate (H_2bta^{2-}) coordinated copper(II) mononuclear complex, $[Cu(\mathbf{L1})(C_6H_2(COO)_2(COOH)_2)]$ (**2**) have been synthesized and structurally characterized by a combination of analytical, spectroscopic, and crystallographic methods. The complex **1** exhibits a novel 1D polymeric structure with copper(II) centers and bridging fumarate ligands. The complex **2** shows a monomeric structure with a square pyramidal coordination geometry around the copper(II) ion. In **2** the pentavalent around the copper atom is completed with four nitrogen atoms from the macrocycle and one oxygen atom from the H_2bta^{2-} ligand.

Introduction

Transition metal complexes containing aromatic polycarboxylate ligands have received considerable attention due to their interesting structures and potential applications [1-3]. Recently, macrocyclic complexes with bridging aromatic polycarboxylate ligands have been proved to be good building blocks for the construction of coordination polymers and multidimensional networks [4,5]. The bridging ligands such as 1,4-benzenedicarboxylate [4], 1,3-benzenedicarboxylate [5,6], 1,3,5-benzenetricarboxylate [4,5], H_4bta [7-9], benzenehexacarboxylate [10], and aliphatic polycarboxylates [11] have widely been employed. However, macrocyclic copper(II) coordination complexes formed with aliphatic polycarboxylate or H_4bta ligands are less explored [12]. A number of factors have been understood to influence the structural motifs of the copper(II) complexes with polycarboxylate ligands [11]. Some of them are the distance between the carboxyl groups, and the presence of hydrogen bonding interactions between the macrocyclic ligand and bridging polycarboxylate ligands. Since our previous research revealed that the structure of the copper(II) complexes with the macrocyclic ligand **L1** depend on the nature of the bridging polycarboxylate ligands as well as the hydrogen bonding interactions involved [12], we have therefore conducted an investigation of systems [Cu(**L1**)]$\cdot$2ClO_4–fumarate and

[Cu(**L1**)]·2ClO$_4$– H$_4$bta to better understand the copper(II) coordination behaviors and hydrogen bonding interactions, with the fumarate ligand having the shorter distance between the carboxylate groups compared to that found in [Cu(**L1**)(terephthalato)]$_n$·2nH$_2$O [12] and the H$_2$bta^{2-} ligand possessing a variety of coordination modes and hydrogen bonding abilities. Reported herein are the 1D copper(II) coordination polymer **1** and the mononuclear copper(II) complex **2**, in which various types of hydrogen bonding interactions play an important role to determine the copper(II) coordination geometries. The details of the structures of **1** and **2** and the pre-organization of N–H directionality with its role in profacial selection of anion binding are discussed in this report.





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 Paragon 1000 FT-IR spectrophotometer over the range 4000 and 400 cm^{-1}. UV/Vis diffuse reflectance spectra using samples diluted with $BaSO_4$ were recorded with a Shimadzu 2401 PC UV/Vis recording spectrophotometer. Elemental analyses were performed by the Korea Research Institute of Chemical Technology, Taejon, Korea. The precursor complex $[Cu(\mathbf{L1})]\cdot 2ClO_4$ was prepared according to the literature procedures previously reported [13]. *Safety note.* Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of the materials should be prepared, and these should be handled with care.

Synthesis of **1**

To a DMF solution (10 ml) of $[Cu(\mathbf{L1})]\cdot 2ClO_4$ (300 mg, 0.5 mmol) was added an aqueous solution (10 ml) of fumarate (80 mg, 0.5 mmol). Blue crystals were obtained in a week. Suitable crystals of **1** for X-ray diffraction studies and subsequent spectroscopic measurements were manually collected under the microscope. Anal. Calcd. for $C_{24}H_{54}N_4O_{10}Cu$: C, 46.28%; H, 8.68%; N, 9.00%. Found C, 46.03%; H, 8.35%; N, 8.96%. IR (Nujol, cm^{-1}): 3391 (OH), 3064 (NH), 1669, 1556 (CO). UV/Vis ($BaSO_4$, λ_{max}, nm): 215, 273, 541.

Synthesis of **2**

To a DMF solution (10 ml) of [Cu(**L1**)]·2ClO_4 (300 mg, 0.5 mmol) was added to a methanol (5 ml) solution of 1,2,4,5-benzenetetracarboxylic acid (127 mg, 0.5 mmol). Several drops of pyridine were added to a resulting solution. Reddish purple crystals were obtained in a week. Suitable crystals of **1** for X-ray diffraction studies and subsequent spectroscopic measurements were manually collected under the microscope. Anal. Calcd. for $C_{30}H_{46}N_4O_9Cu$: C, 53.71%; H, 6.86%; N, 8.36%. Found C, 53.58%; H, 7.07%; N, 8.38%. IR (Nujol, cm^{-1}): 3440 (OH), 3203, 3087 (NH), 1697, 1581 (CO). UV/Vis ($BaSO_4$, λ_{max}, nm): 226, 265, 541.

Crystal data for **1** *and* **2**

Single crystals of **1** and **2** were prepared as described above. A crystal of dimensions 0.20 x 0.14 x 0.14 mm^3 for **1** (0.40 x 0.34 x 0.34 mm^3 for **2**) was employed for structural analysis at 150(1) K on a Nonius KappaCCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Crystal data for **1**: $C_{24}H_{54}N_4O_{10}Cu$, FW = 622.25, triclinic, space group P-1, a = 7.86400(10), b = 9.2070(2), c = 10.9340(2) Å, α = 88.0590(9), β = 76.1890(9), γ = 80.1820(11)°, V = 757.50(2) Å^3, Z = 1, D_{calc} = 1.364 Mg/m^3. A total of 10,189 reflections were measured, 3349 reflections were unique (R_{int} = 0.021). μ = 0.778

mm^{-1}, $2.71 < \theta < 27.30^{\circ}$, $0 \leq h \leq 10$, $-11 \leq k \leq 11$, $-13 \leq l \leq 14$, R1 = 0.0251, wR2 = 0.0644 ($I > 2\sigma(I)$), R1 = 0.0263, wR2 = 0.0653 (all data), GOF = 1.070, largest diff. peak and hole = 0.313 and –0.394 eÅ^{-3}. Crystal data for **2**: $C_{30}H_{46}N_4O_9Cu$, FW = 670.25, monoclinic, space group Cc, a = 13.2578(3), b = 14.1575(4), c = 17.7378(5) Å, β = 110.3380(10), V = 3121.78(14) Å^3, Z = 4, D_{calc} = 1.426 Mg/m^3, A total of 11,995 reflections were measured, 6176 reflections were unique (R_{int} = 0.032). μ = 0.759 mm^{-1}, $2.82 < \theta < 27.51^{\circ}$, $-17 \leq h \leq 17$, $-18 \leq k \leq 16$, $-23 \leq l \leq 22$, R1 = 0.0294, wR2 = 0.0748 ($I > 2\sigma(I)$), R1 = 0.0307, wR2 = 0.0758 (all data), GOF = 1.033, largest diff. peak and hole = 0.247 and –0.386 eÅ^{-3}. For **1** and **2**, the data frames were integrated and scaled using the DENZO-SMN package [14]. The structures were solved and refined, using the SHELXTL\PC V5.1 package [15]. Hydrogen atoms were included in calculated positions, except for those involving hydrogen bonding specifically for the hydrogen atoms of the water molecules and those bonded to the oxygen atoms of the carboxyl groups, which were refined with isotropic thermal parameters.

Results and discussion

The macrocyclic ligand **L1** in **1** and **2** adopts the classical *trans* III (*R,R,S,S*) conformation with both of the ethylene bridges replaced by *trans*-cyclohexane.

The ligand **L1** is one of the 16 possible diastereoisomers of **L**.

As illustrated in Fig. 1.1, the structure of **1** consists of an 1D coordination polymer with a basic {[Cu(**L1**)(μ-$O_2CCH=CHCO_2$)]·$6H_2O$} unit. The coordination environment around the central copper(II) ion shows a Jahn–Teller distorted octahedron in the chain direction with four Cu–N bonds and two Cu–O contacts. The four Cu–N distances are in the range 2.0190(10)–2.0235(9) Å and shorter than the Cu-O distance of 2.7295(9) Å. The long Cu–O interatomic distance of 2.7295(9) Å is comparable with that determined in the related [Cu(**L1**)(terephthalato)]$_n$·2$n$$H_2O$ (Cu-O = 2.7323 Å) system [12]. Such a long contact is maintained by hydrogen bonding interactions between secondary amines of the macrocycle and carboxylate groups of the fumarate ligand {N(1)-H(1N)···O(2)#1 = 2.8420(13) Å; N(2)-H(2N)···O(1) = 2.9583(13) Å}. Additional hydrogen bonding interactions are observed in **1** by an intervention of lattice water molecules (Fig. 1.1 and Table 1.2). As the macrocyclic ligand skeleton adopts the *trans* III conformation, the pre-organization of N–H directionality with its role in profacial selection of anion binding through hydrogen bonding interactions is achieved, and this may explain the long Cu–O contact. In addition, the axis along O(1)#1–Cu(1)–O(1) is not perpendicular to the macrocyclic four nitrogen plane, and tilts {N(2)–Cu(1)–O(1)=75.42(3)°} toward N(2)#1 and N(2) directions due to the aforementioned hydrogen bonding interactions.

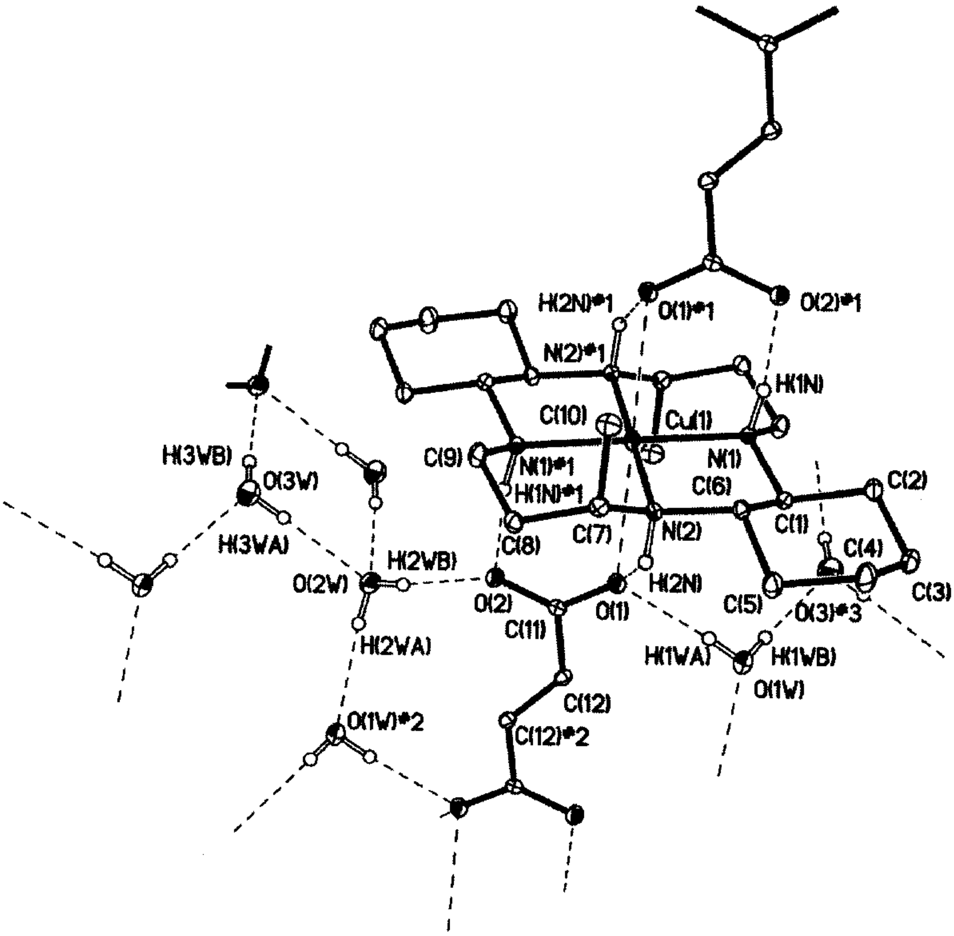


Fig. 1.1 Structure of **1** showing the numbering scheme. Hydrogen atoms other than those participating in hydrogen bonding are omitted for clarity.

Table 1.1

Selected bond lengths (Å) and angles (°) for $\{[Cu(\mathbf{L1})(O_2CCH{=}CHCO_2)]\cdot 6H_2O\}_n$ (**1**)

Cu(1)–N(1)	2.0235(9)
Cu(1)–N(2)	2.0190(10)
Cu(1)–O(1)	2.7295(9)
O(1)–C(11)	1.2674(14)
O(2)–C(11)	1.2567(15)
C(12)–C(12)#2	1.325(2)
N(2)#1–Cu(1)–N(2)	180.00(15)
N(2)#1–Cu(1)–N(1)	95.38(4)
N(2)–Cu(1)–N(1)	84.62(4)
N(1)–Cu(1)–N(1)#1	180.0
N(2)#1–Cu(1)–O(1)	104.58(3)
N(2)–Cu(1)-O(1)	75.42(3)
N(1)–Cu(1)-O(1)	96.34(3)
N(1)#1–Cu(1)–O(1)	83.66(3)
C(12)#2–C(12)–C(11)	123.32(14)

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

Table 1.2

Hydrogen bonds for **1** (Å and °)

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1N)...O(2)#1	0.93	1.92	2.8420(13)	170.9
N(2)-H(2N)...O(1)	0.93	2.34	2.9583(13)	123.4
O(1W)-H(1WA)...O(1)	0.79(2)	2.01(2)	2.8006(15)	176(2)
O(1W)-(1WB)...O(3W)#3	0.78(2)	2.12(2)	2.9062(19)	175(2)
O(2W)-(2WA)...O(1W)#2	0.78(2)	2.10(2)	2.8836(17)	175(2)
O(2W)-H(2WB)...O(2)	0.78(2)	2.04(2)	2.8143(15)	173(2)
O(3W)-H(3WA)...O(2W)	0.80(2)	2.07(2)	2.8640(17)	175(2)
O(3W)-(3WB)...O(2W)#4	0.84(3)	2.18(3)	3.0133(19)	176(2)

Symmetry transformations used to generate equivalent atoms: #1 -*x*+1,-*y*+1,-*z*+1; #2 -*x*+2,-*y*,-*z*+1; #3 *x*,*y*,*z*-1; #4 -*x*+1,-*y*,-*z*+2.

In **2** the copper atom is five-coordinate with bonds to the four secondary amine nitrogen atoms of the macrocyclic ligand and to the oxygen atom of the H_2bta^{2-} ligand (Fig. 1.2). The basic structure of the macrocyclic unit in **2** is similar to **1** with an average Cu–N interatomic distance of ~2.033 Å. However, the coordination environment about the copper(II) ion considerably is different from that of **1**, showing that the one end of the H_2bta^{2-} dianion is coordinated to the central copper atom while the other end remains free. The sixth axial site is vacant. The Cu(1)–O(1) distance of 2.2539(13) Å is ~15% longer than the other related Cu–O bonds. The average Cu–O distance of 1.966 ± 0.030 Å, determined for five structures, is found in a previous report [16]. The uncoordinated oxygen atoms of the carboxylate groups in the H_2bta^{2-} ligand are all involved in forming either inter- or intramolecular hydrogen bonds. The dianionic H_2bta^{2-} ligand in this molecule serves as two functions. One is as a coordinated axial ligand {Cu(1)–O(1); 2.2539(13) Å}, while the other is a counteranion to maintain the molecule as a charge-balanced species. Four carboxyl groups of the H_2bta^{2-} dianion are divided into three kinds by different bonding environments in **2**. The carboxyl group O(1)C(27)O(2) coordinates to Cu(1) with one oxygen atom O(1) in monodentate fashion. The uncoordinated oxygen atom O(2) acts as hydrogen bond acceptors {N(2)–H(2C)···O(2)=2.871(2) Å; O(1W)–H(1WA)···O(2) 2.754(2) Å}. The two C–O bonds in the carboxyl group O(1)C(27)O(2) are almost same

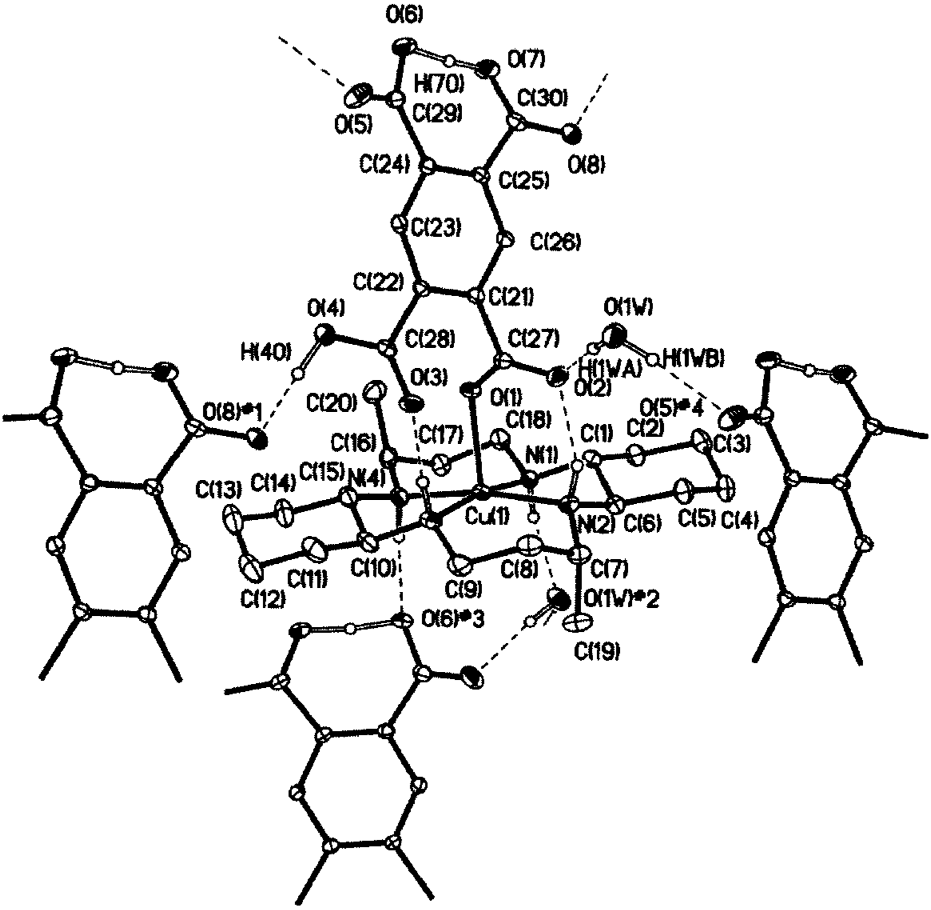


Fig. 1.2 Structure of **2** showing the numbering scheme. Hydrogen atoms other than those participating in hydrogen bonding are omitted for clarity.

Table 1.3

Selected bond lengths (Å) and angles (°) for Cu(**L1**)($C_6H_2(COO)_2(COOH)_2$)]·H_2O **(2)**

Cu(1)–N(1)	2.003(2)
Cu(1)–N(2)	2.042(2)
Cu(1)–N(3)	2.0396(19)
Cu(1)–N(4)	2.0470(19)
Cu(1)–O(1)	2.2539(13)
O(1)–C(27)	1.248(3)
O(2)–C(27)	1.245(3)
O(3)–C(28)	1.212(3)
O(4)–C(28)	1.317(3)
O(5)–C(29)	1.227(3)
O(6)–C(29)	1.309(3)
O(7)–C(30)	1.271(3)
O(8)–C(30)	1.233(3)
N(1)–Cu(1)–N(3)	171.48(8)
N(1)–Cu(1)–N(2)	84.49(6)
N(3)–Cu(1)–N(2)	95.42(8)
N(1)–Cu(1)–N(4)	93.94(8)
N(3)–Cu(1)–N(4)	84.57(8)
N(2)–Cu(1)–N(4)	169.41(8)
N(1)–Cu(1)–O(1)	99.85(7)
N(3)–Cu(1)–O(1)	88.71(7)
N(2)–Cu(1)–O(1)	95.27(7)
N(4)–Cu(1)–O(1)	95.31(7)

Table 1.4

Hydrogen bonds for **2** (Å and °)

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(4)-H(4O)...O(8)#1	0.96(5)	1.63(5)	2.571(2)	168(5)
O(6)-H(7O)...O(7)	1.19(5)	1.21(5)	2.388(3)	168(5)
N(1)-H(1B)...O(1W)#2	0.93	1.97	2.876(3)	164.9
N(2)-H(2C)...O(2)	0.93	2.00	2.871(2)	156.2
N(3)-H(3C)...O(3)	0.93	2.06	2.979(2)	169.8
N(4)-H(4C)...O(6)#3	0.93	2.12	3.044(2)	172.2
O(1W)-H(1WA)...O(2)	0.89(2)	1.87(2)	2.754(2)	176(3)
O(1W)-H(1WB)...O(5)#4	0.89(2)	1.95(2)	2.833(3)	175(3)

Symmetry transformations used to generate equivalent atoms:

#1 $x+1/2,y-1/2,z$; #2 $x,-y+1,z-1/2$; #3 $x+1/2,-y+1/2,z-1/2$: #4x+1/2,y+1/2,z.

with interatomic distances C(27)–O(1)=1.248(3) Å and C(27)–O(2)=1.245(3). The *ortho*-carboxyl group O(3)C(28)O(4) shows a carboxylic acid form. The C(28)–O(4) bond bearing the hydrogen atom is longer than the C(28)–O(3) bond {C(28)–O(3) = 1.212(3) Å and C(28)–O(4)=1.317(3)}. The *meta*- and *para*-carboxyl groups O(5)C(29)O(6) and O(7)C(30)O(8) lie under similar bonding environments caused by an intramolecular hydrogen bond between O(7) and O(6) {O(6)–H(7O)···O(7)=2.388(3) Å}. The hydrogen atom on the carboxylic group was found on O(7). Thus, the H_2bta^{2-} ligand in the present complex **2** exhibits a "coordinated ligand anion", which is supported by hydrogen bonding interactions. The pre-organized secondary amines, a lattice water molecule, and the H_2bta^{2-} dianion participate in the multiple hydrogen bonding interactions as hydrogen bond donors and/or acceptors (Fig. 1.2 and Table 1.4).

In summary, two compounds (**1** and **2**), based on the copper(II) macrocycles and the polycarboxylate ligands fumarate or H_2bta^{2-}, show different structural motifs. The [Cu(**L1**)]·2ClO$_4$–fumarate system affords the 1D copper(II) coordination polymer **1**, whereas the [Cu(**L1**)]·2ClO$_4$– H_4bta system gives the H_2bta^{2-} coordinated copper(II) mononuclear complex **2**. Although the 1D coordination polymer with the copper(II) macrocyclic ligand and the aliphatic polycarboxylate building blocks contains similar polymeric chains observed in [Cu(**L1**)(terephthalato)]$_n$·2nH$_2$O [12], there are considerable differences in the hydrogen bonding systems. Clearly, the hydrogen bonding interactions in **1** and **2** play an important role to determine the coordination geometries about the copper(II) ions.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center. (CCDC), CCDC No. 187093 for **1** and CCDC No. 187094 for **2**.

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CHAPTER II

Polymeric nickel(II) and copper(II) complexes with H_2bta^{2-} ions as bridging ligands (H_2bta^{2-} = 1,2,4,5-benzenetetracarboxylic acid dianion)

Abstract

Two new complexes of composition $\{[Ni(\mathbf{L2})(H_2bta^{2-})]\cdot 2H_2O\}_n$ (**1**) {**L2** = 1,4,8,11-tetraazacyclotetradecane} and $\{[Cu(\mathbf{L2})(H_2bta^{2-})]\cdot H_2O\}_n$ (**2**) were obtained by reacting $[Ni(\mathbf{L2})]\cdot 2ClO_4$ or $[Cu(\mathbf{L2})]\cdot 2ClO_4$ and H_2bta^{2-}, and their structures were determined by analytical, spectroscopic, and X-ray diffraction methods. The blue complex **1** and violet complex **2** consist of 1D polymeric chains with nickel(II) or copper(II) macrocycles and bridging H_2bta^{2-} ligands, respectively. In **1** the COO^- groups on the 1,4-positions of the H_2bta^{2-} ligand are coordinated to the central nickel(II) atom, but in **2** the COOH groups on the 1,5-positions of the H_2bta^{2-} ligand are involved in interacting with the central copper(II) atom through un unusual carbonyl coordination.

Introduction

Transition metal macrocyclic complexes with bridging aromatic polycarboxylate ligands have been shown to be good building blocks for the construction of coordination polymers and multi-dimensional supramolecular networks [1-8]. Among the various aromatic polycarboxylate ligands, H_2bta^{2-} is especially of interest because of its various coordination features toward the transition metal ions [7,9-10]. In previous studies, we reported that the carboxyl groups on the H_2bta^{2-} can induce versatile coordination modes with transition metal macrocyclic complexes and can act as hydrogen bond donors and/or acceptors through inter- and/or intramolecular fashion [11-13]. During our further investigation of the nickel(II) and copper(II) macrocyclic chemistry of H_2bta^{2-}, we have prepared and characterized novel 1D nickel(II) and copper(II) coordination polymers **1** and **2**. In **1** the COO^- groups on the 1,4-positions of the H_2bta^{2-} ligand coordinate to the central nickel(II) atom and the COOH groups on the 2,5-positions participate in the intermolecular hydrogen bonds. In **2**, however, the COOH groups on the 1,5-positions of the H_2bta^{2-} ligand are involved in interacting with the central copper(II) atom through an unusual carbonyl coordination. In both complexes, various types of hydrogen bonding interactions play an important role in reinforcing the metal - ligand ligations as well as in determining the shapes of the H_2bta^{2-} dianions. The details of the structures and properties of **1** and **2** are discussed in this report.

Experimental

Materials and Methods

All chemicals used in this work were of reagent grade and were used without further purification. Infrared spectra were measured as Nujol mulls between KBr plates using a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer over the 4000 and 400 cm^{-1} range. UV/Vis diffuse reflectance spectra using samples diluted with $BaSO_4$ were recorded with a Shimadzu 2401 PC UV-Vis recording spectrophotometer. Elemental analyses were performed by the Korea Research Institute of Chemical Technology, Taejon, Korea. The precursor complexes [Ni(**L2**)]$\cdot 2ClO_4$ and [Cu(**L2**)]$\cdot 2ClO_4$ were prepared according to the literature procedures previously reported [14].

Synthesis of **1** *and* **2**

To an aqueous (20 ml) solution of [Ni(**L2**)]$\cdot 2ClO_4$ (228 mg, 0.5 mmol) was added a methanol solution (20 ml) of 1,2,4,5-benzenetetracarboxylic acid (127 mg, 0.5 mmol). The mixture was allowed to stand in an open beaker at ambient temperatures. Blue crystals of **1** were obtained in a week. The violet crystals of **2** were obtained similarly using [Cu(**L2**)]·2ClO$_4$ instead of [Ni(**L2**)]·2ClO$_4$. Suitable crystals of **1** and **2** for X-ray diffraction studies and subsequent spectroscopic measurements were manually collected under the microscope. Anal. Calcd. for $C_{20}H_{32}N_4O_{10}Ni$ (**1**) : C, 43.86; H, 5.85; N, 10.23. Found C, 44.13; H, 6.04; N, 10.32 %. IR (Nujol, cm^{-1}) : 3456 (OH), 3278, 3170 (NH), 1706, 1580, 1398 (COO). UV/Vis (BaSO$_4$, λ_{max}, nm) : 368, 518, 675. Anal. Calcd. for $C_{20}H_{30}N_4O_9Cu$ (**2**) : C, 44.94; H, 5.62; N, 10.49. Found C, 45.11; H, 5.78; N, 10.58 %. IR (Nujol, cm^{-1}) : 3438 (OH), 3231, 3166 (NH), 1555, 1360 (COO). UV/Vis (BaSO$_4$, λ_{max}, nm) : 541.

Crystal data for **1** *and* **2**

Single crystals of **1** and **2** were prepared as described above. A crystal of dimensions 0.30 x 0.30 x 0.14 mm^3 for **1** (0.36 x 0.30 x 0.14 mm^3 for **2**) was employed for structural analysis at 150(1) K on a Nonius KappaCCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Crystal data for **1**: $C_{20}H_{32}N_4O_{10}Ni$, FW = 547.21, triclinic, space group P1, a =

8.5950(2), b = 8.7670(2), c = 9.2860(2) Å, α = 65.2180(14), β = 81.3610(12), γ = 75.2070(12)°, V = 613.48(2) Å^3, Z = 1, D_{calc} = 1.481 Mg/m^3. A total of 9021 reflections were measured, 2808 reflections were unique (R_{int} = 0.0547). μ = 0.851 mm^{-1}, $2.77 < \theta < 27.51$°, $-10 \leq h \leq 11$, $-11 \leq k \leq 11$, $-12 \leq l \leq 12$, R1 = 0.0324, wR2 = 0.0739 ($I > 2\sigma(I)$), R1 = 0.0353, wR2 = 0.0757 (all data), GOF = 1.074, largest diff. peak and hole = 0.340 and –0.541 eÅ^{-3}. Crystal data for **2**: $C_{20}H_{30}N_4O_9Cu$, FW = 534.02, triclinic, space group P-1, a = 9.5410(2), b = 9.6570(2), c = 14.6470(3) Å, α = 76.1970(9), β = 73.4770(9), γ = 61.8780(12)°, V = 1132.32(4) Å^3, Z = 2, D_{calc} = 1.566 Mg/m^3, A total of 13302 reflections were measured, 5180 reflections were unique (R_{int} = 0.0502). μ = 1.024 mm^{-1}, $2.56 < \theta < 27.50$°, $-12 \leq h \leq 12$, $-12 \leq k \leq 12$, $-19 \leq l \leq 19$, R1 = 0.0336, wR2 = 0.0865 ($I > 2\sigma(I)$), R1 = 0.0415, wR2 = 0.0911 (all data), GOF = 1.048, largest diff. peak and hole = 0.437 and –0.692 eÅ^{-3}. For **1** and **2**, the data frames were integrated and scaled using the DENZO-SMN package [15]. The structures were solved and refined, using the SHELXTL\PC V5.1 package [16]. Hydrogen atoms were included in calculated positions, except for those involving hydrogen bonding specifically for the hydrogen atoms bonded to the oxygen atoms of the carboxyl groups and water molecules and for the hydrogen atoms bonded to the nitrogen atoms of the secondary amines, which were refined with isotropic thermal parameters. In **2** the one of the carboxylate groups is disordered over two sites {C(19), O(5) and O(6)}. The disorder occurs because of rotation about the C(14)-C(19) bond.

Results and discussion

Descriptions of structures for **1** *and* **2**

As illustrated in Fig. 2.1, the structure of **1** consists of a 1D coordination polymer with a basic {[Ni(**L2**)(H_2bta^{2-})]·$2H_2O$} unit. The coordination environment around the central nickel(II) ion is described as a distorted octahedron with four Ni-N bonds from the macrocycle and two Ni-O bonds from the H_2bta^{2-} ligand. In **1** the Ni atom sits on an inversion center. The Ni-N bond distances are in the range 2.0586(15) - 2.0646(14). It is well understood 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) [17,18]. The Ni-O interatomic distance of 2.1722(10) Å is comparable to the previously reported values in the related systems {$[Ni(\mathbf{L2})(tp^{2-})]_n \cdot 4nH_2O$: Ni-O = 2.129(5) Å; $[Ni_2(\mathbf{L2})_2(tp^{2-})(H_2O)_2]\cdot(ClO_4)_2$: Ni-O = 2.106(4) and 2.125(4) Å, where tp^{2-} = terephthalate dianion; $[Ni(\mathbf{L2})(HOC_6H_4COO^-)_2]$: Ni-O = 2.1100(14) Å } [2,19,20].

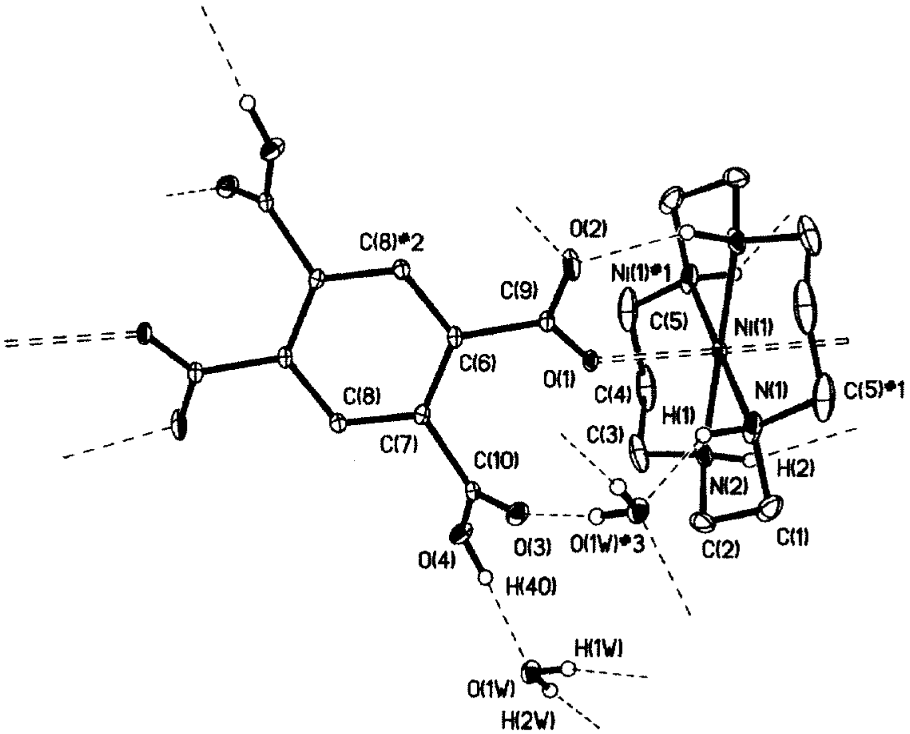


Fig. 2.1 The structure of $\{[\mathrm{Ni}(\mathbf{L2})(\mathrm{H_2bta^{2-}})]\cdot 2\mathrm{H_2O}\}_n$ **(1)** showing the numbering scheme. Hydrogen atoms other than those participating in hydrogen bonding are omitted for clarity.

Table 2.1

Selected interatomic distances (Å) and angles (°) for $\{[\mathrm{Ni}(\mathbf{L2})(\mathrm{H_2bta^{2-}})]\cdot 2\mathrm{H_2O}\}_n$ (**1**)

Ni(1)-N(1)	2.0586(15)
Ni(1)-N(2)	2.0646(14)
Ni(1)-O(1)	2.1722(10)
O(1)-C(9)	1.2551(18)
O(2)-C(9)	1.2553(19)
O(3)-C(10)	1.2136(19)
O(4)-C(10)	1.3139(18)
N(1)-Ni(1)-N(1)#1	180
N(1)#1-Ni(1)-N(2)#1	85.49(7)
N(1)-Ni(1)-N(2)#1	94.51(7)
N(2)#1-Ni(1)-N(2)	180
N(1)#1-Ni(1)-O(1)	89.68(5)
N(1)-Ni(1)-O(1)	90.32(5)
N(2)#1-Ni(1)-O(1)	93.36(5)
N(2)-Ni(1)-O(1)	86.64(5)

Symmetry transformations used to generate equivalent atoms:

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

In **1** the macrocyclic ligand skeleton adopts the well-known *trans* III conformation [1,21], thus, the preorganization of N-H directionality with its role in profacial selection of anion binding through hydrogen bonding interactions is achieved. Apart from the Ni-O bonds, two kinds of hydrogen bonds contribute to the formation of the polymer {N(2)-H(2)···O(2)#1 = 2.8379 (18) Å, N(1)-H(1)···O(1W)#3 = 3.0635 (19) Å, O(1W)-H(1W)···O(3)#3 = 2.7375 (16) Å; symmetry codes: #1 –x,-y,-z, #3 –x,-y-1,-z+1} (Fig. 2.1). In the H_2bta^{2-} anion in **1**, the carboxylate groups and carboxylic acid groups do not lie in the phenyl ring plane since the dihedral angle between the carboxylate and the aromatic ring {O(1)C(9)C(6)C(7)} is 35.5° and the dihedral angle between the carboxylic acid and the aromatic ring{O(3)C(10)C(7)C(6)} is 51.2°.

In the previous studies, we have shown that the diverse shapes of the H_4bta, H_3bta^{1-}, and H_2bta^{2-}, where the shapes vary with the degree of deprotonation and the types of hydrogen bonding systems [11-13]. The shape of the present H_2bta^{2-} anion may be comparable to that found in [Ni(**L3**)]·(H_2bta^{2-})·(H_4bta) {**L3** = 3,10-bis(2-hydroxyethyl)-1,3,5,8,10,12-hexaazacyclotetradecane} [12]. However, the coordination properties of the H_2bta^{2-} dianions toward the nickel(II) ions are totally different from each other, showing that the COO^- groups on the 1,4-positions of the H_2bta^{2-} ligand in **1** coordinate to the central nickel(II) ion to form

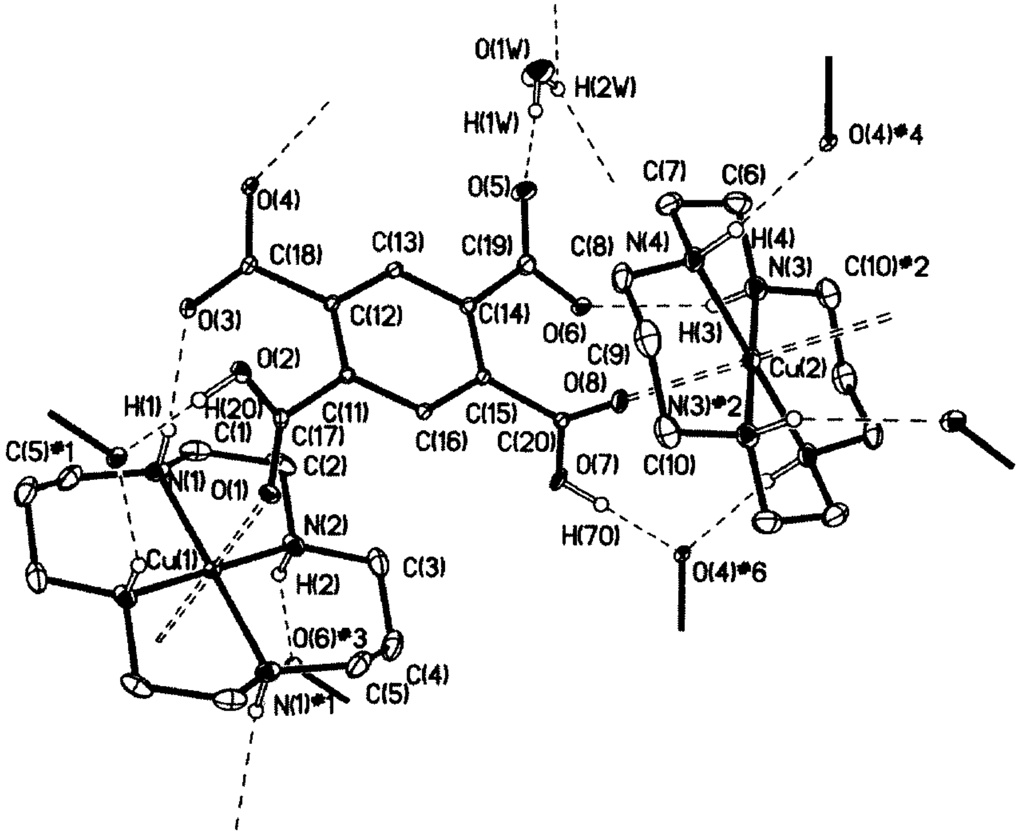


Fig. 2.2 The structure of {[Cu(**L2**)(H$_2$bta^{2-})]·H$_2$O}$_n$ (**2**) showing the numbering scheme. Hydrogen atoms other than those participating in hydrogen bonding are omitted for clarity.

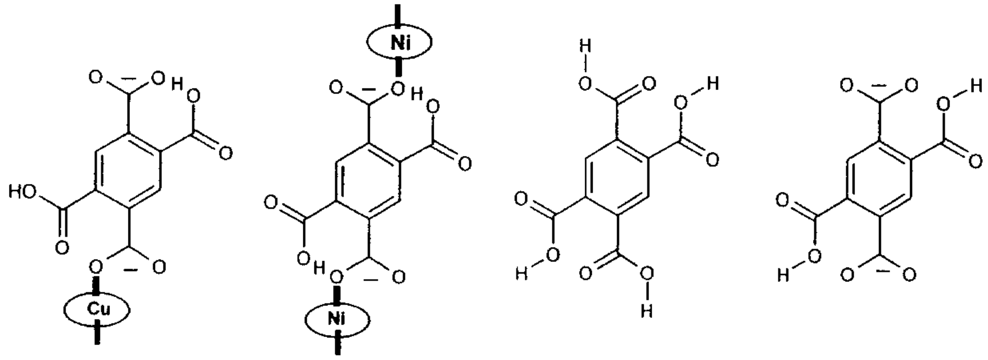
Table 2.2

Selected interatomic distances (Å) and angles (°) for $\{[\mathrm{Cu}(\mathbf{L2})(\mathrm{H_2bta}^{2-})]\cdot \mathrm{H_2O}\}_n$ (**2**)

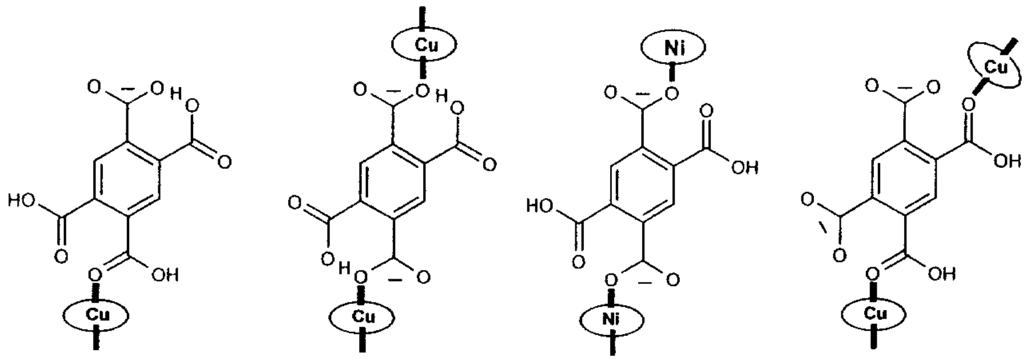
Cu(1)-N(1)	2.0065(16)
Cu(1)-N(2)	2.0318(16)
Cu(2)-N(3)	2.0224(17)
Cu(2)-N(4)	2.0240(16)
Cu(1)-O(1)	2.5274(13)
Cu(2)-O(8)	2.3844(12)
O(1)-C(17)	1.234(2)
O(2)-C(17)	1.288(2)
O(3)-C(18)	1.230(2)
O(4)-C(18)	1.287(2)
O(5)-C(19)	1.241(3)
O(6)-C(19)	1.277(4)
O(7)-C(20)	1.292(2)
O(8)-C(20)	1.218(2)
N(1)-Cu(1)-N(1)#1	180
N(1)-Cu(1)-N(2)#1	94.12(7)
N(1)-Cu(1)-N(2)	85.88(7)
N(2)#1-Cu(1)-N(2)	180
N(1)-Cu(1)-O(1)	90.73(5)
N(1)#1-Cu(1)-O(1)	89.27(5)
N(2)#1-Cu(1)-O(1)	78.07(5)
N(2)-Cu(1)-O(1)	101.93(5)
N(3)-Cu(2)-N(3)#2	180
N(3)-Cu(2)-N(4)	85.89(7)
N(3)-Cu(2)-N(4)#2	94.11(7)
N(3)-Cu(2)-O(8)	86.62(6)
N(4)-Cu(2)-O(8)	87.25(5)
N(3)-Cu(2)-O(8)#2	93.38(6)
N(4)-Cu(2)-O(8)#2	92.75(5)

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

a blue octahedral high-spin d^8 nickel(II) ion with the COOH groups on the 2,5-positions participating in the intermolecular hydrogen bonds. On the other hand, the H_2bta^{2-} dianion in $[Ni(\mathbf{L3})]\cdot(H_2bta^{2-})\cdot(H_4bta)$ is not involved in interacting with the central nickel(II) ion resulting in the formation of a yellow square-planar low-spin d^8 nickel(II) ion (Chart 1).



btc^{2-} in ref 11 **btc^{2-} in ref 12** **btc in ref 12** **btc^{2-} in ref 12**



btc^{-} in ref 13 **btc^{2-} in ref 13** **this work** **this work**

Chart 1. Versatility of H_2bta^{2-} and their moieties in coordination, hydrogen bonding, and the degree of deprotonation.

In **2** there are two half copper(II) complexes (each of which have crystallographic inversion symmetry), one H_2bta^{2-} counter ion, and one molecule of water in the asymmetric unit. All these species participate in the formation of a 1D undulated polymer **2** (Fig. 2.2). The basic structure of each macrocyclic unit in **2** is similar to each other with an average Cu-N interatomic distances of ~ 2.019 and 2.023 Å. However, there is a slight difference between the two Cu-O interatomic distances {Cu(1)-O(1) = 2.5274(13), Cu(2)-O(8) = 2.3844(12) Å}. Two structurally important features are found in **2**. One is a carbonyl coordination of the carboxylic acid groups of the H_2bta^{2-} to the copper(II) ions. Carbonyl coordination to the copper(II) ion is rare and unusual. The reported copper(II)-carbonyl oxygen atom distances are 2.444(8) and 2.453(8) Å by Colacio et al. [22] and 2.4814(11) Å by Kim et al. [13], respectively. Most of our recent studies on the macrocyclic nickel(II) and copper(II) complexes with H_2bta^{2-} ligands indicate that the COO^- groups favorably interact with metal ions than the COOH groups. Another one is an involvement of 1,5-COOH groups rather than 1,4-COO^- groups of the H_2bta^{2-} ligand to the copper(II) ions in coordination resulting in the formation of the undulated 1D coordination polymer (Chart 1). To our best knowledge, this is the first example of the H_2bta^{2-} ligand which preferably coordinates to the copper(II) ions through 1,5-COOH groups. As is usual, the H_2bta^{2-} is not planar with all four carboxyl groups deviating from the aromatic ring {O(8)C(20)C(15)C(14) = 83.1°, O(2)C(17)C(11)C(12) = -52.2°, O(3)C(18)C(12)C(11) = -37.8°, O(5)C(19)C(14)C(13) = 32.3°}. The participation of 1,5-COOH groups in coordination and the non-planarity of the H_2bta^{2-} in **2** are believed to facilitate the inter-molecular hydrogen bonding interactions. Again, the macrocyclic ligand skeleton in **2** retains the *trans* III conformation with preorganized N-H directionality which makes it easier to interact with the H_2bta^{2-} in the proface through intermolecular hydrogen bonding interactions {N(1)-H(1)···O(3) = 2.950(2) Å, N(3)-H(3)···O(6) = 3.47 (3) Å} (Fig. 2.2). The hydrogen bonding interactions in **1** and **2** play an important role in determining the whole structures of the molecules as well as the coordination geometries about the metal ions and the shapes of the H_2bta^{2-} dianions. As is usual in the coordination polymers and supramolecules, the complexes **1** and **2** are insoluble in common solvents such as methanol, water, acetonitrile, and DMF, etc.

Supplementary material

Crystallographic data have been deposited at the Cambridge Crystallographic Data Center (CCDC), CCDC Nos. 200348 for **1** and 200347 for **2**.

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CHAPTER III

Polymeric, dimeric, and monomeric zinc(II) tetraaza macrocyclic complexes formed with $[Zn(\mathbf{L2})(ClO_4)]\cdot ClO_4$ and organic polycarboxylate ligands

Abstract

Four new zinc(II) complexes of the composition $\{[Zn(\mathbf{L2})(tp^{2-})]\cdot H_2O\}_n$ (**1**), $\{[Zn(\mathbf{L2})(H_2bta^{2-})]\cdot 2H_2O\}_n$ (**2**), $[Zn_2(\mathbf{L2})_2(ox^{2-})]\cdot 2ClO_4\cdot 2DMF$ (**3**), and $[Zn(\mathbf{L2})(H_2btc^{-})_2]\cdot 2DMF$ (**4**), where **L2** = 1,4,8,11-tetraazacyclotetradecane (cyclam), tp^{2-} = terephthalic acid dianion, H_2bta^{2-} = 1,2,4,5-benzenetetracarboxylic acid dianion, ox^{2-} = oxalic acid dianion, DMF = N,N-dimethylformamide, H_2btc^{-} = 1,3,5-benzenetricarboxylic acid anion, have been synthesized and structurally characterized by a combination of analytical, spectroscopic and crystallographic methods. The structures of (**1**) and (**2**) show one-dimensional coordination polymers in which each zinc ion is bridged by the tp^{2-} or H_2bta^{2-} anion, respectively. In the complex (**3**), the oxalate anion bridges two macrocyclic zinc cations $[Zn(\mathbf{L2})]^{2+}$ to form a dimer. The compound (**4**) is

made up of a macrocyclic zinc cation $[Zn(\mathbf{L2})]^{2+}$ and two H_2btc^- anions, where the H_2btc^- anions occupy trans sites at the zinc(II) ion.

Introduction

In recent years many interests have been focused on the design and synthesis of low dimensional coordination polymers constructed by the reaction of metal ions with multifunctional ligands such as polycarboxylates owing to their intriguing structural features and potential applications [1-10]. The bridging ligand is one of the important factors that influence the structures of the coordination polymers. Multidentate polycarboxylate anions such as terephthalate [6,7], 1,2,4,5-benzenetetracarboxylate [5,10], 1,3,5-benzenetricarboxylate [4], and oxalate [10,11] are well-known versatile ligands able to chelate and bridge metal ions leading to the formation of polynuclear systems. In particular, polyaza macrocyclic complexes with multi-connecting ligands have been proved to be good building blocks for the construction of coordination polymers and multi-dimensional supramolecular networks [4,7,12]. In this context, the $[Zn(\mathbf{L2})]^{2+}$ cation and polycarboxylate anions could be attractive building blocks for the construction of coordination polymers or supramolecular networks, in that there is a macrocyclic skeleton with rigid coordination sites and pre-organized arrangement of N-H directionality. In this contribution we report the results of a systematic study of macrocyclic zinc(II) carboxylato complexes in which the X-ray diffraction studies reveal polymeric, dimeric, and monomeric zinc(II) structures, $\{[Zn(\mathbf{L2})(tp^{2-})]\cdot H_2O\}_n$ (**1**), $\{[Zn(\mathbf{L2})(H_2bta^{2-})]\cdot 2H_2O\}_n$ (**2**), $[Zn_2(\mathbf{L2})_2(ox^{2-})]\cdot 2ClO_4\cdot 2DMF$ (**3**), and $[Zn(\mathbf{L2})(H_2btc^{-})_2]\cdot 2DMF$ (**4**) synthesized from the reactions between $[Zn(\mathbf{L2})(ClO_4)]\cdot ClO_4$ and various organic polycarboxylate ligands.

Experimental

Materials and methods

All chemicals used in this work were of reagent grade and were used without further purification. Infrared 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}. Elemental analyses were performed by the Korea Research Institute of Chemical Technology, Taejon, Korea. Suitable crystals of (**1**) – (**4**) for X-ray diffraction studies and subsequent spectroscopic measurements were manually collected under the microscope. *Caution: The perchlorate salts used in this study are potentially explosive and should be handled in small quantities.*

Synthesis of $[Zn(\mathbf{L2})ClO_4]\cdot ClO_4$

A solution of $Zn(ClO_4)_2\cdot 6H_2O$ (3.717 g, 9.98 mmol) in methanol (20 cm^3) was added to a solution of **L2** (2 g, 9.98 mmol) dissolved in methanol (30 cm^3). The reaction mixture was refluxed for 1 h and then cooled to room temperature. A white precipitate was obtained, which was filtered-off, washed with methanol and finally air-dried. Microanalytical results and i.r. spectra indicate that the formula of the white precipitate agrees with the formula $[Zn(\mathbf{L2})ClO_4]\cdot ClO_4$. Anal. Calcd. for $C_{10}H_{24}N_4Cl_2O_8Zn$: C, 25.84; H, 5.17; N, 12.06. Found C, 26.17; H, 5.18; N, 11.97 %. IR (Nujol, cm^{-1}): 3268 (NH), ~1117 (ClO_4), ~1090 (ClO_4).

Synthesis of $\{[Zn(\mathbf{L2})(tp^{2-})]\cdot H_2O\}_n$ (**1**)

To a DMF (10 cm^3) solution of $[Zn(\mathbf{L2})ClO_4]\cdot ClO_4$ (166 mg, 0.357 mmol) was added dropwise an aqueous solution (10 cm^3) of 1,4-benzenedicarboxylic acid disodium salt (75 mg, 0.357 mmol). The solution was allowed to stand at room temperature for several days until transparent rod crystals formed. Anal. Calcd. for $C_{18}H_{30}N_4O_5Zn$ (**1**): C, 48.23; H, 6.70; N, 12.50. Found C, 48.38; H, 6.83; N, 12.45 %. IR (Nujol, cm^{-1}): 3391 (OH), 3234, 3173 (NH), 1573, 1370 (COO).

Synthesis of $\{[Zn(\mathbf{L2})(H_2bta^{2-})]\cdot 2H_2O\}_n$ (**2**)

To a DMF (10 cm^3) solution of $[Zn(\mathbf{L2})ClO_4]\cdot ClO_4$ (166 mg, 0.357 mmol) was added dropwise a DMF solution (10 cm^3) of 1,2,4,5-benzenetetracarboxylic acid (91 mg, 0.357 mmol). The solution was allowed to stand at room temperature for several days until transparent cubic crystals formed. Anal. Calcd. for $C_{20}H_{32}N_4O_{10}Zn$ (**2**): C, 43.33; H, 5.78; N, 10.11. Found C, 43.74; H, 5.81; N, 10.09 %. IR (Nujol, cm^{-1}): 3449 (OH), 3224, 3164 (NH), 1693, 1572, 1340, 1310 (COO).

Synthesis of $[Zn_2(\mathbf{L2})_2(ox^{2-})]\cdot 2ClO_4\cdot 2DMF$ (**3**)

To a DMF (10 cm^3) solution of $[Zn(\mathbf{L2})ClO_4]\cdot ClO_4$ (166 mg, 0.357 mmol) was added dropwise an aqueous solution (10 cm^3) of potassium oxalate monohydrate (66 mg, 0.357 mmol). The solution was allowed to stand at room temperature. Hexagonal plate crystals were obtained in several days. Anal. Calcd. for $C_{28}H_{62}N_{10}O_{14}Cl_2Zn_2$ (**3**): C, 34.84; H, 6.42; N, 14.51. Found C, 35.20; H, 6.44; N, 14.44 %. IR (Nujol, cm^{-1}): 3270, 3250 (NH), 1633, 1313, 790 (COO), 1095 (ClO_4).

Synthesis of $[Zn(\mathbf{L2})(H_2btc^-)_2]\cdot 2DMF$ (**4**)

To a DMF (10 cm^3) solution of $[Zn(\mathbf{L2})ClO_4]\cdot ClO_4$ (166 mg, 0.357 mmol) was added dropwise a DMF solution (10 cm^3) of 1,3,5-benzenetricarboxylic acid (75 mg, 0.357 mmol). The solution was allowed to stand at room temperature for several days until transparent rod crystals formed. Anal. Calcd. for $C_{34}H_{48}N_6O_{14}Zn$ (**4**): C, 49.15; H, 5.78; N, 10.12. Found C, 49.07; H, 5.78; N, 10.03 %. IR (Nujol, cm^{-1}): 3450 (OH), 3248, 3169 (NH), 1703, 1622, 1557 (COO).

X-ray crystallography

A summary of selected crystallographic data for (**1**) – (**4**) is given in Table 3.1. X-ray data were collected on a Nonius KappaCCD diffractometer, using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). 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 [13]. The structures were solved and refined, using the SHELXTL\PC V5.1 package [14]. 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 carboxyl groups and those bonded to the nitrogen atoms, which were refined with isotropic thermal parameters.

Results and discussion

The structure of (**1**) consists of a one-dimensional coordination polymer with a basic [Zn(**L2**)(tp^{2-})] unit (Fig. 3.1). The coordination environment around the central zinc(II) ion shows a slightly distorted octahedron in the chain direction with four Zn-N and two Zn-O bonds. The Zn atom sits on an inversion center. The four Zn-N distances are in the range 2.1083(15)-2.1114(15) Å and the Zn-O distances are 2.1559(12) Å. The Zn-O distance of 2.1559(12) Å is slightly longer than those found in non-macrocyclic systems {[Zn(tp^{2-})(H_2O)$_2$]$_n$; Zn-O = 2.011(2) Å, ([Zn(2,2'-bpy)(1,2-tp^{2-})(H_2O)]$_n$; Zn-O = 2.025(5) Å) [6,15], possibly due to the steric hindrance of the macrocyclic ligand. Selected interatomic distances and angles for (**1**) are listed in Table 3.2. One of the pertinent structural features found in (**1**) is the pre-organization of N-H groups of the macrocycle with its role in profacial selection of tp^{2-} anion binding through hydrogen bonding interactions (N(1)-H(1)···O(2) = 2.971(2) Å). Similarly to other macrocyclic-tp^{2-} system [7], there are two different series of one-dimensional coordination polymers running

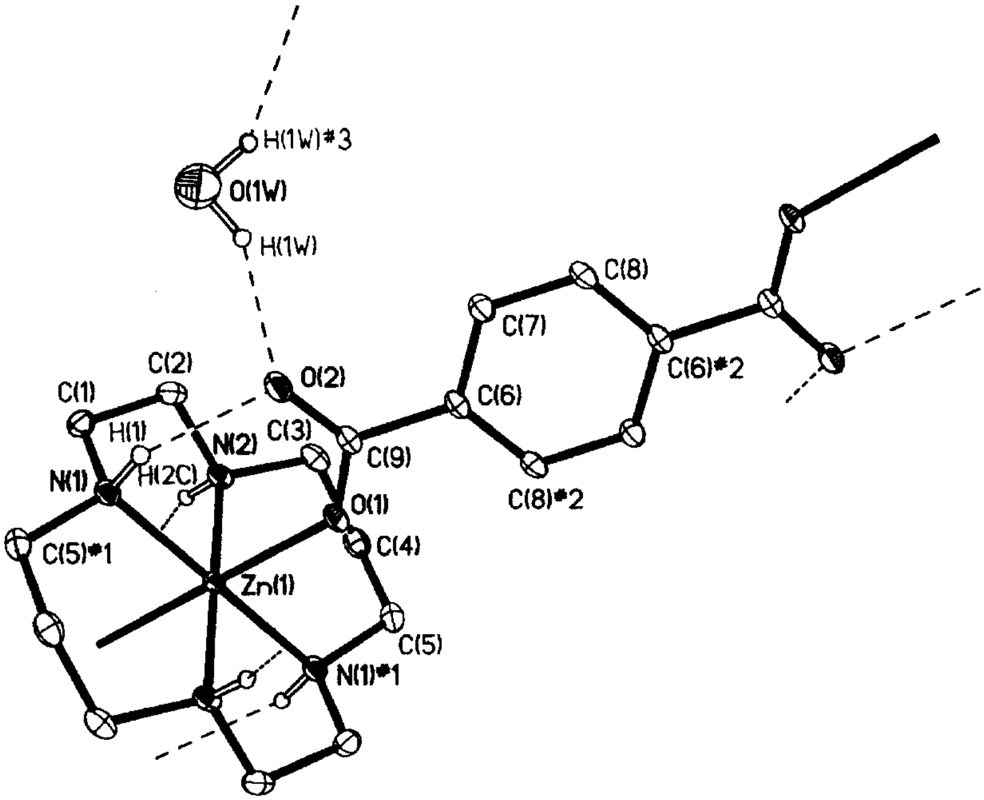

Fig. 3.1 Molecular structure of (**1**) with atom-labeling scheme. Hydrogen atoms other than those participating in hydrogen bonding are omitted for clarity.

toward different directions in (**1**). The two different chains are interconnected by water molecules through hydrogen bonding interactions (O(1W)-H(1W)···O(2) = 2.857(2) Å), resulting in the formation of an ultimate three-dimensional network.

In (**2**) the basic coordination pattern of the anion toward the zinc(II) is very similar to that in (**1**). The polymeric one-dimensional chain is formed toward the axial direction of the $[Zn(\mathbf{L2})]^{2+}$ cation (Fig. 3.2). The Zn-O distance of 2.2839(14) Å is even longer than that observed in (**1**). It seems that the increased steric hindrance by the introduction of two more carboxyl groups in the H_2bta^{2-} anion prevents the anion from approaching closely to the zinc(II) macrocycle. Selected interatomic distances and angles for (**2**) are listed in Table 3.2. Apart from the Zn-O bonds in (**2**), the hydrogen bond between the pre-organized N-H groups of the macrocycle and the COO^- of the H_2bta^{2-} contributes to the formation of a polymer (N(1)-H(1)···O(2)#1 = 2.876 (2) Å, symmetry codes: #1 –x+1,-y+1,-z+1). The salient structural feature of (**2**) is the observation of only a single series of one-dimensional coordination polymers running toward the crystallographic c directions, as described earlier the two different series of coordination polymers running toward different directions were observed in (**1**). Water molecules mediate in interconnecting each polymeric chain through hydrogen bonding interactions to form two-dimensional plane in (**2**). The shape of the H_2bta^{2-} anion

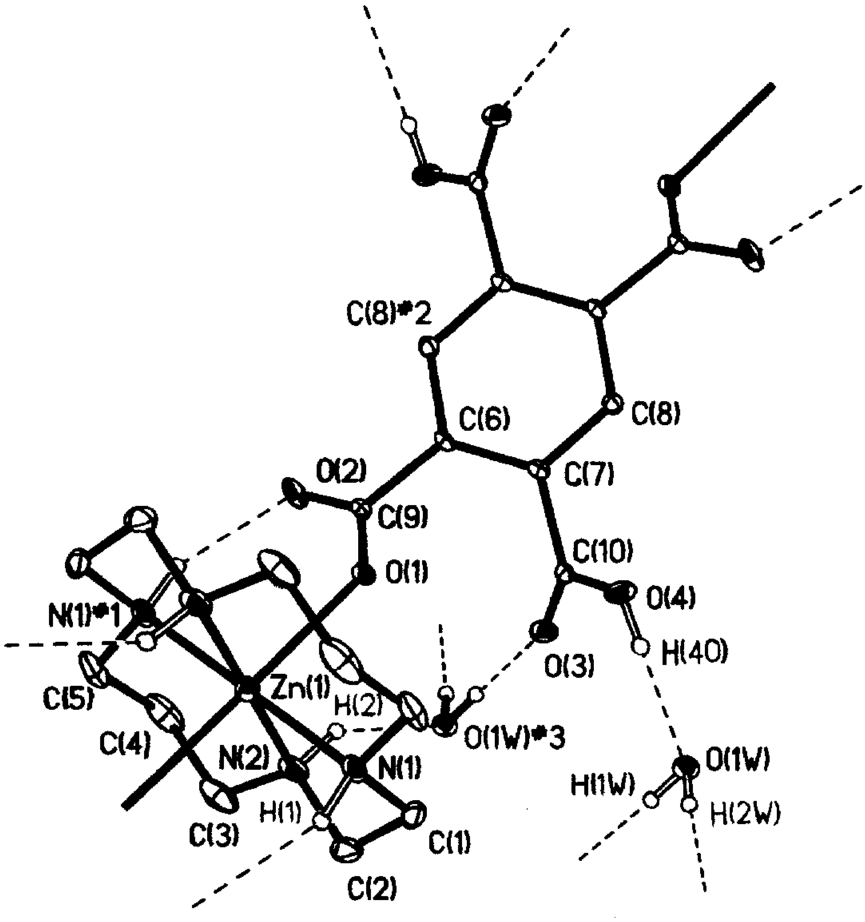

Fig. 3.2 Molecular structure of (2) with atom-labeling scheme. Hydrogen atoms other than those participating in hydrogen bonding are omitted for clarity.

resembles to that found in [Ni(**L1**)]·(H_2bta^{2-})·(H_4bta) {**L1** = 3,10-bis(2-hydroxyethyl)-1,3,5,8,10,12-hexaazacyclotetradecane} [16]. As is often the examples [12,17,18], the carboxylate groups and carboxylic acid groups of the present H_2bta^{2-} anion do not lie in the phenyl ring plane since the dihedral angle between the carboxylate and the aromatic ring {O(1)C(9)C(6)C(7)} is 31.8° and the dihedral angle between the carboxylic acid and the aromatic ring {O(3)C(10)C(7)C(6)} is 54.2°. In the recent studies, we have reported various shapes of the H_4bta, H_3bta$^-$, and H_2bta^{2-}, where the shapes vary with the degree of deprotonation and the types of hydrogen bonding systems [8].

The structure of (**3**) consists of binuclear [Zn_2(**L2**)$_2$(ox^{2-})]$^{2+}$ cations which are hydrogen bonded to perchlorate anions and solvent DMF molecules. There is a crystallographic inversion center at the middle of point of the C(11)-C(11)#1 (#1 = -x+1,-y+1,-z+1) bond of the bridging oxalate ion. A view of the molecule is shown in Fig. 3.3. Selected interatomic distances and angles are listed in Table 3.2. The coordination environment around the zinc(II) ion is described as a distorted octahedron with four nitrogen atoms from the macrocycle and two oxygen atoms from the bridging oxalate ion. In (**3**) the macrocyclic ligand skeleton adopts a folded *cis* conformation in a manner observed in *cis*-[Ni_2(**L2**)$_2$(μ-ox^{2-})]·2NO_3 and [(Ni**L3**)$_2$(μ-ox^{2-})]·2ClO_4 [11,19], showing the *RRRR* set of nitrogen configurations.

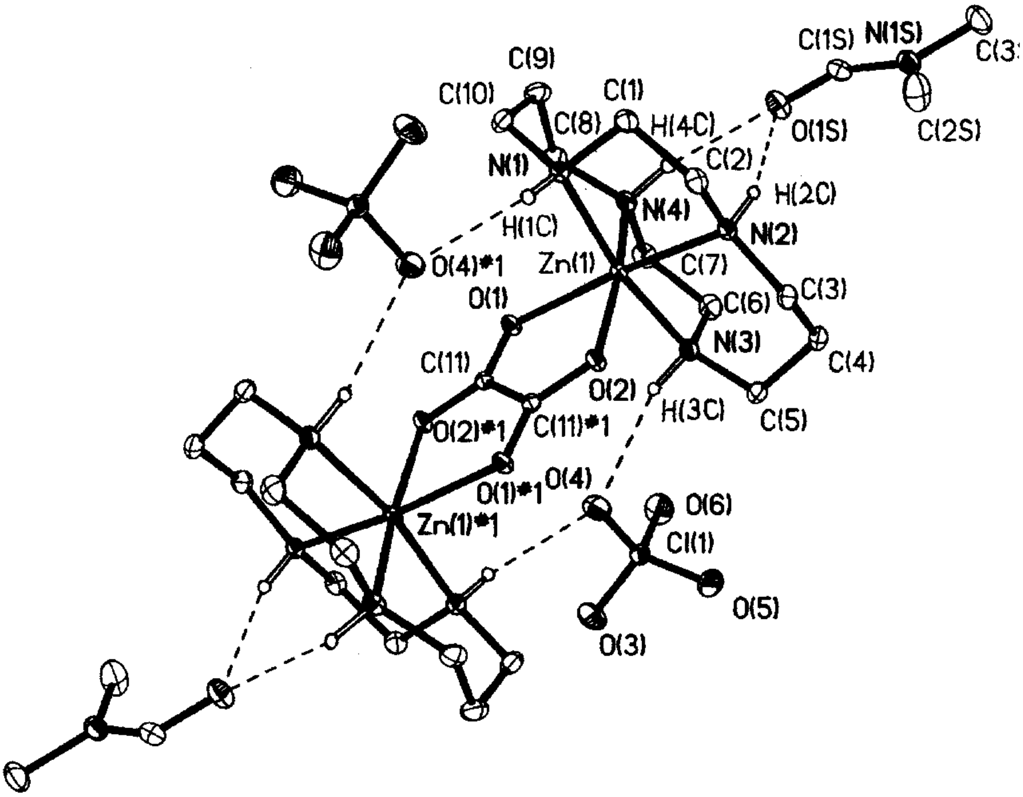

Fig. 3.3 Molecular structure of (**3**) with atom-labeling scheme. Hydrogen atoms other than those participating in hydrogen bonding are omitted for clarity.

The four Zn-N distances of 2.1429(14) – 2.1658(14) Å in (**3**) are slightly longer than the values found in *trans* zinc(II) complexes {Table 3.2 and [Zn(**L4**)X_2], **L4** = 2,5,9,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane; Zn-N = 2.096(5), 2.092(4) Å (X = H_2O); Zn-N = 2.111(3), 2.099(3) Å (X = N_3^-); Zn-N = 2.088(5), 2.098(4) Å (X = NCS^-)} [20]. The two Zn-O distances of 2.1175(11) and 2.1397(11) are slightly shorter than those found in a related macrocyclic *trans* zinc(II) system {*catena*-(μ-CrO_4-*O,O'*)[Zn(**L5**)Zn(**L4**)]·$3H_2O$ **L5** = 3,5,10,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane; Zn-O = 2.175(2), 2.402(2) Å} [21]. Apart from the bridging oxalate ligand, two ClO_4^- anions play a role in mediating the two macrocycles by weak hydrogen bonds (N(1)-H(1C)···O(4)#1 = 3.0572(19), N(3)-H(3C)···O(4) = 3.1092(19) Å; #1 –x+1,-y+1,-z+1). The four N-H groups in (**3**) are also pre-organized, however, the patterns of the pre-organization observed in (**3**) are different from those observed in (**1**), (**2**) and (**4**) as the macrocycle is folded. The two hydrogen atoms on nitrogen atoms N(1) and N(3) as hydrogen bond donors face to the oxygen atoms of perchlorate anions, and the remaining two hydrogen atoms on N(2) and N(4) face to the oxygen atoms of solvent DMF molecules, assisting in the formation of an ultimate dimeric compound (**3**).

The structure of (**4**) consists of $[Zn(\mathbf{L2})]^{2+}$ cation, two H_2btc^- anions, solvent DMF molecules. In (**4**), the coordination geometry around the zinc(II) ion reveals

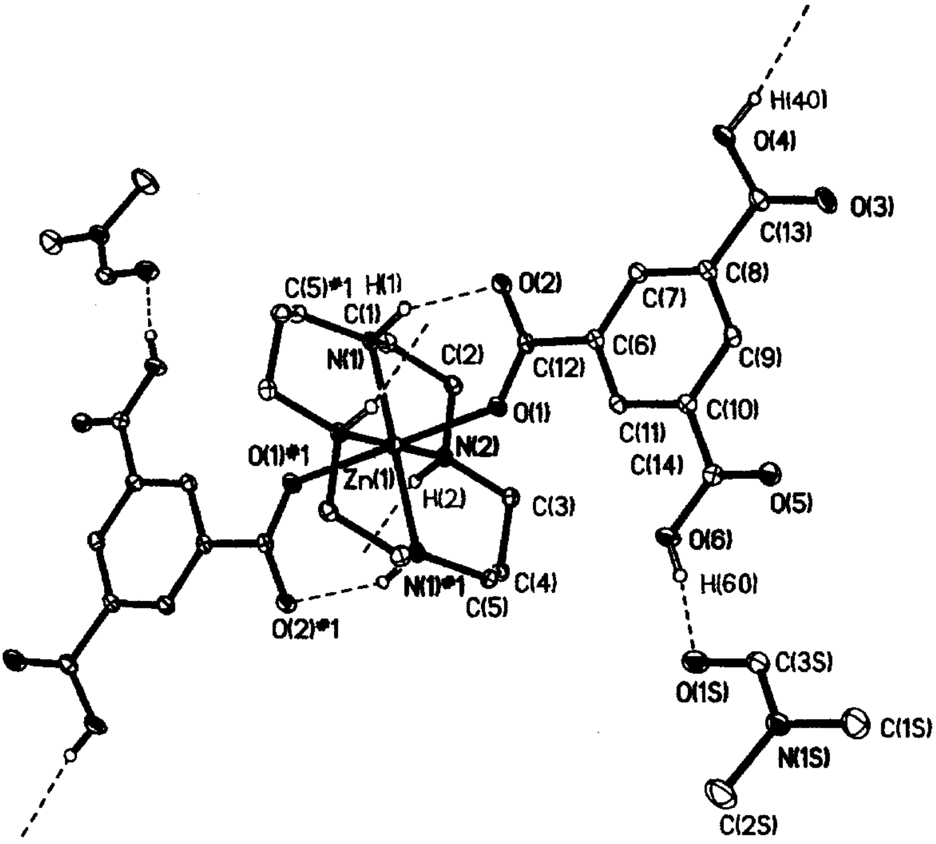

Fig. 3.4 Molecular structure of (**4**) with atom-labeling scheme. Hydrogen atoms other than those participating in hydrogen bonding are omitted for clarity.

a six-coordinated axially distorted octahedron with four nitrogen atoms from the macrocycle and two oxygen atoms from the carboxylate groups of H_2btc^- anions. An inversion center exists on the central zinc(II) ion. Fig. 3.4 shows a drawing of (**4**) with the atom labeling scheme. Selected interatomic distances and angles are listed in Table 3.2. The Zn-O distance of 2.2222(12) Å and the Zn-N distances of 2.0923(16) – 2.1128(15) Å are normal and fall on those found in such complexes [21]. The macrocyclic ligand adopts a type-III configuration with the appropriate *RRSS* arrangement of the four chiral nitrogen centers. The H_2btc^- anion is always involved in the formation of the complex (**4**) although an acid form H_3btc is used during the synthesis. Two sets of N-H are observed in (**4**) and each set participates in the formation of hydrogen bonding interactions as hydrogen bond donors.

The crystals (**1**) – (**4**) retain their transparency for several weeks in a refrigerator, but they lose solvent molecules in a couple of days upon exposure to the atmosphere as evidenced by elemental analyses.

Table 3.1 Crystal data and details of structural determinations for **(1)** – **(4)**

	(1)	(2)
Empirical formula	C18 H30 N4 O5 Zn	C20 H32 N4 O10 Zn
Formula weight	447.83	553.87
Temperature	150(1) K	150(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic
Space group	C2/c	P1
Unit cell dimensions	a = 16.3442(5) Å	a = 8.5540(3) Å
	b = 16.2092(6) Å	b = 8.7040(3) Å
	c = 8.9481(3) Å	c = 9.4100(4) Å
	β = 119.435(2)°	α = 64.9920(12)°
		β = 82.6640(13)°
		γ = 75.7960(14)°
Volume	2064.58(12) $Å^3$	615.29(4) $Å^3$
Z	4	1
Calculated density	1.441 Mg/m^3	1.495 Mg/m^3
Absorption coefficient	1.226 mm^{-1}	1.059 mm^{-1}
F(000)	944	290
Crystal size (mm)	0.30 x 0.20 x 0.20	0.20 x 0.12 x 0.06
θ range for data collection	2.60-27.48°	2.64-27.52°
Index range	$-21 \leq h \leq 20$, $-21 \leq k \leq 21$,	$-10 \leq h \leq 11$, $-10 \leq k \leq 11$,
	$-10 \leq l \leq 11$	$-12 \leq l \leq 12$
Reflections collected	7841	5213
Independent reflections	2364 [R(int) = 0.0384]	2662 [R(int) = 0.0534]
Completeness to θ = 27.45°	99.6 %	93.7 %
Data / restraints / parameters	2364 / 0 / 134	2662 / 0 / 172
Goodness-of-fit on F^2	1.047	1.082
Final R indices [I>2sigma(I)]	R1 = 0.0307, wR2 = 0.0777	R1 = 0.0375, wR2 = 0.0875
R indices (all data)	R1 = 0.0414, wR2 = 0.0838	R1 = 0.0487, wR2 = 0.0959
Largest diff. peak and hole	0.426 and -0.476 e .$Å^{-3}$	0.364 and -0.713 e. $Å^{-3}$

Table 3.1 Continued

	(3)	(4)
Empirical formula	C28 H62 Cl2 N10 O14 Zn2	C34 H48 N6 O14 Zn
Formula weight	964.52	830.15
Temperature	150(1) K	150(1) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/n	P2(1)/n
Unit cell dimensions	a = 13.2202(2) Å	a = 8.41700(10) Å
	b = 12.0175(2) Å	b = 20.7650(4) Å
	c = 13.3587(2) Å	c = 11.3520(2) Å
	β = 103.8190(10)°	β = 110.7621(10)°
Volume	2060.92(6) Å^3	1855.24(5) Å^3
Z	2	2
Calculated density	1.554 Mg/m^3	1.486 Mg/m^3
Absorption coefficient	1.367 mm^{-1}	0.739 mm^{-1}
F(000)	1012	872
Crystal size (mm)	0.40 x 0.40 x 0.35	0.22 x 0.20 x 0.16
θ range for data collection	2.58 to 27.49°	2.62 to 27.45°
Index range	$-17 \le h \le 16$, $-15 \le k \le 14$, $-17 \le l \le 17$	$-10 \le h \le 10$, $-26 \le k \le 26$, $-14 \le l \le 14$
Reflections collected	16540	17072
Independent reflections	4706 [R(int) = 0.0447]	4225 [R(int) = 0.0674]
Completeness to θ = 27.45°	99.4 %	99.7 %
Data / restraints / parameters	4706 / 0 / 256	4225 / 0 / 261
Goodness-of-fit on F^2	1.055	1.045
Final R indices [I>2sigma(I)]	R1 = 0.0287, wR2 = 0.0706	R1 = 0.0383, wR2 = 0.0903
R indices (all data)	R1 = 0.0343, wR2 = 0.0737	R1 = 0.0545, wR2 = 0.0974
Largest diff. peak and hole	0.383 and -0.491 e. Å^{-3}	0.374 and -0.670 e. Å^{-3}

Table 3.2 Selected bond distances (Å) and angles (°) for (**1**) – (**4**)

(1)		(2)	
Bond distances		Bond distances	
Zn(1)-N(1)	2.1083(15)	Zn(1)-N(1)	2.0971(19)
Zn(1)-N(2)	2.1114(15)	Zn(1)-N(2)	2.0978(19)
Zn(1)-O(1)	2.1559(12)	Zn(1)-O(1)	2.2839(14)
O(1)-C(9)	1.260(2)	O(1)-C(9)	1.247(3)
O(2)-C(9)	1.260(2)	O(2)-C(9)	1.255(3)
		O(3)-C(10)	1.209(3)
		O(4)-C(10)	1.316(3)
Bond angles		Bond angles	
N(1)-Zn(1)-N(1)#1	180	N(1)-Zn(1)-N(1)#1	180
N(1)-Zn(1)-N(2)	85.35(6)	N(1)-Zn(1)-N(2)	85.47(8)
N(1)#1-Zn(1)-N(2)	94.65(6)	N(1)#1-Zn(1)-N(2)	94.53(8)
N(1)-Zn(1)-O(1)	92.14(6)	N(1)-Zn(1)-O(1)	87.54(6)
N(1)#1-Zn(1)-O(1)	87.86(6)	N(1)-Zn(1)-O(1)#1	92.46(6)
N(2)-Zn(1)-O(1)	92.60(5)	N(2)-Zn(1)-O(1)#1	89.22(7)
N(2)#1-Zn(1)-O(1)	87.40(5)	N(2)-Zn(1)-O(1)	90.78(7)
O(1)-Zn(1)-O(1)#1	180	O(1)-Zn(1)-O(1)#1	180
#1 –x+1/2, -y+1/2, -z+1		#1 –x+1, -y+1, -z+1	

Table 3.2 Continued

(3)		(4)	
Bond distances		Bond distances	
Zn(1)-N(1)	2.1598(14)	Zn(1)-N(1)	2.0923(16)
Zn(1)-N(2)	2.1490(13)	Zn(1)-N(2)	2.1128(15)
Zn(1)-N(3)	2.1429(14)	Zn(1)-O(1)	2.2222(12)
Zn(1)-N(4)	2.1658(14)	Zn(1)-O(2)	2.1397(11)
Zn(1)-O(1)	2.1175(11)	O(1)-C(12)	1.261(2)
Zn(1)-O(2)	2.1397(11)	O(2)-C(12)	1.257(2)
O(1)-C(11)	1.2543(19)	O(3)-C(13)	1.207(2)
O(2)-C(11)#1	1.2554(19)	O(4)-C(13)	1.325(2)
		O(5)-C(14)	1.217(2)
		O(6)-C(14)	1.321(2)
Bond angles		Bond angles	
O(1)-Zn(1)-O(2)	78.74(4)	N(1)-Zn(1)-N(1)#1	180
O(1)-Zn(1)-N(3)	92.43(5)	N(1)-Zn(1)-N(2)	84.76(6)
O(2)-Zn(1)-N(3)	95.50(5)	N(1)#1-Zn(1)-N(2)	95.24(6)
O(1)-Zn(1)-N(2)	166.71(5)	N(1)-Zn(1)-O(1)	91.07(5)
O(2)-Zn(1)-N(2)	88.31(5)	N(1)-Zn(1)-O(1)#1	88.93(5)
N(3)-Zn(1)-N(2)	91.78(5)	N(2)-Zn(1)-O(1)#1	89.41(5)
O(1)-Zn(1)-N(1)	95.20(5)	N(2)-Zn(1)-O(1)	90.59(5)
O(2)-Zn(1)-N(2)	92.86(5)	O(1)-Zn(1)-O(1)#1	180
N(3)-Zn(1)-N(1)	169.64(5)		
N(2)-Zn(1)-N(1)	82.35(5)		
O(1)-Zn(1)-N(4)	91.84(5)		
O(2)-Zn(1)-N(4)	170.16(5)		
N(3)-Zn(1)-N(4)	81.95(6)		
N(2)-Zn(1)-N(4)	101.24(5)		
N(1)-Zn(1)-N(4)	90.79(5)		
#1 –x+1,-y+1,-z+1		#1 –x+1, -y+1, -z+1	

Supplementary material

Crystallographic data have been deposited at the Cambridge Crystallographic Data Center (CCDC), CCDC Nos. 208587 - 208590 for (**1**) – (**4**).

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Korean Abstract

$\{[\mathrm{Cu}(\mathbf{L1})(\mathrm{fumarato})]\cdot 6\mathrm{H_2O}\}_n$, $[\mathrm{Cu}(\mathbf{L1})(\mathrm{H_2bta^{2-}})]$, $\{[\mathrm{Ni}(\mathbf{L2})(\mathrm{H_2bta^{2-}})]\cdot 2\mathrm{H_2O}\}_n$, $\{[\mathrm{Cu}(\mathbf{L2})(\mathrm{H_2bta^{2-}})]\cdot \mathrm{H_2O}\}_n$, $\{[\mathrm{Zn}(\mathbf{L2})(\mathrm{tp^{2-}})]\cdot \mathrm{H_2O}\}_n$, $\{[\mathrm{Zn}(\mathbf{L2})(\mathrm{H_2bta^{2-}})]\cdot 2\mathrm{H_2O}\}_n$, $[\mathrm{Zn_2}(\mathbf{L2})_2(\mathrm{ox^{2-}})]\cdot 2\mathrm{ClO_4}\cdot 2\mathrm{DMF}$, and $[\mathrm{Zn}(\mathbf{L2})(\mathrm{H_2btc^-})_2]\cdot 2\mathrm{DMF}$ (**L1**=3,14-dimethyl-2,6,13,17-tetraazatricyclo[$14.4.0^{1.18}.0^{7.12}$]docosane, **L2** = 1,4,8,11-tetraazacyclotetradecane, $\mathrm{tp^{2-}}$ = terephthalic acid dianion, $\mathrm{H_2bta^{2-}}$ = 1,2,4,5-benzenetetracarboxylic acid dianion, $\mathrm{ox^{2-}}$ = oxalic acid dianion, $\mathrm{H_2btc^-}$ = 1,3,5-benzenetricarboxylic acid anion)의 조성을 갖는 8개의 새로운 화합물을 합성하였고 분석, 분광학 및 결정학적 방법을 통해 구조적 특성들을 알아낼 수 있었다. 일부 착화합물의 경우, 각 금속 이온을 polycarboxylate anion이 다리연결을 함으로써 1차원의 배위 폴리머를 형성하였다. 모든 착화합물에서 다양한 형태의 수소결합 상호작용과 미리 자리잡고있는 N-H의 방향이 carboxylate anion의 형태 결정 뿐만 아니라 금속-리간드 결합을 강화하는데 중요한 역할을 한다.

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