

Macrocyclic Zinc(II) Coordination Polymers Constructed from Aromatic and Cyclohexane Dicarboxylate Ligands

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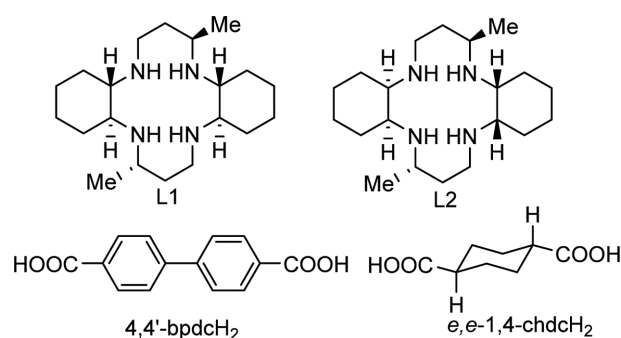
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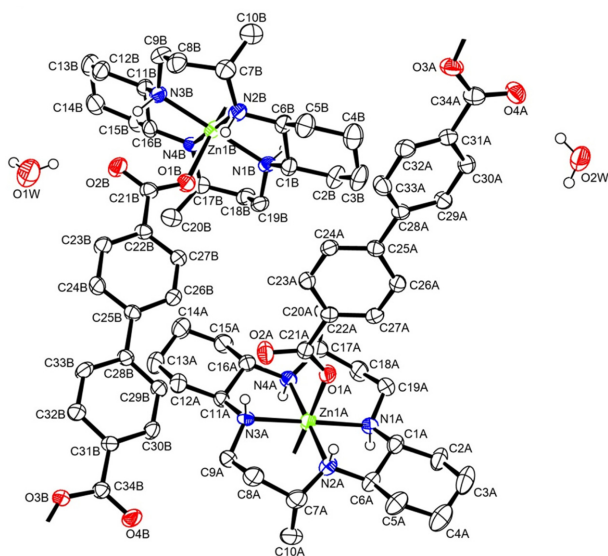
Great efforts have been made on the design and construction of supramolecular coordination polymers not only due to their fascinating structural features but also their potential in conventional and emerging applications.^{1–8} Metal complexes of azamacrocyclics along with multidentate ligand linkers have been considered as good building blocks for the formation of supramolecular coordination polymers.⁹ During the formation of final structures, intermolecular forces such as hydrogen bonds, π - π interactions, and CH- π interactions, etc are frequently involved.^{10,11} Rational design and the synthetic strategy of supramolecular coordination polymers *via* a self-assembly process largely depend on the selection of metal ion connectors and bridging ligand linkers. Thus, the metal complex of tetraazamacrocyclic **L** which bears *trans*/*cis*-fused cyclohexane rings on a cyclam backbone could potentially extend its structure to the axial direction of metal ion by the coordination of bridging ligands, resulting in the formation of 1D coordination polymer. In addition, the macrocycle **L** and its zinc(II) complex attracted attention due to their revealing anti-HIV activity.¹² Rigid organic linkers, in particular, aromatic polycarboxylates have widely been employed to generate coordination polymers with macrocyclic metal ion connectors.^{13,14} In contrast, flexible organic building blocks have been far less exploited as their backbone flexibility makes the resulting coordination polymers difficult to predict and control. However, the flexibility of organic linkers is all the better preferred by researchers to design and construct a new class of coordination polymers in spite of the above mentioned demerits.^{15,16} Recent articles about the development of flexible ligands in the realm of coordination polymers substantiate the importance of flexible ligands.^{17,18} An aromatic dicarboxylic acid, bpdcH₂ (bpdc = 4,4'-biphenyl dicarboxylate), may be a good candidate as an organic building block for the construction of supramolecular coordination polymer due to its coordinating ability and the possibility of inter-

molecular interactions arising between the aromatic rings. Though the bpdcH₂ molecule contains rigid aromatic rings, it also exhibits flexibility *via* rotation about a carbon-carbon single bond. Another best known flexible ligand is 1,4-chdcH₂ (1,4-chdc = 1,4-cyclohexane dicarboxylate) which can adopt three different conformations, i.e. *e,e*-*trans*-1,4-chdcH₂, *a,e*-*cis*-1,4-chdcH₂ and *a,a*-*trans*-chdcH₂. The 1,4-chdcH₂ molecule can show versatile coordination modes to metal ions depending on the degree of deprotonation and participate in intermolecular interactions by acting as hydrogen bond donors and/or acceptors. With the purpose to try and find out coordination polymers having fascinating structural features, we employed the macrocyclic zinc(II) complex as a metal ion connector, and dicarboxylates bpdc and *e,e*-*trans*-1,4-chdc as bridging ligand linkers (Scheme 1). From the self-assembly processes of an appropriate combination of metal ion and bridging dicarboxylate ligands, we obtained the complexes of [Zn(**L1**)(bpdc)]·0.75H₂O (**1**) and [Zn(**L1**)(*e,e*-*trans*-1,4-chdc)]·2H₂O (**2**), which form coordination polymers in crystalline solids. In this contribution, we describe the details of the structural, supramolecular, thermal, and spectroscopic properties of **1** and **2**.

The structure of **1** contains two independent macrocycles with solvated water molecules, and consists of 1D



Scheme 1. Structures of **L1**, **L2**, 4,4'-bpdcH₂, and *e,e*-*trans*-1,4-chdcH₂.



As shown in Figure 2(a), two 1D chains (yellow) pair up through C7A-H $\cdots\pi$ (centroid of phenyl ring) ($d(\text{C}\cdots\pi) = 2.688 \text{ \AA}$) interactions between the macrocycle in one chain and bridging bpdC ligands in another chain to form a double stranded supramolecular polymer. Due to these interactions, two phenyl rings in the bridging bpdC ligands are twisted with respect to the carbon-carbon bond with a dihedral angle (C26A-C25A-C28A-C33A) of 153.52° . However, no such secondary interactions either between the yellow double stranded polymers or between the green 1D chains are found. Ultimately, the 1D chains (green chain lying on crystallographic b direction) run over the yellow double stranded polymers in a slanted fashion like a plywood, resulting in the formation of 2D sheets (Figure 2(b)). The short contacts $d(\text{H3B}\cdots\text{C25A}) = 2.809 \text{ \AA}$, $d(\text{H3B}\cdots\text{C24A}) = 2.662 \text{ \AA}$, $d(\text{O2A}\cdots\text{H26B}) = 2.406 \text{ \AA}$, $d(\text{O2A}\cdots\text{H29B}) = 2.679 \text{ \AA}$, and $d(\text{C26B}\cdots\text{H12B}) = 2.818 \text{ \AA}$ are observed near the intersection of double strands and green 1D chains.

The structure **2** is composed of a zinc(II) macrocycle and a bridging ligand *e,e*-trans-1,4-chdc with two lattice water molecules. The structure exhibits a 1D coordination polymer with a basic $[\text{Zn}(\text{L1})]$ (*e,e*-trans-1,4-chdc) unit (Figure 3). The zinc(II) ion coordination geometry is completed by four Zn-N and two Zn-O bonds. Table 3 contains important bond distances and angles for **1**. The zinc atom sits on an inversion center. The Zn-N distances are normal with $2.0939(9) \text{ \AA}$ and $2.1263(9) \text{ \AA}$. The Zn-O distance of $2.1948(8) \text{ \AA}$ is comparable to the those for related zinc(II) complexes ($[\text{Zn}(\text{L1})(\text{oxalate})]\cdot 3\text{H}_2\text{O}\cdot 0.5\text{DMF}$; Zn-O = $2.205(3)$, $2.248(3) \text{ \AA}$,²² $[\text{Zn}(\text{L2})(\text{oxalate})]\cdot 3.5\text{H}_2\text{O}$; Zn-O = $2.2175(17)$, $2.2352(12) \text{ \AA}$,²³ $[\text{Zn}(\text{cyclam})](\text{maleate})\cdot 3\text{H}_2\text{O}$; Zn-O = $2.1968(16)$, $2.2840(16) \text{ \AA}$).²⁴

The 1D coordination polymer chain is connected to each other by the mediation of lattice water molecules to form

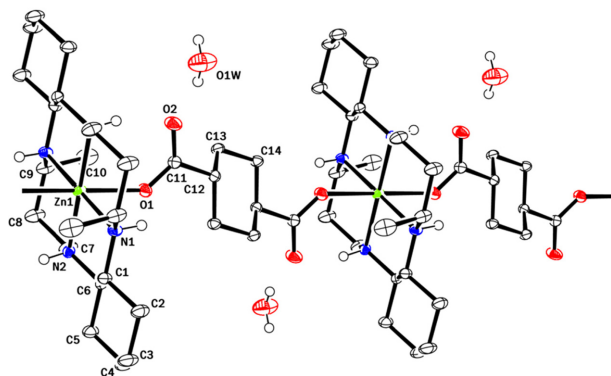


Figure 3. Molecular structure of **2** with atom-labeling scheme (50% thermal ellipsoids). Hydrogen atoms other than those on nitrogen atoms and water molecules are omitted for clarity.

Table 3. Selected bond distances (\AA) and angles ($^\circ$) for **2**

Zn1-N1	2.1263(9)	Zn1-N2	2.0939(9)
Zn1-O1	2.1948(8)	O1-C11	1.2588(13)
O2-C11	1.2550(14)		
N2-Zn1-N1	83.58(3)	N2-Zn1-N1#1	96.42(3)
N2-Zn1-O1#1	92.40(3)	N2-Zn1-O1	87.60(3)
N1-Zn1-O1#1	98.86(4)	N1-Zn1-O1	81.14(4)

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

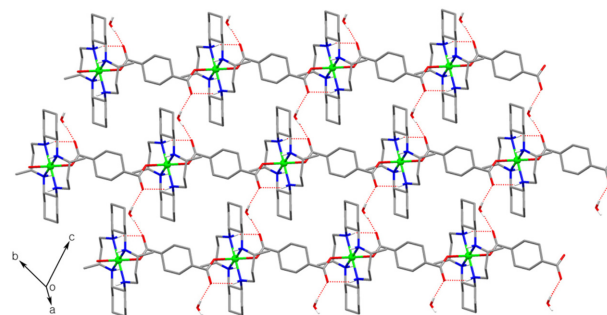


Figure 4. Extended structure of 1D coordination polymers in **2**.

Table 4. Hydrogen bonds for **2** (\AA and $^\circ$)

D-H \cdots A	d(D-H)	d(H \cdots A)	d(D \cdots A)	$\angle(\text{DHA})$
N1-H1N \cdots O1	0.86(15)	2.30	2.811(2)	118.2
N2-H2N \cdots O2#1	0.42(15)	2.15	2.946(2)	158.0
O1W-H1WA \cdots O2	0.82(2)	2.06	2.864(2)	168(2)
O1W-H1WB \cdots O1#3	0.79(2)	2.12	2.906(2)	174(2)

Symmetry code: #1 $-x+1, -y+1, -z+1$ #2 $-x, -y+2, -z$ #3 $-x+1, -y+1, -z$

2D sheet, but neither direct inter chain interactions nor interactions between the sheets are observed in **2** (Figure 4, Table 4). As usually found in the tetraazamacrocyclic metal complexes with carboxylate ligands, the Zn-O coordination bond is supported by the hydrogen bond arising from the pre-organized N-H groups of the macrocycle and carboxylate group (N2-H2N \cdots O2#1: $d(\text{D}\cdots\text{A}) = 2.946(2) \text{ \AA}$, $\angle(\text{DHA}) = 158.0^\circ$).

The infrared spectrum of **1** displays characteristic bands of the bpdC bridging ligands at 1592 , 1540 cm^{-1} (ν_{asCOO}) and 1380 cm^{-1} (ν_{sCOO}).²⁵ Two weak bands at 3220 cm^{-1} and 3125 cm^{-1} can be assigned to the N-H stretchings of the macrocycle. The broad band at 3345 cm^{-1} is originated from O-H stretching of the lattice water molecules. The infrared spectrum of **2** shows strong absorptions at 1572 cm^{-1} (ν_{asCOO}) and 1384 cm^{-1} (ν_{sCOO}) due to the *e,e*-trans-1,4-chdc bridging ligands. The band at 3160 cm^{-1} is assignable to the N-H stretchings of the macrocycle. In addition, the broad band at 3410 cm^{-1} indicates the O-H stretching of the lattice water molecules. The weak band at 1649 cm^{-1}

is originated from bending vibration of lattice water molecules ($\delta\text{H}_2\text{O}$) (Figures S1 and S2).

TGA curves for **1** show a first weight loss of 2.0% (calcd. 2.0%) over ca. 30–150 °C, corresponding to the loss of a lattice water molecule. Final residues (observed 12.4%, calculated 12.4%) were remained above 540 °C with ZnO composition. TGA curves for **2** were obtained with dehydrated powder due to the instability of **2** even in the crystalline state in air. Weight losses of 86.0% over ca. 320–550 °C was observed, corresponding to the losses of macrocycles and bridging ligands. Final residues (obsd. 14.0%, calcd. 14.2%) were remained above 550 °C with ZnO composition (Figures S3 and S4).

In conclusion, two zinc(II) complexes $[\text{Zn}(\text{L1})(\text{bpdc})] \cdot 0.75\text{H}_2\text{O}$ (**1**) and $[\text{Zn}(\text{L1})(e,e\text{-trans-1,4-chdc})] \cdot 2\text{H}_2\text{O}$ (**2**) have been prepared and structurally characterized. The complex **1** which contains the macrocycle **L1** and bridging bpdc ligands exhibits a 2D zinc(II) supramolecular coordination polymer in crystalline solid. Two different 1D chains exist in the complex **1**. One of the chains runs along the crystallographic *c* axis with pairing up to form a double stranded supramolecular polymer. The other chain along the crystallographic *b* direction runs over the 1D double stranded polymers in a slanted fashion, resulting in the formation of 2D sheets. The structure **2** exhibits a 1D coordination polymer with a basic $[\text{Zn}(\text{L1})(e,e\text{-trans-1,4-chdc})]$ unit. The 1D coordination polymer chain is connected to each other by the mediation of lattice water molecules to form 2D sheet, but neither direct inter chain interactions nor interactions between the sheets are observed in **2**.

EXPERIMENTAL

Materials, Methods and Apparatus

All commercially available chemicals were used as received. Water was distilled before use. IR spectra of solid samples (KBr pellets) were recorded on a Perkin-Elmer Spectrum X spectrophotometer between 4000 cm^{-1} and 400 cm^{-1} . The elemental analyses (C, H, N) were performed on samples using a CE Instruments EA-1110 Elemental Analyzer at KRICT, Korea. The free ligand **L1**, $\text{Zn}(\text{L1})(\text{NO}_3)_2$ and Na_2bpdc were synthesized by literature procedures.^{24,26,27}

Synthesis of **1**

To a DMF (10 mL) solution of $\text{Zn}(\text{L1})(\text{NO}_3)_2$ (53 mg, 0.1 mmol) was added a stoichiometric amount of Na_2bpdc (29 mg, 0.1 mmol) in water (10 mL), which was allowed to stand in an open beaker at ambient temperature. After a week, colorless crystals of **1** were obtained. Yield: >90% based

on $\text{Zn}(\text{L1})(\text{NO}_3)_2$. Anal. Calcd. for $\text{C}_{34}\text{H}_{49.50}\text{ZnN}_4\text{O}_{4.75}$ (**2**): C, 62.29%; H, 7.61%; N, 8.55%. Found C, 62.69%; H, 7.57%; N, 8.66%. IR (KBr, cm^{-1}): 3491, 3345 (νOH), 3220, 3125 (νNH), 1592, 1540 (ν_{asCOO}), 1380 (ν_{sCOO}).

Synthesis of **2**

To a DMF (10 mL) solution of $\text{Zn}(\text{L1})(\text{NO}_3)_2$ (263 mg, 0.5 mmol) was added an aqueous solution of *e,e*-trans-1,4-chdcH₂ (86 mg, 0.5 mmole) and five pipette drops of triethylamine. The mixture was left until colorless blocks of **2** formed. The crystals were filtered and dried in air. Yield: 67% based on $\text{Zn}(\text{L1})(\text{NO}_3)_2$. Anal. Calc. for $\text{C}_{28}\text{H}_{54}\text{N}_4\text{O}_6\text{Zn} \cdot 2\text{H}_2\text{O}$: C, 58.72%; H, 8.74%; N, 9.79%. Found C, 58.75%; H, 8.91%; N, 9.88%. IR (KBr, cm^{-1}): 3413 (νOH), 3160 (νNH), 1649 ($\delta\text{H}_2\text{O}$), 1572 (ν_{asCOO}), 1384 (ν_{sCOO}).

X-ray Crystallography

Table 5 contains a summary of selected crystallographic data and structure refinement details for **1** and **2**. Data were collected on a Nonius Kappa CCD (for **1**) or a Bruker Kappa APEX-DUO CCD (for **2**) diffractometer, using graphite monochromated Mo K α radiation. A combination of ϕ and ω (with κ offsets) scans were used to collect sufficient

Table 5. Crystal data and structure refinement for **1** and **2**

	1	2
Empirical formula	$\text{C}_{34}\text{H}_{49.50}\text{ZnN}_4\text{O}_{4.75}$	$\text{C}_{28}\text{H}_{54}\text{ZnN}_4\text{O}_6$
Formula weight	655.65	608.12
Temperature(K)	150(1)	147(2)
Wavelength(Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	P $\bar{1}$	P $\bar{1}$
<i>a</i> (Å)	15.3733(3)	8.9144(6)
<i>b</i> (Å)	8.9144(6)	10.1473(7)
<i>c</i> (Å)	15.9971(4)	10.3340(7)
α (°)	117.0640(12)	63.698(2)
β (°)	102.9830(12)	87.799(2)
γ (°)	99.3420(13)	66.688(2)
Volume(Å ³)	3250.52(12)	758.87(9)
<i>Z</i>	4	1
<i>D</i> _{calcd} (Mg/m ³)	1.340	1.331
Abs coefficient(mm ⁻¹)	0.802	0.855
Independent refl	14684 [R(int) = 0.0633]	3528 [R(int) = 0.0206]
Goodness-of-fit on F ²	1.018	1.058
Final R indices [I > 2 σ (I)]	R ₁ = 0.0590, wR ₂ = 0.1359	R ₁ = 0.0215, wR ₂ = 0.0530
R indices (all data)	R ₁ = 0.1263, wR ₂ = 0.1651	R ₁ = 0.0239, wR ₂ = 0.0542

data. The Denzo-SMN package was used to process the data frames.²⁸ The structures were solved and refined using the SHELXTLPC V6.1 package.²⁹ Refinement was performed by full-matrix least squares on F^2 using all data (negative intensities included). Crystallographic data for the structures reported here have been deposited with CCDC (Deposition Nos. CCDC-743544 (**1**) and CCDC-1059162 (**2**)). These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, E-mail: deposit@ccdc.cam.ac.uk

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Supporting Information. IR spectra and TGA curves for the complexes **1** and **2** are available (Figures S1–S4).

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