Ki-Young Choi*

2D Hydrogen-bonded polymer assembled by zinc(II) tetraaza macrocyclic complex and 1,2-cyclopentanedicarboxylic acid

Abstract: The self-assembly of $[Zn(L)(H_2O)_2]\cdot Cl_2$ and 1,2-cyclopentanedicarboxylic acid generates a 2D hydrogen-bonded polymer [Zn(L)(Hcpdc)] (L=3,14-dimethyl-2,6,13,17-tetraazatricyclo[14,4,$0^{1,18}0^{7,12}$]docosane, H_2cpdc= 1,2-cyclopentanedicarboxylic acid) (**1**). Complex **1** is characterized by X-ray crystallography, spectroscopy, and thermogravimetric analyzer. The crystal structure of **1** shows a distorted octahedral coordination geometry around the zinc (II) ion, with the four secondary amines of the macrocycle and two carboxylate oxygen atoms of the $Hcpdc^-$ ligand in the *trans* position. The compound crystallizes in the monoclinic system $P2_1/c$ with a=8.6002(10), b=10.4906(11), c=19.008(2) Å, β (°)=92.949(7)°, V=1712.6(3) $Å^3$, Z=2. The IR spectrum and TGA behavior of the compound are significantly affected by the $Hcpdc^-$ ligand.

Keywords: 1,2-cyclopentanedicarboxylic acid; 2D hydrogen-bonded polymer; crystal structure; tetraaza macrocycle; zinc(II) complex.

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Introduction

The self-assembly of the coordination polymers with specific network topologies has received great attention due to its potential usage in many areas of science and technology (Tecila et al., 1990; Tsukube et al., 1991; Lehn et al., 1992; Lawrence et al., 1995; Choi et al., 1999a,b; Cotton et al., 2001; Lu et al., 2001; Park et al., 2007a,b; Kim et al., 2008; Kwag et al. 2010a,b; Sen et al., 2013). Especially, hydrogen bonding is one of the key interactions for the process of molecular aggregation and recognition in nature, which creates novel structures of molecular assembly (Lehn et al., 1992). For example, the compound $[Ni(L)(H_2O)_2]_{0.5}[Ni(L)(H_2O)_2]_{0.5}$ (L=3,14-dimethyl-2,6,13,17-tetraazatricyclo[14,4,$0^{1,18}$,$0^{7,12}$] docosane) assembles in the solid state to form a 1D chain linked by an intermolecular hydrogen bond (Choi et al., 1999b). In addition, a 3D supramolecular network $[Ni(cyclam)(H_2O)_2]_3[(btc)_3]_2\cdot 24H_2O$ (btc=1,3,5-benzenetricarboxylate) was assembled by $[Ni(cyclam)(H_2O)_2]^{2+}$ and btc^{3-} ligand in water *via* hydrogen bonds, which is regarded as a molecular floral lace (Choi et al., 1999a). The hydrogen-bonding interactions, therefore, play a significant role in aligning the molecules and the polymer strands in the crystalline solids.

In the present paper, we report the synthesis, crystal structure, and chemical properties of the 2D hydrogen bonded polymer $[Zn(L)(Hcpdc)_2]$ (**1**), which was assembled by $[Zn(L)(H_2O)_2]\cdot Cl_2$ (L=3,14-dimethyl-2,6,13,17-tetraazatricyclo[14,4,$0^{1,18}$,$0^{7,12}$]docosane) and 1,2-cyclopentanedicarboxylic acid (H_2cpdc). The structure of L ligand is shown in Scheme 1.

Results and discussion

An Oak Ridge Thermal Ellipsoid Plot (ORTEP) (Farrugia, 1997) of $[Zn(L)(Hcpdc)_2]$ (**1**) with the atomic numbering scheme is shown in Figure 1. Selected bond lengths and angles are listed in Table 1. The macrocyclic ligand skeleton of the present compound takes the *trans*-III(*R*,*R*,*S*,*S*) conformation with two chair six-membered and two gauche five-membered chelate rings. The zinc atom lies on a center of inversion. The coordination environment around the central zinc(II) ion is described as a distorted octahedron with four Zn-N bonds from the macrocycle and two Zn-O bonds from $Hcpdc^-$ ligand. The zinc atom and four N atoms of the macrocycle are exactly in a plane. The Zn-N (secondary amine) distance of 2.077(2) and 2.118(2) Å is similar to that observed for octahedral zinc(II) complexes with 14-membered tetraaza macrocycle ligands (Choi, 1998a; Choi et al., 1997, 1998b). The axial Zn-O(1) distance of 2.290(1) Å is slightly longer than the equatorial Zn-N bond distances, giving an axially elongated octahedral

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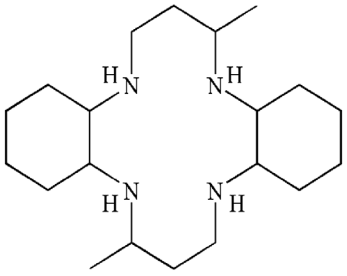

Scheme 1 3,14-dimethyl-2,6,13,17-tetraazatricyclo[14,4,$0^{1.18}0^{7.12}$]-docosane (L).

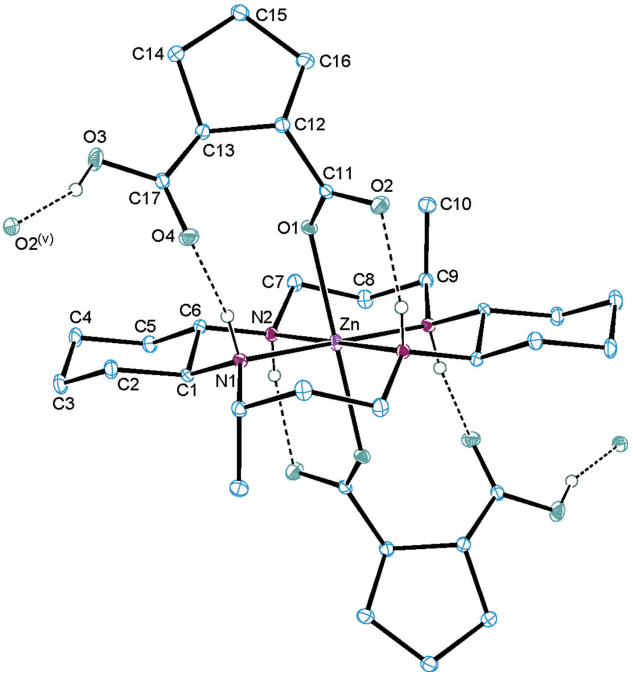

Figure 1 An ORTEP drawing (30% probability ellipsoids) of [Zn(L)$(Hcpdc)_2$] (**1**) with the atomic numbering scheme.
The hydrogen bonds are shown as dashed lines.

geometry. The N-Zn-N angles of the six-membered chelate ring are larger than those of the five-membered chelate ring. Furthermore, the axial Zn-O(1) linkage is not perpendicular to the ZnN_4 plane with N(1)-Zn-O(1) and N(2)-Zn-O(1) angles of 97.58(6) and 86.88(6)°, respectively. The Zn-O(1)-C(11) angle and C(11)-O(1) distance relative to the Hcpdc⁻ ligand are 126.1(1)° and 1.260(2) Å, respectively. The deprotonated one among the two Hcpdc⁻ carboxylic groups is bonded to the zinc atom. Interestingly, the two secondary amines N(1) and N(2) form intramolecular hydrogen bonds with the carboxylate oxygen atoms of Hcpdc⁻ ligand [N(1)-H(1)···O(4)^{iv} 3.022(2) Å, 157.5°; N(2)-H(2)···O(2)^{iv} 2.799(2) Å, 153.0°; symmetry code (iv): -x+1, -y, -z+2]. Furthermore, the protonated oxygen atom O(3)

Table 1 Selected bond distances (Å) and angles (°) for [Zn(L)$(Hcpdc)_2$] (**1**).

Zn-N(1)	2.117(2)	Zn-N(2)	2.077(2)
Zn-O(1)	2.290(1)	C(11)-O(1)	1.259(2)
C(11)-O(2)	1.260(2)	C(17)-O(3)	1.313(2)
C(17)-O(4)	1.220(2)		
N(1)-Zn-N(2)	96.21(6)	N(1)-Zn-N(2)^{iv}	83.79(6)
N(1)-Zn-O(1)	97.54(5)	N(2)-Zn-O(1)	86.87(5)
N(1)^{iv}-Zn-O(1)	82.46(5)	N(2)^{iv}-Zn-O(1)	93.13(5)
Zn-O(1)-C(11)	126.3(1)	O(1)-C(11)-O(2)	123.7(2)
O(3)-C(17)-O(4)	123.6(2)		

Symmetry codes: (i) x+1, y, z; (ii) x, y+1, z; (iii) -x+1, y+1/2, -z+3/2; (iv) -x+1, -y, -z+2.

in the Hcpdc⁻ ligand forms the intermolecular hydrogen bond to an adjacent deprotonated oxygen atom O(2) of the Hcpdc⁻ [O(3)-H(3)···O(2)^{v}; 2.515(2) Å, 159(3)°; symmetry code (v): -x+1, y-1/2, -z+3/2-x+3/2, y+1/2, -z+3/2]. This interaction gives rise to a 2D hydrogen-bonded polymer (Figure 2 and Table 2).

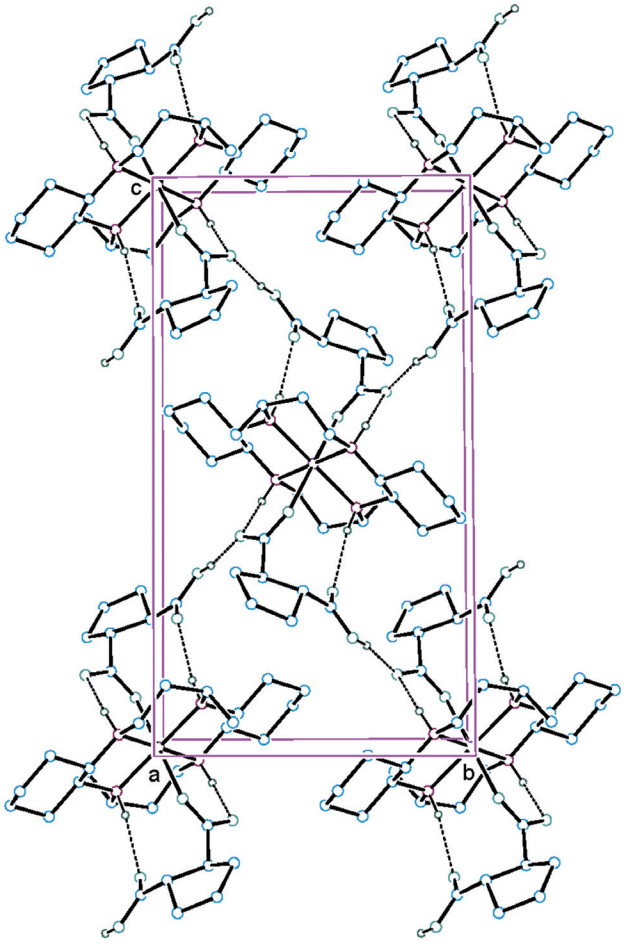

Figure 2 A packing diagram of [Zn(L)$(Hcpdc)_2$] (**1**).
The hydrogen bonds are shown as dashed lines.

Table 2 Hydrogen bonding parameters (Å, °) for [Zn(L)(Hcpdc)$_2$] (**1**).

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)
N(1)-H(1)···O(4)^{iv}	0.87(2)	2.21(2)	3.024(2)	156(2)
N(2)-H(2)···O(2)^{iv}	0.89(2)	1.95(2)	2.800(2)	159(2)
O(3)-H(3)···O(2)^{v}	0.86(3)	1.69(3)	2.514(2)	160(3)

Symmetry codes: (iv) -x+1, -y, -z+2; (v) -x+1, y-1/2, -z+3/2.

The IR spectrum of **1** shows a band at 3126 cm^{-1} corresponding to the ν(NH) of the coordinated secondary amines of the macrocycle. Two strong bands exhibit ν_{as}(COO) stretching frequency at 1617 cm^{-1} and ν_{sym}(COO) at 1372 cm^{-1}, respectively. The value of Δν (245 cm^{-1}) indicates that the carboxylate groups coordinated to the zinc(II) ion only as a monodentate ligand (Bakalbassis et al., 1991; Cao et al., 2002). The TGA diagram of **1** further supports the structure determined by X-ray diffraction method (Figure 3). The compound was heated in the temperature range 25–900°C in nitrogen gas. The first weight loss is observed from 266 to 342°C, which is due to the loss of two Hcpdc$^-$ ligands (observed, 40.3%; calculated, 41.6%). A second weight loss corresponding to the macrocycle (observed, 46.1%; calculated, 47.0%) is found in the temperature range 342–510°C. Further weight loss is observed in the temperature range 510–900°C corresponding to the ZnO residue (observed, 11.1%; calculated, 11.4%). The formation of ZnO accompanies the decomposition of the macrocycle ligand in the zinc(II) complex (Dong et al., 1999).

Conclusions

The crystal structure of complex **1** shows a distorted octahedral coordination geometry around the zinc (II) ion, with the four secondary amines of the macrocycle and two carboxylate oxygen atoms of the Hcpdc$^-$ ligand in the *trans* position. Interestingly, the intramolecular and intermolecular hydrogen bonds in the complex generate a 2D hydrogen-bonded polymer. The IR spectrum and TGA behavior of the compound are significantly affected by the Hcpdc$^-$ ligand.

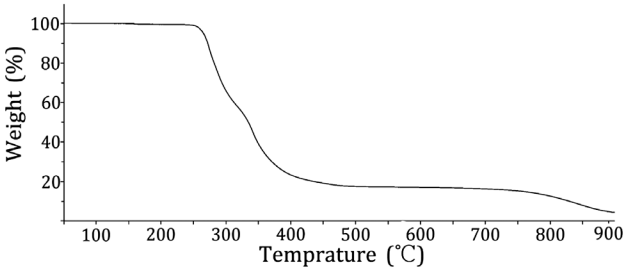

Figure 3 Thermogravimetric curve of [Zn(L)(Hcpdc)$_2$] (**1**).

Table 3 Crystallographic data for [Zn(L)(Hcpdc)$_2$] (**1**).

Empirical formula	$C_{34}H_{58}N_4O_8Zn$
Formula weight	716.21
Temperature (K)	100(2)
Crystal color/habit	Silver/block
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	8.6002(10)
b (Å)	10.4906(11)
c (Å)	19.008(2)
β (°)	92.949(7)
V (Å^3)	1712.6(3)
Z	2
D_{calc} (Mg m^{-3})	1.389
Absorption coefficient (mm^{-1})	0.774
F(000)	768
Crystal size (mm^3)	0.20×0.10×0.02
θ range (°)	2.15–28.40
Limiting indices	$-11\le h\le 11$, $-14\le k\le 8$, $-25\le l\le 22$
Reflection collected/ unique	16114/4281 (R_{int}=0.0395)
Reflection used	4998
Absorption correction	SADABS
Max./min. transmission	0.9847 and 0.8606
Data/restraints/ parameters	4281/0/226
Goodness of fit on F^2	1.041
Final *R* indices [$I>2\sigma(I)$]	R_1[a]=0.0383, wR_2[b]=0.0822
R indices (all data)	R_1=0.0504, wR_2=0.0891
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0347P)^2+0.9081P]$ with $P=(F_o^2+2F_c^2)/3$
Largest difference peak and hole (eÅ^{-3})	0.379 and -0.504

[a]$R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$.
[b]$wR_2=[\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Experimental section

Materials and physical measurements

All chemicals used in the syntheses were of reagent grade and were used without further purification. The macrocycle 3,14-dimethyl-2,6,13,17-tetraazatricyclo[14,4,0^{1,18},0^{7,12}]docosane (L) was prepared according to the literature method (Kang et al., 1991). IR spectra were recorded with a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer (Perkin Elmer, Waltham, MA, USA) using KBr pellets. DSC and TGA (Mettler Toledo, Lausanne, Switzerland) were performed under

flowing nitrogen at a heating rate of 10°C min^{-1} using an SDT 2960 Thermogravimetric Analyzer. Elemental analyses (C, H, N) were performed on a Perkin-Elmer CHN analyzer.

Synthesis of [Zn(L)(Hcpdc)$_2$] (1)

To an aqueous solution (20 mL) of [Zn(L)(H_2O)$_2$]·Cl_2 (254 mg, 0.5 mmol) (Choi et al., 1997) was added sodium 1,2-cyclopentanedicarboxylate (202 mg, 1.0 mmol) in water (10 mL). The mixture was heated to reflux for 1 h and then cooled to room temperature. The solution was filtered to remove insoluble material. After, the filtrate was allowed to stand at room temperature until silver crystals formed. The product was recrystallized from hot water. Yield: 437 mg (61%). Calc. (found) for $C_{34}H_{58}N_4O_8Zn$: C, 57.02 (57.14); H, 8.16 (8.23); N, 7.82 (7.71)%. IR (KBr, cm^{-1}): ν(NH) 3126 cm^{-1}, ν_{as}(COO) 1617 cm^{-1}, ν_{sym} (COO) 1372 cm^{-1}. mp=312°C.

X-ray crystallography

Single crystal X-ray diffraction measurement for **1** was carried out on a Bruker APEX II CCD diffractometer using graphite-monochromated Mo-Kα radiation (λ=0.71073 Å). Intensity data were measured at 100(2) K by the ω-2θ technique. Accurate cell parameters and an orientation matrix were determined by the least-squares fit of 25 reflections. The intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied with the SADABS program (Sheldrick, 1996). The structure was solved by direct methods (Sheldrick, 2008a), and the least-squares refinement of the structure was performed by the SHELXL-97 program (Sheldrick, 2008b). All atoms except all hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions, allowing them to ride on their parent C atoms with U_{iso}(H)=1.2U_{eq}(C or N). The crystallographic data, conditions used for the intensity collection, and some features of the structure refinement are listed in Table 3. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 1008195, for **1**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.uk or http://www.ccdc.cam.ac.uk).

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