

1D Coordination Polymer $\{[\text{Zn}(\text{L1})(\text{H}_2\text{pm})]\cdot\text{H}_2\text{O}\}_n$: An Unusual Coordination of 1,5-COO⁻ Groups of H₂pm to Zinc(II) Ions

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Macrocyclic transition metal complexes with polycarboxylate ligands have been proved to be good building blocks for the construction of coordination polymers and supramolecular networks.¹⁻⁶ Coordination polymers are generally composed of metal ion 'connectors' and multidentate ligand 'linkers', and the dimensionality of coordination polymers can be tuned by controlling the coordination sites of metal ion 'connectors' for multidentate ligand 'linkers'.¹ Thus, the construction of 1D coordination polymers is possible to be achieved by blocking equatorial sites of metal ions with polyazamacrocycles and leaving axial sites open for bridging ligands. Among multidentate ligand 'linkers', H₄pm (pm = pyromellitate, 1,2,4,5-benzenetetracarboxylate) is one of the attracting linkers due to its versatile coordination tendencies of carboxylic acid groups to metal ions depending on the degree of deprotonation.⁷⁻¹⁷ Moreover, the carboxylic acid groups of H₄pm in metal complexes can act as hydrogen bond donors and/or acceptors *via* inter- and/or intramolecular fashion in extending the structures. In this report we describe the synthesis and structure of an undulated 1D coordination polymer $\{[\text{Zn}(\text{L1})(\text{H}_2\text{pm})]\cdot\text{H}_2\text{O}\}_n$ (**1**) built by taking advantage of the directionality of zinc(II) macrocycles and the ability of H₂pm ligands to bridge between zinc(II) ions, where the bridging H₂pm ligand shows an unusual coordination of 1,5-COO⁻ groups to zinc(II) ions.

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. Elemental analysis was performed by the Korea Research Institute of Chemical Technology, Daejeon, Korea. The free ligand **L1** was prepared according to a literature procedure.^{18,19} The precursor complex Zn(L1)(NO₃)₂ was prepared by refluxing ligand **L1** (3.36 g, 1.0 mmole) and Zn(NO₃)₂·6H₂O (3 g, 1.01 mmole) in stirring methanol for a day, filtering, washing with methanol, and finally drying in air. The white powder of Zn(L1)(NO₃)₂ was obtained in 95% (5.0 g) yield.

Synthesis of 1. To a DMF/H₂O solution of Zn(L1)(NO₃)₂ (526 mg, 1.0 mmole) was added a DMF solution of H₄pm (254 mg, 1.0 mmole). The mixture was allowed in an open beaker at room temperature. Colorless blocks of **1** were obtained in a week. Suitable crystals of **1** for X-ray diffraction studies and other measurements were manually collected under a microscope. Doubly deprotonated H₂pm anions were always involved in the structure of **1** even in the absence of a base. Yield >90%. Anal. Calcd. for C₃₀H₄₆ZnN₄O₈: C, 53.56; H, 6.84; N, 8.33; O, 21.42%. Found C, 53.51; H, 7.35; N, 8.76; O, 20.48%. IR (Nujol, cm⁻¹): 3425 (νOH), 3240, 3183 (νNH), 3145, 1709 (ν_{as} COO from COOH), 1587, 1531 (ν_{as} COO from COO⁻), 1335 (ν_s COO from COO⁻).

An attempt to prepare a similar zinc(II) coordination polymer by the reaction between Zn(L2)(NO₃)₂ and H₄pm was unsuccessful.

X-ray Crystallography. A summary of selected crystallographic data and structure refinement for **1** is given in Table 1. X-ray data were collected on a Nonius Kappa CCD diffractometer, using graphite monochromated Mo K_α radiation (λ = 0.71073 Å). A combination of 1° φ and ω (with κ offsets) scans were used to collect sufficient data. The data frames were integrated and scaled using the Denzo-SMN package.²⁰ The structure was solved and refined using the SHELXTL/PC V6.1 package.²¹ Refinement was performed by full-matrix least squares on F² using all data (negative intensities included). Hydrogen atoms were included in

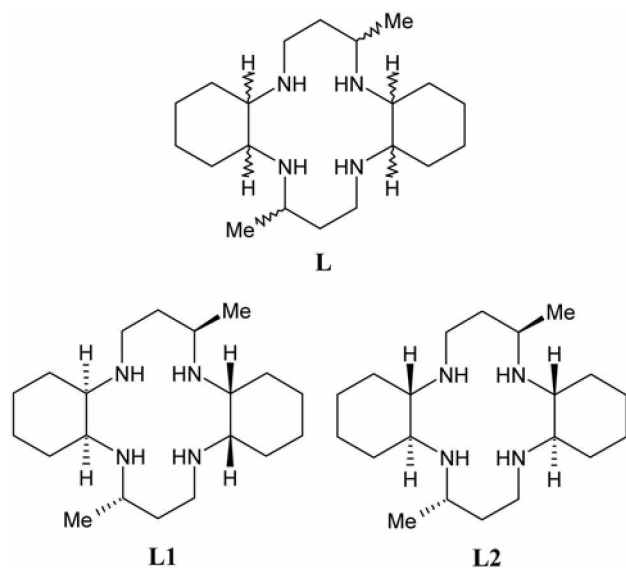


Table 1. Crystal data and structure refinement for **1**

Empirical formula	C ₃₀ H ₄₆ N ₄ ZnO ₉
Formula weight	672.08
Temperature (K)	150(2)
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P $\bar{1}$
Unit cell dimensions	a = 10.7864(11) Å b = 12.855(2) Å c = 12.8584(17) Å α = 75.423(7) $^\circ$ β = 67.982(8) $^\circ$ γ = 70.936(9) $^\circ$
Volume	1545.2(4) Å ³
Z	
Density (calcd)	1.445 Mg/m ³
Absorption coefficient	0.855 mm ⁻¹
Independent reflections	5142 [R(int) = 0.117]
Goodness-of-fit on F ²	1.038
Final R indices [I > 2 σ (I)]	R ₁ = 0.0748, wR ₂ = 0.1973
R indices (all data)	R ₁ = 0.1134, wR ₂ = 0.2173

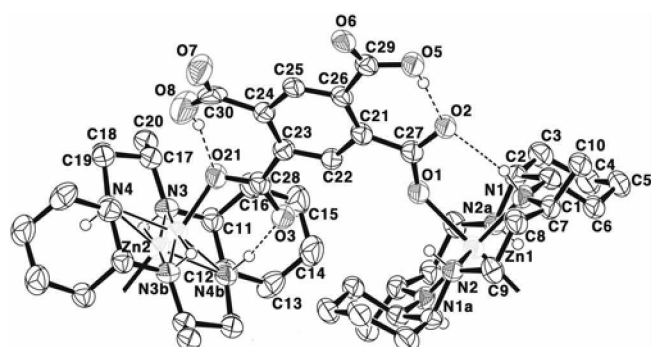


Figure 1. Molecular structure of **1** with atom-labeling scheme. Hydrogen atoms other than those participating in hydrogen bonding are omitted for clarity. Selected bond distances (Å) and angles ($^\circ$): Zn1-N1, 2.102(4); Zn1-N2, 2.126(5); Zn2-N3, 2.263(5); Zn2-N4, 2.118(5); Zn1-O1, 2.207(4); Zn2-O21, 2.170(3); Zn2-N3#2, 2.044(5); Zn2-N4#2, 2.057(4); N1-Zn1-N2, 96.34(16); N1-Zn1-N2#1, 83.66(16); N1-Zn1-O1, 89.27(14); N2-Zn1-O1, 90.93(15); N1-Zn1-O1#1, 90.73(14); N3-Zn2-N4, 89.40(17); N3-Zn2-O21, 104.61(16); N4-Zn2-O21, 95.82(16); N3#2-Zn2-N4#2, 97.49(18); N3#2-Zn2-N4, 84.60(18); N4#2-Zn2-N4, 157.61(7); N3#2-Zn2-O21, 96.00(17); N4#2-Zn2-O21, 106.07(16); N3-Zn2-N3#2, 159.03(7); N3-Zn2-N4#2, 80.71(17). Symmetry code: #1 $-x+1, -y+1, -z+1$; #2 $-x+2, -y, -z$

calculated positions. The crystals seemed to be twinned and/or the diffraction pattern was effected by the fact that atom Zn2 was slightly displaced from the center of symmetry causing it to be disordered. The structure contained two unique Zn atoms (Figure 1) for asymmetric unit and gave the predicted 1D structure. Some other residual electron density presumed water located in a void could not be resolved. The program SQUEEZE was used to remove this residual density.²² The program suggested one molecule of water per asymmetric unit, therefore this was added to the formula.

Results and Discussion

The complex **1** was obtained by reacting Zn(L1)(NO₃)₂ and H₂pm in DMF/H₂O. The structure of **1** exhibits the undulated 1D coordination polymer {[Zn(L1)(H₂pm)]·H₂O}_n with a basic [Zn(L1)(H₂pm)]·H₂O unit. The 1D chains are linked together *via* the face-to-face π - π interactions between the aromatic rings of coordinated H₂pm ions to generate an extended supramolecular structure (Figure 2). For the π - π stacking interaction, the interplanar separation of the aromatic rings is 3.79-3.80 Å. The coordination environment around the central zinc(II) is a distorted octahedron with four Zn-N bonds from the macrocycle and two Zn-O bonds from the H₂pm ligands. The Zn-N distances are in the range of 2.102(4)-2.263(5) Å. The Zn-O distances of 2.207(4) and 2.170(3) Å lies within the previously reported values in related systems Zn(L2)(apc)₂:²³ Zn-O = 2.099(2) Å, [Zn₂(xylyl-bicyclam)(OAc)₂](OAc)₂·2CH₃OH;²⁴ Zn-O = 2.089(2), 2.407(2) Å. {[Zn(cyclam)(phthalate)]_n·(CH₃OH)_n;²⁵ Zn-O = 2.220(2), 2.190(2) Å. {[Zn(cyclam)(tp)]·H₂O}_n;²⁶ Zn-O = 2.1559(12) Å. {[Zn(cyclam)(H₂pm)]·2H₂O}_n;²⁶ Zn-O = 2.2839(14) Å. [Zn(cyclam)(H₂btc)]₂·2DMF;²⁶ Zn-O = 2.2222(12). {[Zn(cyclam)(maleate)]·H₂O}_n;²⁷ Zn-O = 2.1968(16), 2.2840(16); where apc = 3-amino-2-pyrazinecarboxylate, tp = terephthalate and btc = 1,3,5-benzenetricarboxylate. Two pertinent features are found in the complex **1**. One is that the complex **1** contains a rigid and sterically hindered macrocycle L1 in which both of the ethylene bridges are replaced by *cis*-fused cyclohexane rings, where the two cyclohexane subunits are *anti* with respect to the plane of the macrocycle. The examples of metal complexes with the macrocyclic ligand L1 are extremely rare.^{18,28,29} We have found three such complexes with nickel(II) ions. However, the structurally characterized zinc(II) complex with L1 has never been reported to date. The present macrocycle L1 is one of the 16 possible diastereoisomers of L. Recent reports show quite different coordination behaviors and chemical properties between transition metal complexes of L1 and L2. For example, the bicarbonate ligands coordinate to the nickel(II) ion of [Ni(L1)(ClO₄)₂] to form the 1D supramolecule {[Ni(L1)(OCO₂H)₂]_n in which the coordination environment around the nickel(II) ion is a

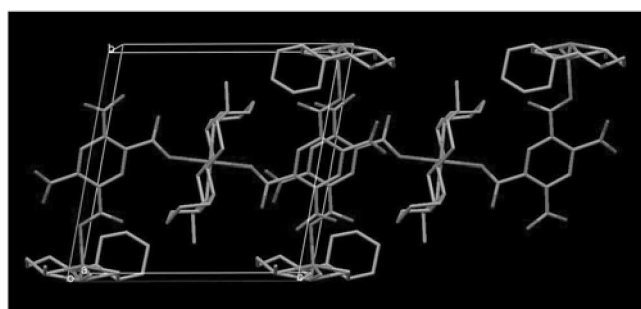
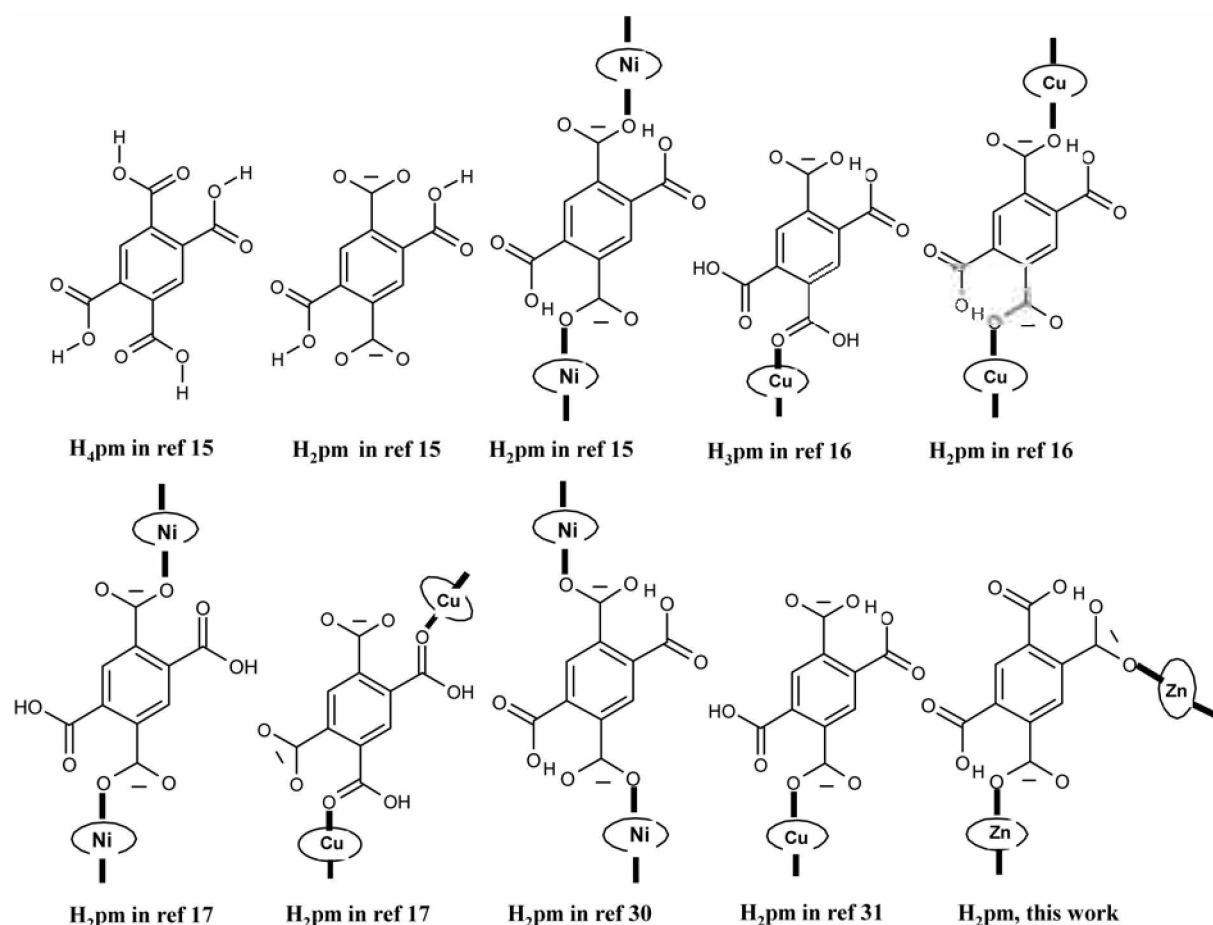


Figure 2. Lattice diagram of **1** showing a 1D coordination polymer; the face-to-face π - π interaction between the aromatic rings of coordinated H₂pm ions is observed in the stacked structure. Hydrogen atoms are omitted for clarity.



Scheme 1. Versatility of H_4pm , H_3pm and H_2pm and their coordination and hydrogen bonding modes.

distorted octahedron, whereas bicarbonate anions do not involve in coordination with the nickel(II) ion of $[Ni(L2)]-(ClO_4)_2$.²⁸ They only remain as counteranions forming a hydrogen bonded supramolecule $\{[Ni(L2)](HCO_3)_2\}_n$, where the geometry around the nickel(II) ion is a square plane. Solution chemistry also indicates that the nickel(II) complex of the *cis*-fused isomer binds various solvent molecules more easily than the nickel(II) complex of the *trans*-fused isomer does.¹⁸ Another noteworthy feature found in **1** is the unusual coordination of 1,5- COO^- groups of H_2pm to zinc(II) macrocycle. Although diverse coordination modes and shapes for H_4pm , H_3pm , H_2pm , and pm moieties are understood depending on the degree of deprotonation and the types of hydrogen bonds involved, the coordination of 1,4- COO^- groups of H_2pm to metal ions is dominant, and the involvement of 1,5- COO^- groups of H_2pm in coordination is unprecedented (Scheme 1).

The previously reported copper(II) complex $\{[Cu(cyclam)-(H_2pm)] \cdot H_2O\}_n$ may be a system to be comparable with the present complex **1**, but the 1,5- $COOH$ groups of H_2pm rather than 1,5- COO^- groups coordinate to copper(II) ions *via* their carbonyls in $\{[Cu(cyclam)(H_2pm)]H_2O\}_n$.¹⁷ As is usual, the macrocyclic skeleton in **1** retains the *trans* III conformation with two sets of pre-organized N-H groups which enable to interact with H_2pm anions in the proface through coordination and intermolecular hydrogen bonds.

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

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O5-H5...O2	0.84	1.59	2.406(5)	164.4
O8-H8...O21	0.84	1.65	2.432(6)	153.6
N1-H1...O2	0.93	2.08	2.970(6)	159.1
N2-H2...O7#3	0.93	2.13	3.048(6)	170.5
N3-H3...O6#4	0.93	2.52	3.370(6)	151.6
N3-H3...O21#2	0.93	2.56	3.133(6)	120.5
N4-H4...O3#2	0.93	2.01	2.897(6)	157.9

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

contributing the formation of the coordination polymer **1**. Each $COOH$ group on 2,4-positions is participating in an intramolecular hydrogen bond with neighboring COO^- groups on 1,5-positions, respectively (Table 2).

The microanalysis supported the structure determined by X-ray diffraction studies and the IR spectrum gave evidences for the presence of the macrocycle and H_2pm ligands.

In conclusion, we have prepared and fully characterized the new 1D undulated zinc(II) coordination polymer **1** in which the macrocyclic ligand L1 contains *cis*-fused cyclohexane rings. The bridging ligand H_2pm in the complex **1** shows the unusual coordination mode to the zinc(II) macrocycle with the involvement of 1,5- COO^- rather than 1,4-

COO⁻ in coordination. We believe that this unusual structure is caused by the involvement of complex inter- and intramolecular hydrogen bonds between the zinc(II) macrocycle 'connectors' and H₂pm 'linkers' (Figure 1 and Table 2), the presence of face-to-face π - π interactions of aromatic rings between the 1D chains (Figure 2) as well as the enhanced rigidity and steric hindrance of the macrocycle L1 by the introduction of *cis*-fused cyclohexane rings and methyl groups on the 14-membered tetraazamacrocyclic.

Supplementary Material. Crystallographic data for the structure have been deposited with Cambridge Crystallographic Data Center (Deposition No. CCDC 623391 for 1). 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, fax: 44 1223 336033, email: deposit@ccdc.cam.ac.uk.

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