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Formation of Molecular Ladder Elements with Macrocyclic Platforms via Linear Bifunctional Ligands

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Reaction between 4-aminopyridine and a dinuclear zinc(II) component of a Robson macrocyclic ligand has resulted in the formation of a molecular ladder element motif. X-ray single crystal structural analysis indicates that two pyridine rings are assembled at the same direction of the macrocycle, which are placed in a nearly parallel way via π–π interactions, forming a concavity structure with a macrocyclic base. It is significantly noted that one hydrogen-bond cycle generated from hydrogen atoms of two amino groups with two perchlorate anions has sustained such an assembly of two 4-aminopyridine species to stand in a face to face pattern through a weak molecular interaction on the macrocyclic platform by one-end coordination bonding. The self-assembly of 4-carboxylic pyridine acid and the same macrocyclic component in the presence of sodium hydroxide has yielded an interesting wheellike complex. Two macrocyclic dinuclear zinc(II) components have been linked through coordination bonding with two pyridine derivatives situated on the same direction of a macrocycle. X-ray structural results suggest that the compound has a unique sandwichlike structure consisting of two macrocyclic covers with two inversely positioned bridging pyridine carboxylic groups in the middle.

Introduction

With the development of supramolecular chemistry, there has been an increasing demand to recognize various interactions as driving forces to an anticipated aggregation state of molecular building blocks via self-assembly.[1] In addition to the traditional intermolecular interactions such as hydrogen bonds, van der Waals interactions, charge-transfer forces, and others,[2] coordination bonding has recently been actively employed to generate the ordered network assisted by metal ions.[3] The facile variety of coordination configurations around metal atoms has offered much privilege for chemists to design and synthesize particular supramolecular systems with diverse architecture and dimensions for exploring new functional materials (such as a nanoporous molecular-based solid or complexes used for transport of energy, charge, ions, and molecules).[3,4] As any crystal structure stands for a balance of forces, one crystal pattern may be either comprised of one kind of interaction or a combination of different categories of interactions.[1,2] In the former case, a single interaction dominates the formation of the related crystal pattern, while in the latter multiple interactions codominate the crystal structure.

In our recent research on the assembly with a macrocyclic dinuclear zinc(II) component (**1**; Chart 1), we have described molecular ladders composed of **1** as macrocyclic platforms and 4,4′-bipyridine as building blocks (Figure 1b).[5] For

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(1) (a) Etter, M. C. *Acc. Chem. Res.* **1990**, *23*, 120. (b) Lawrance, D. A.; Jiang, T.; Levett, M. *Chem. Rev.* **1995**, *95*, 2229. (c) Bernstein, J.; Davis, R. E.; Shimoni, L.; Chang, N.-L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1555. (d) Desijraju, G. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311.

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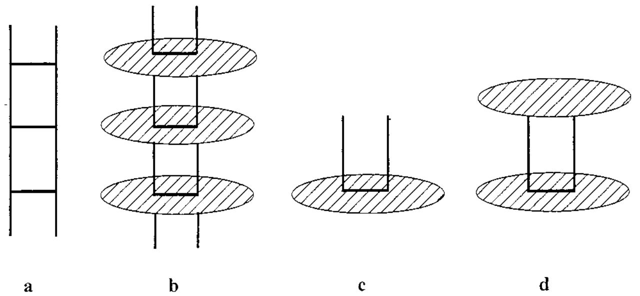
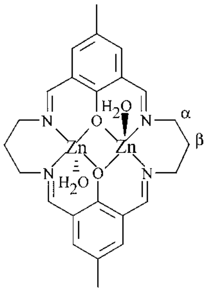


Figure 1. (a) Molecular ladders. (b) Molecular ladders with macrocyclic platforms. (c) Molecular ladder element with a macrocyclic base. (d) Wheellike unit.

Chart 1. Cation of Complex $[Zn_2L(H_2O)_2]^{2+}$ (**1**)[a]



[a] α and β are used to label carbon atoms to distinguish their NMR peaks.

further study, an attempt was made to have 4-aminopyridine (4-ampy) and 4-carboxylic pyridine acid (4-pyCOOH) serve as linear bifunctional ligands to produce analogous molecular ladder motifs. However, ladder elements have been unexpectedly obtained. Herein we report two unique self-assembly examples possessing the unit composed of molecular ladder elements with macrocyclic platforms (Figure 1c,d).

Experimental Section

Physical Measurements. Elemental analyses were measured with a Perkin-Elmer 1400C analyzer. Infrared spectra (400−4000 and 100−600 cm^{-1}) were collected on a Nicolet FTIR 170X spectrophotometer at 298 K using KBr plates. ^1H NMR spectra were obtained in a Bruker 300 or 500 MHz NMR spectrometer. Electrospray ionization (ES) mass spectra were recorded on a Finnigan MAT SSQ 710 mass spectrometer in a scan range of 100−1200 amu. Thermogravimetric analysis−differential thermal analysis (TGA−DTA) data were recorded by a CA Instruments DTA−TGA 2960 type simultaneous analyzer.

Materials. All solvents and chemicals were of analytical grade and used without further purification. 4-Aminopyridine and 4-carboxylic pyridine acid were purchased as commercial chemicals from Aldrich. 4-Methyl-2,6-diformylphenol was prepared with high yield by an improved oxidation method using active manganese(IV) dioxide.[5a] Dinuclear macrocyclic zinc complexes (1) were synthesized via a sodium template method described previously.[6]

Caution! Although no problem was encountered in all our experiments, transition metal perchlorates are potentially explosive and should be handled in small quantities.

Synthesis of $[Zn_2L(4\text{-ampy})_2](ClO_4)_2$ (2). $[Zn_2L(H_2O)_2](ClO_4)_2$ (0.384 g, 0.5 mmol) was dissolved in ethanol (30 cm^3); then 4-aminopyridine (0.094 g, 1 mmol) was added. After refluxing for 1 h, the solution was slowly evaporated to nearly 5 cm^3 under reduced pressure and cooled to room temperature; the yellow precipitate was filtered, washed with a small amount of ethanol, and dried in vacuo. Yield: 0.402 g (87%). Anal. Calcd for $[C_{34}H_{38}N_8O_2Zn_2](ClO_4)_2$: C, 44.37; H, 4.16; N, 12.17. Found: C, 44.67; H, 4.32; N, 12.41. IR (KBr): 3449 and 3361 (NH_2); 1640 (C═N), 1096, 1084, and 624 (ClO_4); 419 and 248 cm^{-1} (Zn−Py). ^1H NMR (500 MHz, DMSO-d_6, 298 K, TMS): δ 8.51 (s, 4H, HC═N), 7.72 (d, 8H, py-H), 7.54 (s, 4H, phenyl), 6.46 (s, 4H, NH_2), 3.85 (t, 8H, αCH_2), 2.29 (s, 6H, CH_3), 1.96 (m, 4H, βCH_2). ES-MS: *m/z* 266 $[Zn_2L]^{2+}/2$.

Synthesis of $[Zn_2L(4\text{-pyCOO})]_2(ClO_4)_2$ (3). Sodium hydroxide (0.04 g, 1 mmol) dissolved in a small amount of water and 4-carboxylic pyridine (0.123 g, 1 mmol) acid in ethanol (20 cm^3) were mixed and kept stirring for 10 min; then a solution of $[Zn_2L(H_2O)_2](ClO_4)_2$ (0.384 g, 0.5 mmol) in 30 cm^3 of ethanol was added. The mixture was refluxed for 1 h, then cooled to room temperature, and filtered. The filtrate was concentrated, and yellow needle crystals were collected and dried in a vacuum. Yield: 0.455 g (90%). Anal. Calcd for $[C_{30}H_{30}N_5O_4Zn_2]_2(ClO_4)_2$: C, 47.93; H, 4.03; N, 9.32. Found: C, 48.14; H, 4.22; N, 9.59. IR (KBr): 1639 (C═N); 1558, 1327, and 773 (O−C−O); 1097, 1084, and 625 (ClO_4); 422 and 254 cm^{-1} (Zn−Py). ^1H NMR (300 MHz, DMSO-d_6, 298 K, TMS): δ 8.49 (s, 4H, HC═N), 7.54 (s, 4H, phenyl), 7.45 (d, 4H, py-H), 3.96 (t, 8H, αCH_2), 2.24 (s, 6H, CH_3), 2.06 (m, 4H, βCH_2). ES-MS: *m/z* 266 $[Zn_2L]^{2+}/2$.

X-ray Crystallography. Crystals of **2a** $\{[Zn_2L(4\text{-ampy})_2](ClO_4)_2 \cdot C_2H_5OH\}$ and **3a** $\{[Zn_2L(4\text{-pyCOO})]_2(ClO_4)_2 \cdot CH_3OH \cdot CH_3CN \cdot H_2O\}$ suitable for X-ray diffraction measurements were grown from the mixed solution of acetonitrile/ethanol (1:1) and acetonitrile/methanol (2:1), respectively, by slow evaporation at room temperature. Since yellow crystals of **2a** and **3a** are not stable in the absence of their mother solution, their single-crystal samples were glue-covered before measurements. Single-crystal diffraction measurements for **2a** and **3a** crystals were carried out on a Bruker SMART 1 K CCD diffractometer system at 293(2) K using graphite monochromated Mo Kα radiation (λ = 0.710 73 Å) at a detector distance of 4 cm and swing angle of −35°. The collected data were reduced by using the program SAINT,[7] and empirical absorption correction was done by using the SADABS[8] program. The structures were solved by direct methods and refined by least-squares method on F_{obs}^2 by using the SHELXTL-PC[9] software package. All non-H atoms were anisotropically refined which were geometrically fixed and allowed to ride on the attached atoms. Hydrogen atoms were inserted in the calculated positions (C−H, 0.96 Å; N−H, 0.90 Å) assigned fixed isotropic thermal parameters at 1.2 times the equivalent isotropic *U* of the atoms to which they are attached and allowed to ride on their respective parent atoms, while hydrogen atoms from water molecules were located from a different map and assigned fixed isotropic thermal parameters. All calculations and molecular graphics were carried out on a PC-586 computer with the SHELXTL PC program package. Solvent molecules of ethanol in **2a**, methanol, water, and acetonitrile molecules in **3a** are observed in the crystal structures of complexes **2a** and **3a**, respectively. The crystallographic results are given in Table 1; major

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Table 1. Crystal Data and Structure Refinement for **2a** and **3a**

	compd **2a**	compd **3a**
empirical formula	$C_{38}H_{48}Cl_2N_8O_{12}Zn_2$	$C_{63}H_{69}Cl_2N_{11}O_{18}Zn_4$
mol wt	1010.48	1600.67
cryst syst	orthorhombic	triclinic
space group	*Pnma*	$P\bar{1}$
a, Å	22.113(3)	11.6520(3)
b, Å	17.181(2)	12.1394(3)
c, Å	11.6611(14)	13.8462(3)
α, deg	90	66.9563(8)
β, deg	90	80.5638(8)
γ, deg	90	76.6348(8)
V, Å^3	4430.2(10)	1747.52(7)
Z	4	1
D_{calcd}, g cm^{-3}	1.515	1.521
μ, mm^{-1}	1.272	1.509
F(000)	2088	822
θ range, deg	1.84−28.29	1.60−29.53
max/min transm	0.7500/0.5922	0.5836/0.5437
no. of params	280	498
reflcns collected/unique	30378/5631	12808/8441
R1, wR2 [$I > 2\sigma(I)$]^a	0.0616, 0.1858	0.0601, 0.1619
goodness of fit on F^2	1.013	0.925
Δ*r*, max/min, e Å^{-3}	1.342/0.785	0.985/1.126

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$; $w = 1/\sigma^2[|F_o|]$.

Table 2. Major Bond Distances (Å) and Angles (deg) for **2a** and **3a**

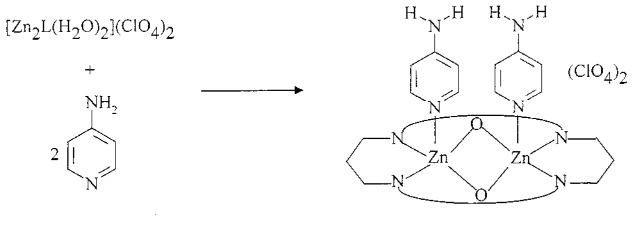
compd **2a**		compd **3a**	
Bond Distances			
Zn(1)−N(2)	2.041(5)	Zn(1)−N(1)	2.044(3)
Zn(1)−N(1A)	2.060(4)	Zn(1)−O(1)	2.044(3)
Zn(1)−N(1)	2.060(4)	Zn(1)−O(2)	2.059(3)
Zn(1)−O(1)	2.070(3)	Zn(1)−N(2)	2.069(4)
Zn(1)−O(1A)	2.070(3)	Zn(1)−N(5)	2.079(3)
		Zn(2)−O(4A)	1.982(2)
Bond Angles			
N(2)−Zn(1)−N(1A)	102.45(15)	N(1)−Zn(1)−O(1)	90.13(12)
N(2)−Zn(1)−N(1)	102.45(15)	N(1)−Zn(1)−O(2)	154.52(12)
N(1A)−Zn(1)−N(1)	95.3(2)	O(1)−Zn(1)−O(2)	75.96(10)
N(2)−Zn(1)−O(1)	103.27(14)	N(1)−Zn(1)−N(2)	94.05(15)
N(1A)−Zn(1)−O(1)	152.44(15)	O(1)−Zn(1)−N(2)	150.00(14)
N(1)−Zn(1)−O(1)	88.66(13)	O(2)−Zn(1)−N(2)	88.17(13)
N(2)−Zn(1)−O(1A)	103.27(14)	N(1)−Zn(1)−N(5)	100.60(13)
N(1A)−Zn(1)−O(1A)	88.66(13)	O(1)−Zn(1)−N(5)	109.30(12)
N(1)−Zn(1)−O(1A)	152.44(15)	O(2)−Zn(1)−N(5)	104.10(11)
O(1)−Zn(1)−O(1A)	75.97(15)	N(2)−Zn(1)−N(5)	99.11(15)
		O(4A)−Zn(2)−N(4)	109.44(14)
		O(4A)−Zn(2)−N(3)	108.77(14)
		O(4A)−Zn(2)−O(2)	97.17(12)
		O(4A)−Zn(2)−O(1)	98.52(11)

bond lengths and bond angles are tabulated in Table 2. Further details are provided in the Supporting Information.

Results and Discussion

Synthesis and Crystal Structure of 2. In our previous study,[6] the crystal structure of the macrocyclic dinuclear zinc(II) complex (**1**) has been reported where the axial position of each zinc(II) atom is occupied by a weakly coordinating water molecule. When 4-ampy was selected to react with **1**, the results of microanalytical and IR spectrum data suggest that two 4-ampy molecules are linked to the macrocyclic unit (a molar ratio of 2:1), but amino groups are uncoordinated (two sharp NH_2 group stretching vibration bands appear at 3449 and 3361 cm^{-1}, respectively, which are analogous to those of free 4-ampy; Scheme 1). So an expected infinite one-dimensional structure cannot be yielded, and it is interesting to specify the coordination fashion of 4-ampy molecules.

Scheme 1. Synthetic Route for Complex **2**



2

Though molecular peaks of complexes **2** and **3** have not been found, the electrospray ionization mass spectra analyses reveal that both complexes have a doubly-charged peak, confirming the production of the macrocyclic compounds. In addition, the ^{1}H NMR spectral data of **2** and **3** are compatible to the expected macrocyclic complex. In addition to signals of hydrogen atoms in the macrocyclic platform, hydrogen atoms attached to amino groups and pyridine rings in **2** and those of the pyridine rings in **3** are also observed. Furthermore, when preparing NMR determination samples, we have found that complexes **2** and **3** are insoluble in any other solvents such as H_2O, CH_3OH, C_2H_5OH, $CHCl_3$, CH_3COCH_3, and CH_3CN except being a little soluble in dimethyl sulfoxide (DMSO), though it is not a good choice in this case. We have obtained satisfactory ^{1}H NMR spectral data of **2** and **3** finally in their saturated DMSO-d_6 solutions, but the solutions are too dilute to record their high-quality ^{13}C NMR spectra.

Description of an X-ray diffraction analysis of **2a** revealed that each zinc(II) atom on the macrocyclic framework has been bound to one 4-aminopydine molecule, preferably resulting in a pyramidal rather than an octahedral coordination environment around the metal atom. The axial position is occupied by the pyridine nitrogen atom due to its stronger coordination ability than that of the amino group and water molecule. However, it is of interest to observe that the amino group is naked uncoordinatedly (Figure 2), and no ladder motifs have been yielded. Contrary to the other known structures of five-coordinate zinc(II) complexes of this macrocyclic ligand,[6] two pyridine rings are set at the same direction of the macrocycle which is slightly bent with the angle of N(2)−Zn(1)−Zn(2) in 93.5°. It is of much significance to note that two pyridine planes are assembled in a nearly parallel way via p−p interactions, forming a concavity structure (Figure 1c). The distance between two pyridine planes is ca. 3.5 Å.

The most important feature is that a hydrogen-bond cycle generated from hydrogen atoms of two amino groups with two perchlorate anions has been formed. Each ClO_4^- group acts as a bridge to link two amino species in the way of N−H···O bonding, consisting of a 12-member hole on top of pyridine rings. The hole with dimensions of ca. 3.77 × 7.29 Å is about 6.21 Å deep to the macrocyclic base. Two hydrogen bonds of one anion group are a little different with H(3BA)···O(5) = 2.346 Å (sym trans: *x*, $^1/_2$ −*y*, *z*),

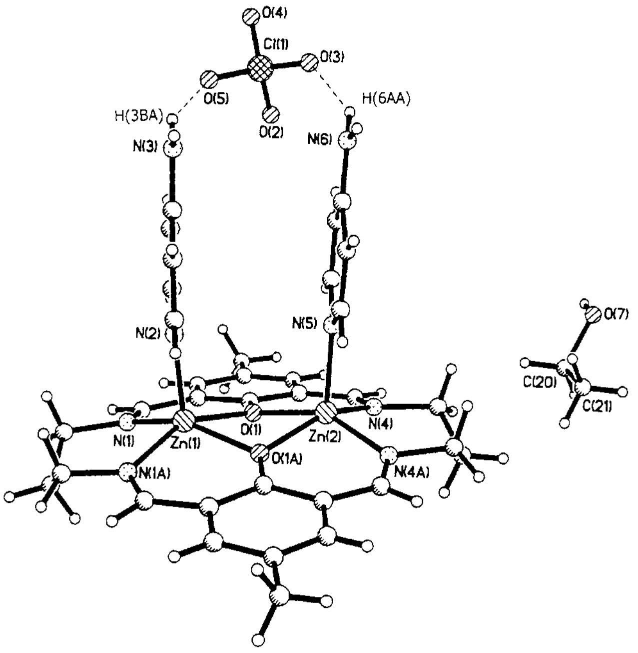


Figure 2. Molecular structure of **2a** cation with the solvent ethanol molecule. To show the metal coordination environment and hydrogen bonds distinctly, only some major atoms, hydrogen atoms involved in H-bonding interactions, and one perchlorate anion are labeled.

H(6AA)···O(3) = 2.213 Å (sym trans: x, $^1/_2$ $-y$, z), and N−H···O angles of 151.9 and 150.7°, respectively. It is suggested that the existence of such a H-bond-formed cycle has supported two 4-aminopyridine species to stand face to face through a weak molecular interaction on the macrocyclic platform by one-end coordination bonding. In our molecular ladder motifs,[5] dinuclear zinc(II) macrocyclic moieties as platforms have been found to play a key role in maintaining the ladder structure, because the coordination bonding between the metal atom and 4,4′-bipyridine is much stronger than the $\pi-\pi$ interaction between pyridine planes to overcome the steric repulsion. But here hydrogen bonding plays a significant part in sustaining such an assembly of 4-aminopyridine molecules. In crystals, it is also observed that each perchlorate anion forms a nonclassic and weak hydrogen bond (C−H···O) with a solvent molecule apart from two strong N−H···O hydrogen bonds. A number of examples on C−H···X hydrogen bonds in organic and organometallic compounds (where X = O, N, and halogen atoms or anions) have been reported, where C−H units frequently function as H-bonding donors and form weak hydrogen bonds with H-bonding acceptors, mainly oxygen and nitrogen.[10] The C−H···O H-bonding here has a length of O(2C)···H(20B) = 2.575 Å (sym trans: $^1/_2$ $-x$, $-y$, $+z$), comparable to those reported.[1d]

Synthesis and Crystal Structure of 3. When 4-pyCOONa was replaced to react with **1**, it was anticipated that a structure

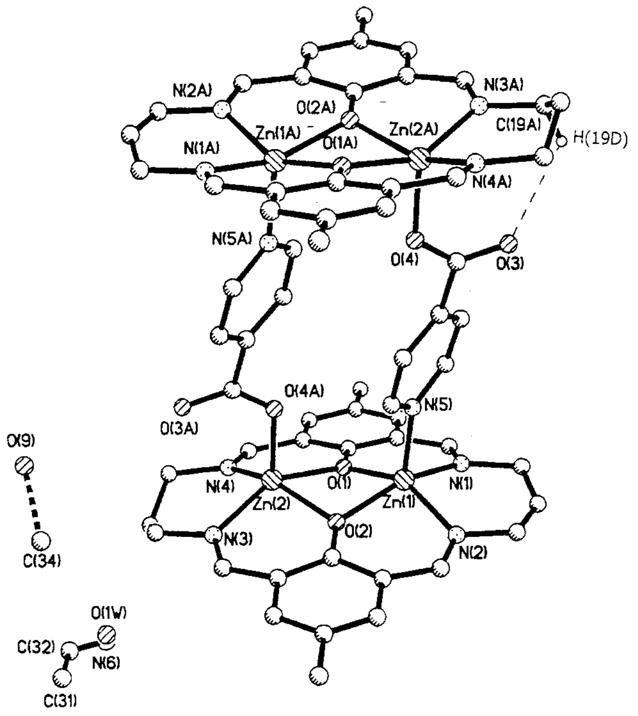
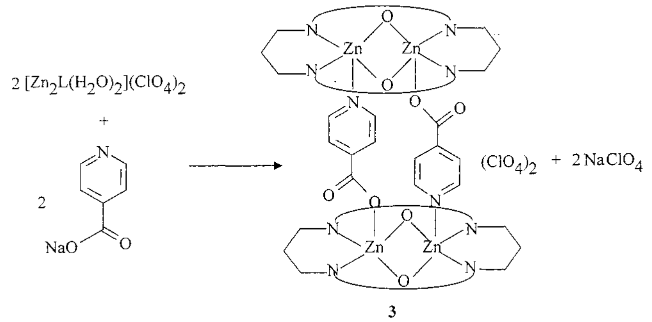


Figure 3. Depiction of the molecular structure of the complex cation in **3a** with its solvent molecules. To make the picture clear, only one hydrogen atom and the heteroatoms are drawn with atomic numbering.

Scheme 2. Synthetic Route for Complex **3**



similar to that of **2** would be obtained (Scheme 2), but at this time the microanalytical result reveals a 1:1 ratio of the macrocyclic unit to 4-pyCOO$^-$. So complex **3** must have a different array compared to that of **2**. It seems important for us to determine the crystal structure of this sample to characterize how 4-pyCOO$^-$ was assembled with **1**.

X-ray crystallographic results of **3a** indicated that two zinc(II) atoms in a macrocyclic framework have a five-coordinating configuration analogous to that of **2a** except that one apical position is taken up by one nitrogen atom and the other by one oxygen atom of 4-carboxylic pyridine acid (Figure 3). Unlike the concave-shaped framework in **2a**, it is of much interest to observe that each carboxylic anion acts as a bridge to link two macrocyclic units by coordination bonding to form a wheellike molecule, with two substituted pyridine groups placed at a reverse position. Although 4-pyridine carboxylic anion works as a linear bifunctional ligand in which the carboxylic anion is monodentative, 1D molecular ladder networks such as 4,4′-bipyridine have not been produced as expected. However, an approximate

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parallelogram consisting of a tetranuclear zinc(II) unit has been formed. Two pyridine rings are parallel to each other with a very short separation of ca. 3.2 Å via $\pi-\pi$ interactions. The Zn−Zn distance in two macrocyclic subunits is 3.182 Å, and the parallelogram is ca. 8.99 × 3.18 Å in lengths with angles of 93.8 and 86.2°, respectively. The resulting cavity is so small that no guest species or molecules can be accommodated. The coordinated C−O unit is not coplanar to the attached pyridine plane but has a torsion angle of ca. 40°. Such a twist provides the necessary space for the configuration deployment of four five-coordinated zinc(II) atoms.

In the crystal packing of complex **3a** exists two C−H···O types of hydrogen bonds. Both of the H-bonding acceptors are from uncoordinated oxygen atoms of 4-pyridine carboxylic anions, but the related H-bonding donors come from different sources. The former arises from solvent methanol molecules and the latter from the first carbon atom of 1,3-propanediamio group of the macrocyclic framework to form intramolecular H-bonds. Such C−H···O H-bonds are H(34A)···O(3D) = 2.473 Å, 107.33° and H(19D)···O(3) = 2.589 Å, 126.60°, respectively. These weak interactions have further stabilized the above-mentioned structure.

Thermal Analyses. TGA−DTA analysis on **2** denotes that the compound is stable in the range of 293−576 K initially, then has a 20.43% weight loss in a range of 577−635 K and stability to 661 K, and finally explodes at 662 K. The data indicate the compound first lost two 4-aminopyridine units and then decomposed. The thermal property of **3** observed is similar to that of **2**, that is to say the sample is unchangeable until 590 K, but it lost 4-carboxylic pyridine acid anion units from 591 to 672 K (loss of weight 16.18%) and then decomposed at 673 K.

The results reported herein offer two unprecedented types of coordination polymers based on the pre-positioned planar dinuclear zinc(II) moiety which has first been used in the self-assembly study to afford macrocyclic platforms. It is concluded that the assembly between **1** and some linear bifunctional building blocks with different size and coordinating groups can be formed to yield molecular ladders or ladder elements. It has been observed that hydrogen bonds and $\pi-\pi$ interactions codominate the motif of assembly in addition to the coordination bonding. We have performed lots of mono- and multifunctional organic ligands to construct some new frameworks with above-mentioned macrocyclic units via coordinating bonds or supramolecular interactions. Some of them react; for example, 8-methylquinoline can form a platelike H-bonding sustained donor−acceptor complex containing macrocyclic dinuclear zinc(II) unit without any coordination bonding interactions,[11] while many ligands react but it is hard to obtain good-quality single-crystal samples, and there is no reaction taking place at all with some other ligands.

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Supporting Information Available: Crystallographic data for **2a** and **3a** including tables of crystal structure refinement data, positional parameters, bond lengths, and bond angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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