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# Notes

## Molecular Ladders with Macrocyclic Platforms

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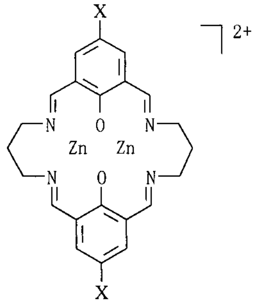
### Introduction

The aggregation of molecular building blocks via self-assembly has recently been of wide interest because the potential of the ordered network directed either by metal ions or by hydrogen bonds offers opportunities to develop new approaches for functional materials.[1] In the former, deliberate designs of transition metals with certain linear bifunctional ligands, e.g., 4,4′-bipyridine and pyrazine, have generated a few classes of coordination polymers with diverse architecture and functions such as one-dimensional molecular chains and ladders,[2] two-dimensional grids and brick walls,[2e,3] and three-dimensional networks.[4] A number of naked metal ions and protected mononuclear metal species have been involved in the metal-assisted self-assembly.[5] Reported here are two unprecedented molecular ladders constructed of a linear functional ligand witha macrocyclic unit (Chart 1) (**1**), a prepositioned dinuclear zinc(II) moiety that has first been used in the self-assembly study to afford macrocyclic platforms.



$[\mathrm{Zn_2L}]^{2+}$ (**1**) : **1a** X = Me, **1b** X = Cl

### Experimental Section

**Physical Measurements.** Elemental analyses were measured with a Perkin-Elmer 1400C analyzer. Infrared spectra (4000−400 $\mathrm{cm}^{-1}$) were collected on a Nicolet FTIR 170X spectrophotometer at 25 °C using KBr plates. $^{1}$H NMR spectra were obtained in a Bruker 500 MHz NMR spectrometer. Electrospray ionization (ES) mass spectra were recorded on a Finnigan MAT SSQ 710 mass spectrometer in a scan range 100−1200 amu. TGA−DTA data were recorded by a CA Instruments DTA-TGA 2960 simultaneous type analyzer.

**Materials.** All solvents and chemicals were of analytical grade and used without further purification. 4-Methyl-2,6-diformylphenol and 4-chloro-2,6-diformylphenol were prepared with high yields according to an improved oxidation method using active manganese(IV) dioxide.[6] Dinuclear macrocyclic zinc complexes (**1**) were synthesized via a sodium template method described previously.[7]

**Synthesis of $[\mathrm{Zn_2L(4,4'\text{-}bipy)_2](ClO_4)_2}$.** Complex **2**, having the empirical formula $[\mathrm{Zn_2L(4,4'\text{-}bipy)_2](ClO_4)_2}$ (bipy = bipyridine), was prepared by refluxing $[\mathrm{Zn_2L(H_2O)_2](ClO_4)_2}$ (**1**) (0.384 g, 0.5 mmol for **1a** and 0.405 g, 0.5 mmol for **1b**) with 4,4′-bipyridine (0.156 g, 1 mmol) in acetonitrile−ethanol (1:1, 40 mL) for 1 h, and then the solutions were slowly evaporated to nearly 5 mL under reduced pressure and cooled to room temperature. Yellow crystalline solids were collected, washed with ethanol, and dried in a vacuum. Yields: **2a**, 0.497 g (92%); **2b**, 0.527 g (94%). The samples obtained above were subjected directly to routine analyses. **2a**. Anal. Calcd for $[\mathrm{C_{24}H_{26}Zn_2N_4O_2(C_{10}H_8N_2)_2](ClO_4)_2\cdot(C_2H_5OH)}$: C, 50.82; H, 4.45; N, 10.31. Found: C, 50.54; H, 4.10; N, 10.55. Main IR ($\mathrm{cm}^{-1}$): 1616(C═N), 1094, and 623 ($\mathrm{ClO_4^-}$). $^{1}$H NMR ($\mathrm{D_2O}$): $\delta$ 8.64(m, 4H, $\mathrm{py_aH}$), 8.33(s, 4H, HC═N), 7.79(m, 4H, $\mathrm{py_bH}$), 7.41(s, 4H, phenyl), 3.99(t, 8H, $\mathrm{CH_2}$), 2.27(s, 6H, $\mathrm{CH_3}$), 2.10(m, 4H, $\mathrm{CH_2}$). ES-MS: *m*/*z* 266 $[\mathrm{Zn_2L}]^{2+}/2$. **2b**. Anal. Calcd for $[\mathrm{C_{22}H_{20}Zn_2N_4O_2Cl_2\ (C_{10}H_8N_2)_2](ClO_4)_2\cdot(C_2H_5OH)}$: C, 46.89 H, 3.76; N, 9.95. Found: C, 46.59; H, 3.55; N, 10.18. Main IR ($\mathrm{cm}^{-1}$): 1642(C═N), 1097, and 624 ($\mathrm{ClO_4^-}$). $^{1}$H NMR ($\mathrm{D_2O}$): $\delta$ 8.49(m, 4H, $\mathrm{py_a}$ H), 8.22(s, 4H, HC═N), 7.64(m, 4H, $\mathrm{py_b}$ H), 7.30(s, 4H, phenyl), 3.84(t, 8H, $\mathrm{CH_2}$), 1.98(m, 4H, $\mathrm{CH_2}$). ES-MS: *m*/*z* 286 $[\mathrm{Zn_2L}]^{2+}/2$.

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**Chart 1.** (a) Molecular Ladders and (b) Molecular Ladders with Macrocyclic Platforms

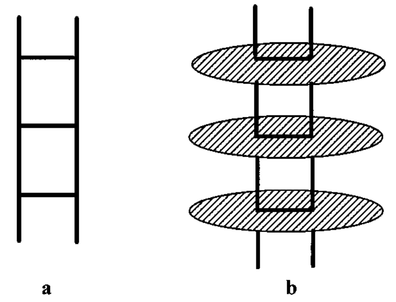


**Table 1.** Crystal Data and Structure Refinement for **2a** and **2b**

| | **2a** | **2b** |
|---|---|---|
| chem formula | $C_{52}H_{64}Cl_2N_8O_{12}Zn_2$ | $C_{23}H_{28}Cl_2N_4O_8Zn$ |
| mol wt | 1194.75 | 624.76 |
| cryst syst | monoclinic | monoclinic |
| space group | *C*2/*c* | *C*2/*c* |
| *a*, Å | 25.7884(3) | 26.2211(4) |
| *b*, Å | 11.7579(2) | 11.8317(1) |
| *c*, Å | 20.1441(3) | 20.8467(4) |
| $\beta$, deg | 121.353(1) | 122.677(2) |
| *V*, Å$^3$ | 5216.13(13) | 5443.88(14) |
| *Z* | 4 | 8 |
| $D_{calcd}$, g cm$^{-3}$ | 1.521 | 1.525 |
| $\mu$, mm$^{-1}$ | 1.094 | 1.152 |
| *F*(000) | 2488 | 2576 |
| $\theta$ range, deg | 5.90−57.50 | 3.70−58.90 |
| max, min transm | 0.764 10, 6219 | 0.8024, 0.6079 |
| no. parameters | 328 | 344 |
| R1, wR2 [$I > 2\sigma(I)$] | 0.0758, 0.1939 | 0.0610, 0.1534 |
| goodness of fit on $F^2$ | 0.954 | 0.930 |
| $\Delta\rho$, max, min, e Å$^{-3}$ | 0.800, −1.026 | 0.601, −0.817 |

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

**X-ray Crystallography.** Single crystals of both **2a** and **2b** grown from a mixed solution of acetonitrile and ethanol at a ratio of 2:1 are subjected to X-ray diffraction measurements. Because crystals of **2a** and **2b** are extremely unstable in the absence of the mother liquor, their single-crystal samples with mother solutions are mounted in quartz tubes for measurements. Thus, single-crystal samples of two complexes are not microanalyzed because of their quick efflorescences. Reflection data for **2a** and **2b** crystals were measured by a Bruker SMART 1K CCD diffractometer system at 293(2) K using graphite monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) at a detector distance of 4 cm and a swing angle of −35°. The collected data were reduced by using the program SAINT,[8] and the empirical absorption correction was done by using the SADABS[9] program. Both structures were solved by direct methods and refined by a least-squares method on $F_{obs}^2$ by using the SHELXTL-PC[10] software package, with 6631 of 18 842 (**2a**) and 6741 of 14 839 (**2b**) [$I > 2\sigma(I)$] unique absorption-corrected reflections. All non-H atoms were anisotropically refined. Except for the water hydrogens in **2b**, all other hydrogen atoms were geometrically fixed and allowed to ride on the attached atoms. The crystallographic results are summarized in Table 1, and selected bond distances and bond angles are listed in Table 2. Further details are provided in Supporting Information.

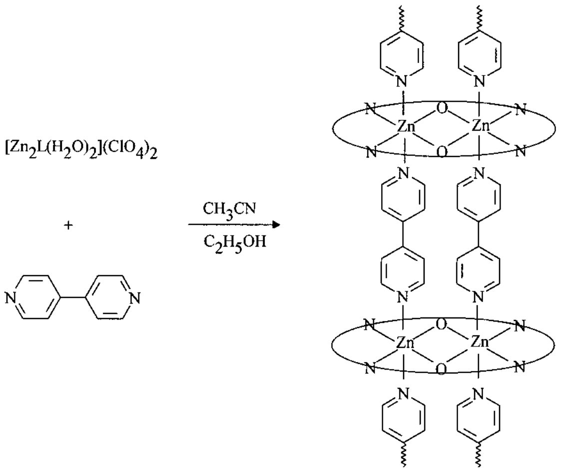
## Results and Discussion

According to the microanalytical data, it can be easily deduced that the ratio of the dinuclear zinc(II) macrocyclic species to 4,4′-bipyridine in two compounds is 1:2. However, it is difficult to specify how two 4,4′-bipyridine units connect to the metal ions in the macrocycle in the same direction or inversely. In our previous work[7b] and others' reports,[11] monofunctional ligands such as water, halogens, and azide anions as well as tetracyanoquinodimethane ligands are found situated on two sides of the macrocyclic plane to reduce the spatial repulsion. Is it the case for 4,4′-bipyridine? To explore the this linear bifunctional ligand via self-assembly with **1** and to learn exactly the coordination environment of each zinc(II) atom, crystal structures of **2a** and **2b** are determined by X-ray diffraction.

**Table 2.** Selected Bond Distances (Å) and Angles (deg) for **2a** and **2b**

| **2a** | | **2b** | |
|---|---|---|---|
| | Bond Distances | | |
| Zn(1)−N(1A) | 2.032(4) | Zn(1)−N(1) | 2.044(3) |
| Zn(1)−N(2A) | 2.019(3) | Zn(1)−O(1) | 2.063(3) |
| Zn(1)−O(1) | 2.044(3) | Zn(1)−N(2) | 2.064(3) |
| Zn(1)−O(1A) | 2.035(3) | Zn(1)−O(1A) | 2.072(2) |
| Zn(1)−N(3) | 2.284(3) | Zn(1)−N(3) | 2.321(3) |
| Zn(1)−N(4B) | 2.444(4) | Zn(1)−N(4B) | 2.401(3) |
| | Bond Angles | | |
| N(2A)−Zn(1)−N(1A) | 100.81(15) | N(1)−Zn(1)−O(1) | 90.72(11) |
| N(2A)−Zn(1)−O(1) | 169.32(13) | N(1)−Zn(1)−N(2) | 100.89(12) |
| N(1A)−Zn(1)−O(1A) | 89.77(13) | O(1)−Zn(1)−N(2) | 168.40(10) |
| N(2A)−Zn(1)−O(1) | 90.54(13) | N(1)−Zn(1)−O(1A) | 169.59(11) |
| N(1A)−Zn(1)−O(1) | 168.24(13) | O(1)−Zn(1)−O(1A) | 78.88(10) |
| O(1A)−Zn(1)−O(1) | 78.82(11) | N(2)−Zn(1)−O(1A) | 89.52(11) |
| N(2A)−Zn(1)−N(3) | 87.88(12) | N(1)−Zn(1)−N(3) | 87.06(10) |
| N(1A)−Zn(1)−N(3) | 89.67(13) | O(1)−Zn(1)−N(3) | 92.39(10) |
| O(1A)−Zn(1)−N(3) | 93.67(11) | N(2)−Zn(1)−N(3) | 88.13(11) |
| O(1)−Zn(1)−N(3) | 93.86(12) | O(1A)−Zn(1)−N(3) | 93.52(10) |
| N(2A)−Zn(1)−N(4B) | 87.30(12) | N(1)−Zn(1)−N(4B) | 87.96(11) |
| N(1A)−Zn(1)−N(4B) | 86.01(13) | O(1)−Zn(1)−N(4B) | 92.41(10) |
| O(1A)−Zn(1)−N(4B) | 92.06(11) | N(2)−Zn(1)−N(4B) | 88.15(11) |
| O(1)−Zn(1)−N(4B) | 91.51(11) | O(1A)−Zn(1)−N(4B) | 92.24(10) |
| N(3)−Zn(1)−N(4B) | 172.81(13) | N(3)−Zn(1)−N(4B) | 173.12(11) |

An X-ray crystal structure study indicated that the coordination environment around each Zn(II) atom in **2a** is a distorted octahedron in which two apical positions are occupied by the bridging ligand, 4,4′-bipyridine (Figure 1). The two axial Zn−N bonds are not equal in length because of the metal atom being a little high over the octahedral base plane.



**2**

The most significant feature is that the crystal structure of **2a**

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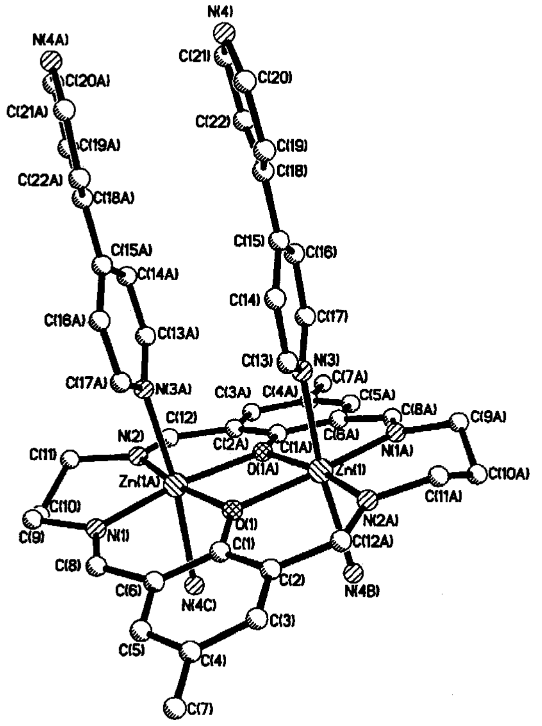

**Figure 1.** Structure of the complex cation of **2a** with the atom-numbering scheme. Hydrogen atoms are omitted for clarity.

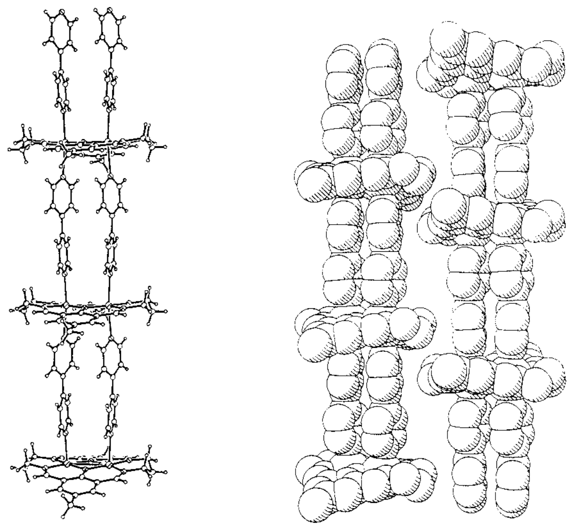
(a) (b)

**Figure 2.** (a) View of the 1-D network and (b) space-filling view of the molecular ladder with macrocyclic platforms and their crystal packing along the *a* axis in **2a**.

exhibits an infinite 1-D molecular ladder motif composed of 4,4′-bipyridine molecules with two zinc atoms of **1a** in very close proximity (<3.2 Å) (Figure 2). Both pyridine ring planes in one 4′,4-bipyridine molecule, staggered with a dihedral angle of 6.3° and paralleled with their counterpart, are perpendicular to the least-squares planes in which two metal atoms are situated. It is of much interest to note that **2a** has rectangular hydrophobic cavities (3.150 Å × 11.758 Å), where the 4,4′-bipyridine ligands connect the Zn(II) ions to serve as the "side rails" (long sides) and where the phenoxy oxygen atoms on the ring link the Zn(II) ions to act as the "rungs" (short sides). To our knowledge, this is the first instance of molecular ladders that have no interpenetrated network entangled or guest molecules clathrated in the ladder cavity. It is suggested that the coordination behavior of the metal atom has played an important role in yielding the framework of the ladder. It is due to the inlay of macrocyclic platforms throughout the structure that has stabilized the resulting ladder motif by overcoming the spatial repulsion between the macrocycle and bipyridine ligands through coordination bonding and by generating $\pi-\pi$ interactions between pyridine rings.

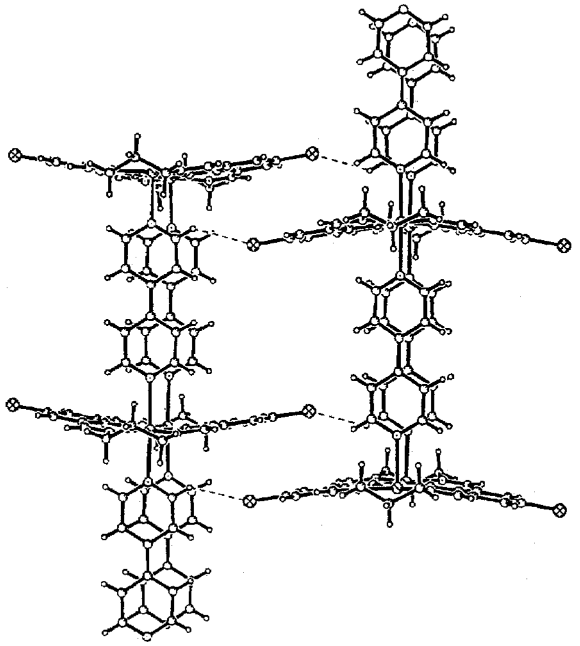

**Figure 3.** View of the 2-D network depicting the connection via nonclassical hydrogen bonds in **2b**.

An X-ray structural analysis revealed that **2b** possesses almost the same molecular ladder motif as **2a**. However, the substituted chlorine atom on the top position of the phenyl ring has led to a distinction of ladder arrays in two crystal patterns. Because of the two phenolic oxygen atoms bridging the two zinc atoms on the macrocyclic ring, this results in the molecular ladder being interrupted by macrocyclic platforms. It is interesting to note that the macrocyclic platforms of the neighboring molecular ladders in **2a** are mutually staggered without any connections, forming a one-dimensional network while in **2b** adjacent ladders are linked by C−H···Cl hydrogen bonding, forming a two-dimensional network (Figure 3). This kind of weak nonclassical hydrogen bonding in **2b** arises from the intermolecular interaction between the top chlorine atom of one macrocyclic framework of one ladder and the hydrogen atom attaching to a pyridine ring of the neighboring ladder. The geometric dimensions of the H-bonding here is 2.898 Å in length and 133.8° in angle. Although the existence of C−H···Cl hydrogen bonds is still controversial,[12] this kind of interaction has been found to be present in more than 100 crystal structural reports, which contain structural patterns like **2b**.[13] In comparison to those in the literature, the length of H···Cl in **2b** is among the values reported.

In addition, C−H···O bonding has also been observed in the crystal structure of both compounds **2a** and **2b**. In **2a**, there are three types of such hydrogen bonds (2.554 Å, 129.01°; 2.593 Å, 141.43°; and 2.591 Å, 132.34°) where the H-bonding acceptor is from one oxygen atom of the perchlorate anions.

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But the related H-bonding donor comes from different sources, the first two from the first carbon atom of the 1,3-propanediamine group of the macrocyclic framework and the last from a pyridine unit. In complex **2b**, such C−H···O H-bonds are 2.564 Å, 156.50° and 2.592 Å, 132.15°, respectively. The H-bonding acceptor is one oxygen atom of perchlorate anions too, but the former H-bonding donor comes from a ArCH═NR group of the macrocyclic framework and the latter from the pyridine unit.

The X-ray determination results reveal that there are methanol and ethanol molecules in the crystal packing of **2a**. It is believed that a small amount of methanol exists in the ethanol that is used without further purification, although the ethanol is so-labeled as analytic grade. While purified ethanol is utilized in **2b**, only an ethanol as well as water molecules is found in its crystal structure.

TGA−DTA analysis of **2a** gives the following: gradual 4.25% weight loss from 15 to 145 °C and stability to 215 °C; then 28.68% weight loss in a range of 216−250 °C and stability to 340 °C; and finally explosion at 341 °C. The data suggest the compound lost solvent molecules and 4′,4-bipyridine units initially and then decomposed. The thermal behavior of **2b** is similar to that of **2a**.

Although the decorated mononuclear metalloporphyrin complexes constructing coordinating polymers and hydrogen-bonding chained polymers have been actively studied recently, macrocyclic dinuclear species are rarely involved in this aspect.[14] The results reported herein offer two new types of coordination polymers based on the macrocyclic dinuclear zinc(II) component. By use of linear 4,4′-bipyridine ligands, 1-D networks and 2-D ones via H-bonding have been isolated. We are in the process of studying other pyridine-based ligands to construct other frameworks with this kind of macrocyclic unit via coordinating bonds or supermolecular interactions. These results will be reported in due course.

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

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