Self-assembled molecular ladders

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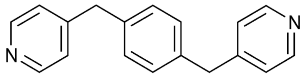
Coordination of a pyridine-based bridging ligand, 1,4-bis(4-pyridylmethyl)benzene (**1**), with cadmium nitrate afforded an infinite ladder complex, the unit structure of which involves a T-shaped assembly of three pyridine rings about a heptacoordinated Cd^{II} atom. The ladder structure was found to expand its cavity volume by enclathrating *p*-dibromobenzene in the cavity. Nearly orthogonal interpenetration of infinite ladders was observed in the solid structure.

Coordination chemistry has been recently taking an important role in controlling 1D, 2D or 3D infinite structures of crystalline compounds.[1] The benefit in employing coordination bonds instead of the frequently employed hydrogen bond[2] is a wide selection of coordination modes of metals. For example, upon coordination in linear, trigonal, square planar or tetrahedral geometries, a rigid bridging ligand gives 1D-rod,[3] 2D-honeycomb,[4] 2D-grid[5] or 3D-diamond[6] infinite structures, respectively.

Of many such coordination polymers, however, infinite ladder structures[7] have attracted scant attention though the corresponding organic ladder polymers have been showing interesting properties. This is probably due to the difficulty in obtaining a T-shaped geometry around the metal, which is essential to get the ladder structure (Scheme 1).[8] In a few old papers, metal nitrate–pyridine complexes were shown to have a T-shaped assembly of three pyridine molecules about the metal in an uncommon heptacoordination geometry.[9] In the expectation of observing ladder structures, we examined the complexation of $Cd(NO_3)_2$ with a variety of bridging ligands possessing pyridine rings at both ends. After examination we found the assembly of an infinite ladder complex from $Cd(NO_3)_2$ and the flexible, very simple ligand **1**. We also found that, due to the flexibility of this ligand, the ladder expands its cavity volume by enclathrating a guest molecule in the cavity. A part of the present study has already been published in a preliminary form.[7a]



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Results and Discussion

Synthesis and crystal structure of the infinite ladder complex $[Cd(\mathbf{1})_{1.5}](NO_3)_2$

When $Cd(NO_3)_2$ was complexed with ligand **1** (1.5 equiv) in ethanol, we obtained X-ray quality single crystals with the empirical formula $[Cd(\mathbf{1})_{1.5}](NO_3)_2$ (complex **A**) in 60% yield.

Scheme 1 Schematic illustration for the assembly of an infinite ladder framework from "T-shaped" units

Crystallographic analysis of this crystal gave the unit structure shown in Fig. 1. There are several interesting aspects. First, the molecular structure involves the expected T-shaped assembly of three pyridine rings. C10 is connected with C′18 whereas C26 and C27 are connected with C″27 and C″26, giving an infinite ladder structure (Fig. 2) in the manner illustrated in Scheme 1. The T-shaped framework of the molecular structure involves coordination angles somewhat deviated from ideal values: N1—Cd1—N2 = 85.5°, N1—Cd1—N3 = 91.6° and N2—Cd1—N3 = 176.1°. Second, there are independent ladders existing along the $a + b$ and $a - b$ vectors of the crystal and these ladders interpenetrate each

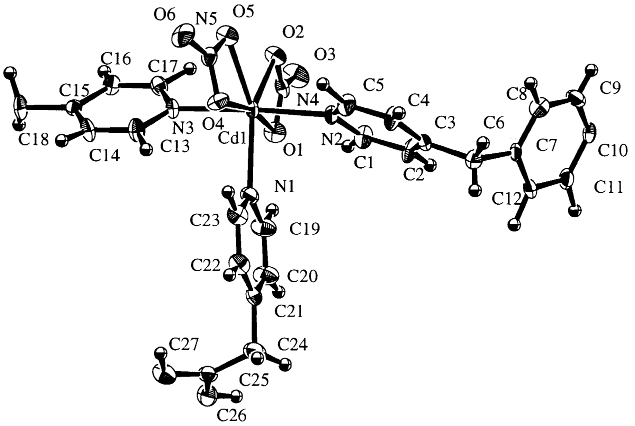

Fig. 1 An ORTEP diagram of the crystal structure of complex **A** showing the 50% probability thermal motion ellipsoid

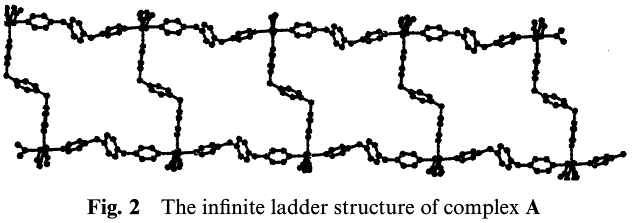

Fig. 2 The infinite ladder structure of complex **A**

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other in the crystal (Fig. 3).[10] The ladder is composed of large 60-membered rings, each of which interlocks with four rings of different ladders. Selected crystal data for the complex are listed in Table 1.

Enclathration of *p*-dibromobenzene by the infinite ladder complex

Because the ladder framework involves a macrocyclic structure, this complex is expected to enclathrate organic guest molecules in the cavity. Thus complexation of $Cd(NO_3)_2$ with ligand **1** was examined in the presence of various guest molecules. Of many aromatic guest molecules, *p*-dibromobenzene was found to be enclathreted to give single crystals with the formula $[Cd(\mathbf{1})_{1.5}](NO_3)_2 \cdot G_{0.5}$ (complex **B**) where G is the guest molecule. The structure was solved by X-ray crystallography (Table 1). The molecular structure is very similar to that of complex **A** except for the existence of half a molecule of *p*-dibromobenzene (Fig. 4). Again, the T-shaped assembly of three pyridine rings is observed and this T-shaped unit makes an infinite ladder structure (Fig. 5), which clearly shows that one guest molecule is enclathrated in the middle of each cavity.

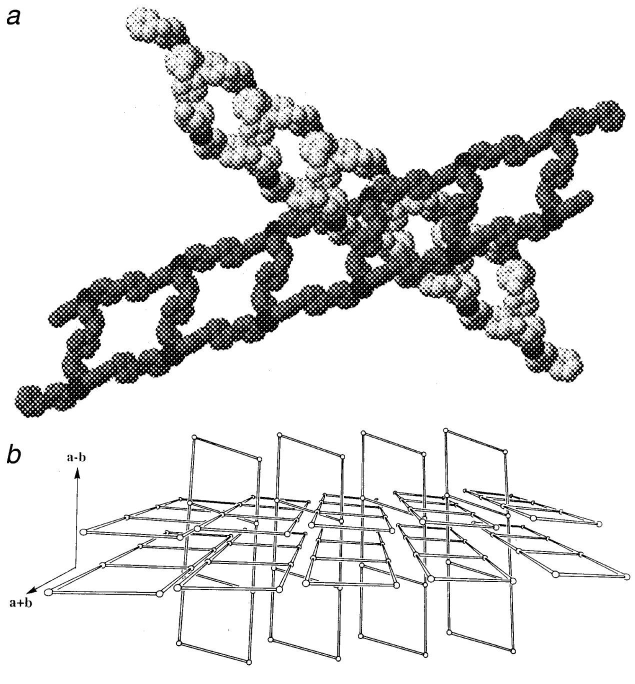

Fig. 3 Interpenetration observed in the crystal structure of complex **A**. (*a*) Two interpenetrating ladders (a CPK presentation). (*b*) Perspective view of the frameworks in **A**. Only the Cd^{II} centers are shown; heavy connections indicate the Cd—**1**—Cd framework

Table 1 Selected crystal data for complexes **A** and **B**

Complex	**A**	**B**
Crystal data		
Chemical formula	$C_{27}H_{24}N_5O_6Cd$	$C_{30}H_{26}N_5O_6CdBr$
Formula weight	626.97	744.88
Crystal size/mm	0.45 × 0.45 × 0.48	0.10 × 0.10 × 0.20
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$ (#15)	$P2_1/n$ (#14)
a/Å	9.664(1)	11.062(4)
b/Å	13.427(2)	12.069(6)
c/Å	20.844(3)	22.68(2)
α/°	90.00	90.00
β/°	94.74(1)	99.51(4)
γ/°	90.00	90.00
U/Å^3	2696(6)	2986(3)
D_{calc}/g cm^{-1}	1.55	1.66
Z	4	4
F(000)	1268	1488
Data Collection		
Radiation/Å	Cu Kα, 1.54178	Mo Kα, 0.71073
μ/cm^{-1}	69.12	21.26
Total data	4410	2142
Unique data	4134	2142
Observed data	3447 [$I > 5.5\sigma(I)$]	886 [$I > 3.0\sigma(I)$]
Refinement		
No. of reflections	3447	884
No. of parameters	448	414
R	0.036	0.055
Rw	0.044	0.050

It is interesting that the ladder enclathrates the guest molecule by expanding the cavity volume as clearly shown by comparing the ring frameworks (Fig. 6). Force field calculations suggested that the driving force for enclathrating the guest molecule is release of strain existing in the ladder framework. Namely, MM2 optimization[11] of the large 60-membered ring of complex **A** gave a conformation very

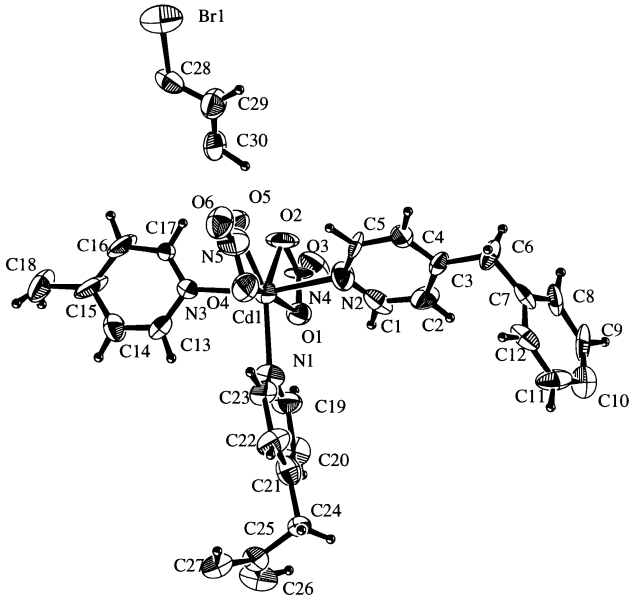

Fig. 4 An ORTEP diagram of the crystal structure of complex **B** showing the 50% probability thermal motion ellipsoid

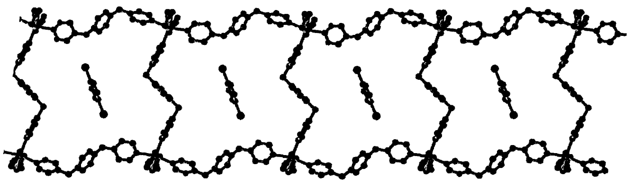

Fig. 5 The infinite ladder structure of complex **B**

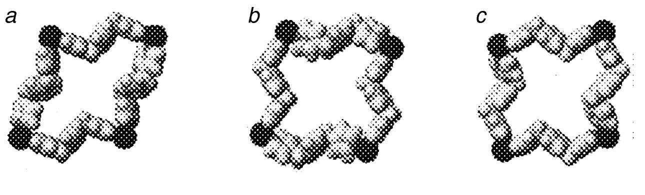

Fig. 6 Large ring structures in: (*a*) complex **A**, (*b*) complex **B** and (*c*) MM2 optimized conformation of complex **A**

similar to that of complex **B**. In addition, due to the enclathration of a guest molecule, the geometry around the metal is still deviated from the ideal T-shape: N1—Cd1—N2 = 94.1°, N1—Cd1—N3 = 99.7°, and N2—Cd1—N3 = 166.1°.

Except for the existence of the guest, essentially there is no significant change in the whole crystal structure of complexes **A** and **B**. Again, we observed the same pattern of interpenetration: the large 60-membered ring in the ladder interlocks with four rings of different ladders. The cross angles of the interpenetrating ladders are 71.4° and 85.9° for complexes **A** and **B**, respectively.

Experimental

1,4-Bis(4-pyridylmethyl)benzene (1)

p-Dibromobenzene (10 mmol) was treated with *n*-BuLi (1.6 M cyclohexane solution, 25 mmol) in THF (50 mL) at −78 °C. After 0.5 h, 4-pyridinecarboxyaldehyde (25 mmol) was added and the mixture was stirred for 1.5 h at room temperature. Addition of water (100 mL) precipitated 1,4-bis(4-pyridylmethyl)benzene (5.1 mmol, 51%) as a pure colorless powder: mp 217–219 °C; ^{1}H NMR ($CDCl_3$, CD_3OD) δ 5.75 (s, 2H, C*H*), 7.33 (s, 4H, C_6H_4), 7.38 (d-like, *J* = 4.6 Hz, 4H, PyH_β) , 8.44 (d-like, *J* = 4.6 Hz, 4H, PyH_α); IR (KBr) 3150, 1660, 1410, 1135, 780, 635 cm^{-1}. HRMS (FAB): calcd for $C_{18}H_{16}N_2O_2$: 293.1290; found, 293.1298. Anal. calcd for $C_{18}H_{16}N_2O_2 \cdot 0.2H_2O$: C, 73.06; H, 5.56; N, 9.04. Found: C, 73.33, H, 5.51; N, 9.08. This compound (0.36 mmol) was dissolved in a mixed solvent of EtOH (20 mL) and 2 M aq HCl (15 mL). To this solution was added 10% Pd-C (11 mg) and the vessel was purged with atmospheric pressure of hydrogen. The mixture was stirred for 9 h at 60 °C under 1 atm of H_2, and then filtered. The filtrate was evaporated *in vacuo* and extracted with CH_2Cl_2 (100 mL × 3). The combined organic layer was dried over anhydrous K_2CO_3 and evaporated. The residue was purified by column chromatography (silica gel, ethyl acetate) and preparative HPLC to give 1,4-bis(4-pyridylmethyl)benzene (0.24 mmol, 65%) as a white powder: mp 107 °C; ^{1}H NMR ($CDCl_3$) δ 3.94 (s, 4 H, CH_2), 7.10 (d-like, *J* = 5.9 Hz, 4H, PyH_β), 7.12 (s, 4H, C_6H_4), 8.44 (d-like, *J* = 5. 3 Hz, 4H, PyH_α); IR (KBr) 3025, 1600, 1508, 1412, 1220, 954, 828, 805, 595, 500, 480 cm^{-1}. Anal. calcd for $C_{18}H_{16}N_2$: C, 83.04; H, 6.19; N, 10.76. Found: C, 82.90; H, 6.12; N, 10.48.

Complexes

Complex A. An ethanol–water (7 : 3) solution of **1** (75 mM) and $Cd(NO_3)_2$ (50 mM) was allowed to stand for 10 days at 20 °C to give a single crystal of complex **A** having the empirical formula $[Cd(\mathbf{1})_{1.5}](NO_3)_2$ in 60% isolated yield. The crystal was subjected to an X-ray diffraction study. Crystal data of complex **A** are shown in Table 1. Anal. calcd for $C_{27}H_{24}N_5O_6Cd$: C, 51.73; H, 3.86; N, 11.17. Found: C, 51.61; H, 3.81; N, 10.98.

Complex B. To an ethanol–water (3 : 2) solution (0.5 mL) of **1** (0.1 mmol) and $Cd(NO_3)_2$ (0.1 mmol) was added a saturated solution of *p*-dibromobenzene in ethanol (1 mL) and the solution was allowed to stand for 1 day at room temperature to give a single crystal of complex **B** having the empirical formula of $[Cd(\mathbf{1})_{1.5}](NO_3)_2 \cdot (C_6H_4Br_2)_{0.5}$. The crystal was subjected to an X-ray diffraction study. Crystal data of complex **B** are shown in Table 1.

CCDC reference number 440/013.

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