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Supramolecular architectures of metallomacrocyclic and coordination polymers with dicarboxylate and 4,4′-bis(imidazol-1-ylmethyl)biphenyl ligands

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Abstract

Four dimeric and polymeric coordination compounds $[Zn_2(bimb)_2(pdc)_2]\cdot 6H_2O$ (**1**), $[Cd_2(bimb)_2(tp)_2]\cdot H_2O$ (**2**), [Cd(bimb)(ada)] (**3**) and [Co(bimb)(ada)] (**4**) (bimb, 4,4′-bis(imidazol-1-ylmethyl)biphenyl; pdc, pyridine-2,6-dicarboxylate; tp, terephthalate and ada, adipate) have been synthesized under hydrothermal conditions. Complex **1** is a discrete dinuclear metallomacrocycle featuring a 34-membered ring, in which the flexible bimb ligand acts as *syn*-conformation. While complexes **2**–**4** are 3D network structures connected by bimb and dicarboxylate ligands, the bimb ligand displays *anti*-confromation.

Keywords: Metallomacrocycle; Coordination polymer; Dicarboxylate; 4,4′-Bis(imidazol-1-ylmethyl)biphenyl; Hydrothermal synthesis

1. Introduction

The rational design of supramolecular architectures having different topologies and functions is one of the important targets in crystal engineering [1–3]. Compared with the classical inorganic compounds, coordination polymers have great advantage of facility for modifiable, flexibility, structural diversity and geometrical control. In this context, the linear, rigid ligand 4,4′-bipyridine is of great importance and widely employed to ligate metal ions as building blocks to construct coordination polymers [4,5]. Their final structures are highly dependent on the metal-to-ligand ratio, as well as on the counterions and guest molecules. The flexible ligands such as 1,2-bis(4-pyridyl)ethane and 1,3-bis(4-pyridyl)propane are also of interest in the construction of flexible microporous coordination polymers [6]. On the other hand, the flexible bridging ligand 1,4-bis(imidazol-1-ylmethyl)benzene (bix) containing imidazole groups with the *syn* and *anti* two conformations has been reported to react with metal ions, furnishing discrete metallomacrocycles, 1D infinite chain, 2D polyrotaxane networks and 3D frameworks with different metal ions [7–19]. 4,4′-Bis(imidazol-1-ylmethyl)-biphenyl (bimb) is a bidentate ligand and can adopt *syn* and *anti* two different conformations (Scheme 1). Compared with 4,4′-bipyridine and bix, bimb is a more flexible ligand and exhibits in various structures with interesting topology. However, the so far known complexes are very limited [20–24]. As a sequel work of our continuing effort in synthesizing coordination polymers with mixed dicarboxylates and N-ligands [25–28] and understanding how the nature of metal ions and the structures of the dicarboxylate ligands affect the structures of the their complexes, flexible bridging ligand bimb was synthesized and employed for the construction of coordination frameworks incorporated with dicarboxylate ligands and different transition metal ions, and dicarboxylates were used in our reaction systems to observe the structural diversity. We report here the synthesis and

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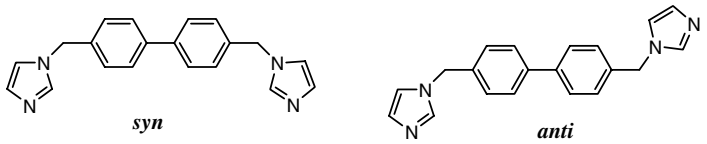

Scheme 1. The '*syn*' and '*anti*' conformations of bimb.

structural characterization of four new complexes, namely $[Zn_2(bimb)_2(pdc)_2]\cdot 6H_2O$ (**1**), $[Cd_2(bimb)_2(tp)_2]\cdot H_2O$ (**2**), [Cd(bimb)(ada)] (**3**) and [Co(bimbb)(ada)] (**4**) (pdc, pyridine-2,6-dicarboxylate; tp, terephthalate and ada, adipate).

2. Experimental

2.1. Materials and general methods

The 4,4′-bis(1-imidazol-1-ylmethyl)biphenyl (bimb) was synthesized according to the literature method [20]. All chemicals were commercially available and used as received without further purification. The C, H and N microanalyses were carried out on an Elementar Vario EL elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Nicolet Magna 750 spectrometer. Thermogravimetric data were collected on a Netzsch TG-209 analyzer in nitrogen atmosphere at a heating rate of 10 °C min^{-1}.

2.2. Hydrothermal syntheses

A mixture of metal salt (0.5 mmol), bimb (0.5 mmol), dicarboxylic acid (0.5 mmol) and NaOH (1.0 mmol) and water (8 ml) was stirred for 15 min in air, then transferred and sealed in a 23 ml Teflon reactor, which was heated at 170 °C for 5 days and then cooled to room temperature at a rate of 5 °C h^{-1}. Crystals were obtained, washed with deionized water and absolute ethanol.

The yield of **1** was 30% based on Zn. $C_{54}H_{54}N_{10}O_{14}Zn_2$ (1196): calcd. C, 54.18; H, 4.51; N, 11.70. Found: C, 54.55; H, 4.52; N, 11.61. FT-IR (KBr, cm^{-1}): 3425 (m, br), 1636 (s), 1592 (m), 1529 (m), 1430 (m), 1368 (s), 1282 (m), 1240 (m), 1109 (m), 955 (m), 853 (m), 815 (m), 755 (m), 732 (m), 694 (m), 659 (m), 511 (m).

The yield of **2** was 331% based on Cd. $C_{56}H_{46}Cd_2N_8O_9$ (1199.81): calcd. C, 56.06; H, 3.86; N, 9.34. Found C, 56.13; H, 3.99; N, 9.55. FT-IR (KBr, cm^{-1}): 3118 (m), 1570 (s), 1517 (m), 1441 (m), 1389 (s), 1283 (m), 1234 (m), 1110 (m), 1084 (m), 1027 (m), 938 (m), 836 (m), 754 (m), 655 (m), 523 (m).

The yield of **3** was 28% based on Cd. $C_{26}H_{26}CdN_4O_4$ (570.92): calcd. C, 54.70; H, 4.59; N, 9.81. Found C, 54.85; H, 4.62; N, 10.02. FT-IR (KBr, cm^{-1}): 3112 (m), 2931 (m), 1550 (s), 1408 (s), 1323 (m), 1283 (m), 1230 (m), 1209 (m), 1109 (m), 1082 (m), 936 (m), 843 (m), 807 (m), 749 (m), 696 (m), 658 (m).

For **4** the yield was 38% based on Co. $C_{26}H_{26}CoN_4O_4$ (517.44): calcd. C, 60.35; H, 5.06; N, 10.83. Found C, 60.48; H, 5.13; N, 10.87. FT-IR (KBr, cm^{-1}): 3140 (m), 2939 (m), 2861 (m), 1604 (s), 1573 (s), 1521 (m), 1502

Table 1
Crystallographic data for **1**–**4**

Complex	**1**	**2**	**3**	**4**
Formula	$C_{54}H_{54}N_{10}O_{14}Zn_2$	$C_{56}H_{46}Cd_2N_8O_9$	$C_{26}H_{26}CdN_4O_4$	$C_{26}H_{26}CoN_4O_4$
Formula weight	1196.47	1199.81	570.92	517.44
Crystal system	Trigonal	Monoclinic	Monoclinic	Monoclinic
Space group	*R*-3	*C*2/*c*	$P2_1/c$	$P2_1/c$
a/Å	24.397(3)	38.661(5)	18.250(2)	17.842(1)
b/Å	24.397(3)	14.519(2)	15.544(2)	15.345(1)
c/Å	24.766(7)	9.213(1)	8.576(1)	8.767(1)
β/°	120	98.201(2)	90.579(3)	96.497(2)
V/Å^3	12766(4)	5119(1)	2432.7(5)	2384.8(3)
Z	9	4	4	4
D_{calcd}/Mg/m^3	1.416	1.557	1.559	1.441
μ(Mo-Kα), mm^{-1}	0.920	0.897	0.938	0.760
F(000)	5640	2424	1160	1076
No. of unique reflections	5571	5566	5189	4255
No. of reflections[$I \geqslant 2\sigma(I)$]	2823	3960	3725	3399
No. of parameters	370	333	316	316
R_{int}	0.059	0.041	0.041	0.029
Goodness of fit refinement	0.964	1.079	1.044	1.066
R_1[a]	0.063	0.061	0.047	0.051
wR_2[b]	0.222	0.175	0.112	0.135

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