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A series of polythreaded architectures based on a long flexible tetracarboxylate ligand and different N-donor ligands

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ABSTRACT

Five new polythreaded coordination networks, $[Co_2(L)(bpp)(H_2O)]\cdot0.25H_2O$ (**1**), $[Co_2(L)(bim)]$ (**2**), $[Co_2(L)(btb)]$ (**3**), $[Co_3(HL)_2(phen)_3]$ (**4**) and $[Ni_2(L)(bpp)_2(H_2O)_2]\cdot2H_2O$ (**5**) (H_4L = 5,5′-(1,3-phenylenebis(methyleneoxy)diisophthalic) acid, bpp = 1,3-di(4-pyridyl)propane, bim = 1,4-bis(imidazol-1-yl)butane, btb = 1,4-bis(1,2,4-triazol-1-yl)butane, phen = 1,10-phenanthroline), have been synthesized by self-assembly of transition-metal salts with a long flexible tetracarboxylate ligand and N-containing ligands. Their structures were characterized by single crystal X-ray diffraction, elemental analyses, X-ray powder diffraction, IR spectra and TG analyses. Compounds **1**–**3** exhibit unusual (2D → 2D) polythreaded frameworks that are built from 2D layers with dangling arms protruding from one side of the layers. Compound **4** displays a unique (2D → 3D) polythreaded framework constructed from 2D layers with two types of lateral arms. Compound **5** is an uncommon (1D → 1D) polythreaded framework that is first assembled from 1D metal–organic nanotubes (MONTs) with lateral arms protruding from one side of the 1D MONTs. In addition, the magnetic properties of them were also studied.

1. Introduction

The design and assembly of metal–organic frameworks (MOFs) have attracted great attention during the past two decades, not only because of their enormous variety of molecular architectures and topologies, but also due to their interesting properties and broad potential applications as new functional materials [1,2]. Entangled systems (catenanes, rotaxanes and molecular knots), an active subject in the field of MOFs, have captivated much attention of chemists because of their intriguing artistic appeal, and more importantly, due to their potential applications originating from the intertwining nature of the lattices [1b,3,4a]. As a result, several fascinating types of entanglement, such as interpenetration, polycatenation, polythreading and other species have been discovered up to now [1b,4]. It is well known that interpenetration and polycatenation need to break rings to separate the individual nets. However, polythreaded networks, which feature rings that are threaded by the adjacent structural units, can be separated without the need for breaking rings [5,6]. Admirable synthetic strategies have been developed for this new type of entanglement in recent years, because polythreaded networks are more flexible than the usual MOFs based entirely on coordination bonds and thus possess potential applications ranging from sensor devices to drug delivery vehicles [1d,7,8].

However, in contrast to the fruitful production of interpenetration and polycatenation structures, polythreaded networks are relatively rare [4b,5d–f,6]. To the best of our knowledge, from the previously reported polythreaded networks almost all are constructed from 0D, 1D or 2D motifs with dangling arms protruding from both sides [1b], and only two (2D → 2D) polythreaded architectures with dangling arms protruding from one side of the layers have been reported [9]. This may be, at least in part, attributed to the fact that the generation of unsymmetrical motifs is more difficult than that of symmetrical motifs. Hence, it is still a current challenge to synthesize polythreaded frameworks that are assembled from 0D, 1D or 2D motifs with dangling arms protruding from one side, and further research is necessary to enrich and develop this branch.

During the course of our attempts to synthesize novel polythreaded networks [10], we chose the long flexible tetracarboxylate ligand 5,5′-(1,3-phenylenebis(methyleneoxy)diisophthalic) acid (H_4L) and different N-containing ligands [1,3-di(4-pyridyl)

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propane (bpp), 1,4-bis(imidazol-1-yl)butane (bim), 1,4-bis(1,2,4-triazol-1-yl)butane (btb) and 1,10-phenanthroline monohydrate (phen) (Scheme 1)] based on the following considerations: (i) H_4L contains two flexible –CH_2–O– spacers in the molecule, thus the two phenylene rings of outer edge can freely twist to meet the requirements of the coordination geometries of metal atoms in the assembly process [11–13]. Due to its varied conformations and geometries, long flexible H_4L ligand showed the ability to produce unique entangled structures [1a,11a]. (ii) The N-containing ligands can acts as lateral arms, thus providing a necessary condition for the formation of polythreading networks. (iii) Only a few coordination compounds containing H_4L ligand have been reported to date [14]. Furthermore, coordination compounds constructed from mixed H_4L and N-donor ligands have never been observed so far. Therefore, much work is still necessary to understand the coordination chemistry of H_4L ligand. In view of these points, we have performed many experiments, and these efforts have led to the isolation of five complexes, namely $[Co_2(L)(bpp)(H_2O)]\cdot0.25H_2O$ (**1**), $[Co_2(L)(bim)]$ (**2**), $[Co_2(L)(btb)]$ (**3**), $[Co_3(HL)_2(phen)_3]$ (**4**) and $[Ni_2(L)(bpp)_2(H_2O)_2]\cdot2H_2O$ (**5**), which exhibit polythreaded character. Their interesting structural motifs and topological analyses will be represented and discussed in detail. In addition, the magnetic properties of compounds **1**–**5** were also investigated.

2. Experimental

2.1. Materials and general methods

All chemicals were commercially purchased and used without further purification. The organic ligands 1,4-bis(imidazol-1-yl)butane (bim) [15a] and 1,4-bis(1,2,4-triazol-1-yl)butane (btb) [15b] were synthesized according to the literature methods. Elemental analyses (C, H, and N) were performed on a Perkin–Elmer 2400 CHN Elemental Analyzer. Co and Ni were determined by a PLASMA-SPEC(I) ICP atomic emission spectrometer. IR spectra were recorded in the range 400–4000 cm^{-1} on a Bio-Rad FTS-185 FT/IR Spectrophotometer using KBr pellets. TG analyses were performed on a NETZSCH STA 449C instrument flowing N_2 with a heating rate of 10 °C min^{-1}. XRPD data were recorded on a XD-3 diffractometer using Cu Kα radiation. Variable-temperature magnetic susceptibility data were obtained on a SQUID magnetometer (Quantum Design, MPMS-7) in the temperature range of 2–300 K with an applied field of 1.0 kOe.

2.2. Synthesis of $[Co_2(L)(bpp)(H_2O)]\cdot0.25H_2O$ (**1**)

A mixture of $Co(NO_3)_2\cdot6H_2O$ (0.1 mmol), H_4L (0.05 mmol), bpp (0.1 mmol), NaOH solution (0.07 mL, 2 M) and distilled water (8 mL) was stirred for about 15 min in air, then transferred and sealed in a 17 mL Teflon-lined autoclave, which was heated at 150 °C for 96 h. After slow cooling to the room temperature, purple block crystals of **1** were obtained (yield: 43% based on H_4L). Elemental analysis (%) Calc. for $C_{37}H_{30.50}Co_2N_2O_{11.25}$: C, 55.48; H, 3.84; Co, 14.71; N, 3.50. Found: C, 55.74; H, 3.98; Co, 14.49; N, 3.37%. IR (KBr pellet): 3445(s), 3383(s), 3080(w), 2935(w), 2870 (w), 1648(m), 1621(s), 1580(s), 1555(s), 1455(s), 1377(s), 1317 (m), 1261(m), 1227(w), 1172(w), 1127(w), 1109(w), 1066(w), 1030(m), 991(w), 969(w), 917(w), 874(w), 858(w), 810m), 780 (m), 724(m), 677(m), 649(w), 614(w), 576(w), 508(w), 448(w).

2.3. Synthesis of $[Co_2(L)(bim)]$ (**2**)

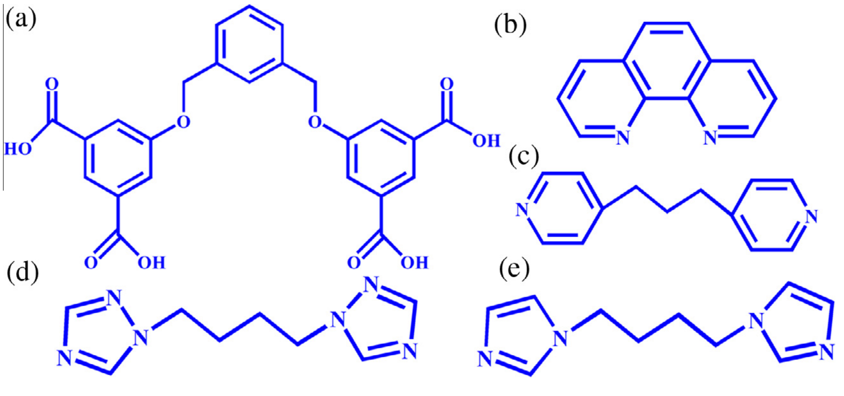
A mixture of $CoCl_2\cdot6H_2O$ (0.2 mmol), H_4L (0.1 mmol), bim (0.1 mmol), NaOH solution (0.2 mL, 2 M) and distilled water (7 mL) was stirred for about 15 min in air, then transferred and sealed in a 17 mL Teflon-lined autoclave, which was heated at 170 °C for 72 h. After slow cooling to the room temperature, purple block crystals of **2** were obtained (yield: 86% based on H_4L). Elemental analysis (%) Calc. for $C_{17}H_{14}CoN_2O_5$: C, 53.00; H, 3.66; Co, 15.30; N, 7.27. Found: C, 53.22; H, 3.48; Co, 15.51; N, 7.09%. IR (KBr pellet): 3443(m), 3129(w), 3114(w), 3079(w), 3056(w), 2948(w), 2918(w), 2863(w), 1610(s), 1572(s), 1524(m), 1492(w), 1451(m), 1410(m), 1373(s), 1318(m), 1264(m), 1230(w), 1181 (w), 1165(w), 1127(w), 1111(m), 1090(w), 1036(w), 967(w), 944 (w), 908(w), 879(w), 836(w), 815(m), 780(m), 744(m), 724(m), 710(m), 678(m), 659(m), 616(w), 513(w), 488(w), 451(w), 436(w).

2.4. Synthesis of $[Co_2(L)(btb)]$ (**3**)

A mixture of $CoCl_2\cdot6H_2O$ (0.2 mmol), H_4L (0.1 mmol), btb (0.1 mmol), NaOH solution (0.5 mL, 2 M) and distilled water (9 mL) and methanol (1 mL) was stirred for about 15 min in air, then transferred and sealed in a 17 mL Teflon-lined autoclave, which was heated at 170 °C for 72 h. After slow cooling to the room temperature, purple block crystals of **3** were obtained (yield: 88% based on H_4L). Elemental analysis (%) Calc. for $C_{32}H_{26}Co_2N_6O_{10}$: C, 49.76; H, 3.39; Co, 15.26; N, 10.88. Found: C, 49.51; H, 3.56; Co, 15.43; N, 10.71%. IR (KBr pellet): 3446(s), 3385(s), 1648(m), 1607(m), 1571(s), 1492(w), 1456(s), 1415(m), 1376(s), 1319(m), 1282(m), 1263(m), 1205(w), 1179(w), 1131(m), 1107(w), 1039 (m), 991(w), 959(w), 935(w), 908(w), 886(w), 799(w), 783(m), 729(m), 675(m), 649(w), 613(w), 555(w), 508(w), 441(w).

2.5. Synthesis of $[Co_3(HL)_2(phen)_3]$ (**4**)

A mixture of $Co(NO_3)_2\cdot6H_2O$ (0.1 mmol), H_4L (0.05 mmol), phen (0.1 mmol), NaOH solution (0.1 mL, 2 M) and distilled water (8 mL) was stirred for about 15 min in air, then transferred and sealed in a



Scheme 1. Structure of H_4L (a,), phen (b), bpp(c), btb (d) and bim (e) ligands.