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Research paper

Syntheses, crystal structures and magnetic properties of five 5,5′-(1,2-phenylenebis(methoxy))diisophthalate coordination polymers

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Five new coordination polymers based on 5,5′-(1,2-phenylenebis(methoxy))diisophthalic acid (H_4L), namely $[Co_3(HL)_2(phen)_2]_n \cdot 2nH_2O$ (**1**), $[Mn_2L(phen)_2]_n \cdot 2nH_2O$ (**2**), $[Cu_2L(4\text{-abpt})_2(H_2O)_2]_n \cdot 2nDMF$ (**3**), $[Co_2L(bpp)_2(H_2O)_3]_n \cdot 3nH_2O$ (**4**) and $\{(CH_3)_2NH_2[Co_2L(\mu_3\text{-}OH)(H_2O)_2] \cdot DMF \cdot H_2O\}_n$ (**5**) (4-abpt = 4-amino-3,5-bis(4-pyridyl)-1,2,4-triazole, bpp = 1,3-bis(4-pyridyl)propane, phen = 1,10-phenanthroline), have been synthesized and characterized by elemental analyses, IR spectra, PXRD, thermogravimetry and X-ray structural analysis. Complex **1** is a 2D coordination polymer constructing from hexadentate HL^{3-} ligand, which contains trinuclear cobalt cluster $[Co_3(COO)_6]$ building block. Complex **2** is a 2D coordination polymer assembled by octadentate L^{4-} ligand. Complex **3** is a 3D metal-organic framework assembled by tetradentate L^{4-} ligand and 4-abpt linker. Complex **4** exhibits a 2D layered network containing 1D $[Co_2L]_n$ nanotube. Complex **5** is a 2D coordination polymer possessing tetranuclear cobalt cluster $Co_4(\mu_3\text{-}OH)_2(COO)_4$. Tetracarboxylate exhibits five types of coordination modes. Thermal analyses demonstrate that complexes **1** and **2** were thermal stable up to 400–450 °C. Variable-temperature magnetic studies indicate that complex **1** has ferrimagnetic coupling in the $[Co_3(COO)_6]$ cluster. Complexes **2** and **5** present antiferromagnetic interactions.

1. Introduction

In recent two decades, coordination polymers (CPs) and metal-organic frameworks (MOFs) have attracted much attention [1], owing to their intriguing structural motifs and multifunctional properties such as luminescence, magnetism, porous absorption, catalysis and sensor [2]. In order to rational design and controlled synthesis, the mixed-ligand strategy has been frequently used to construct diverse coordination polymers with varied topology structures [3]. In contrast to the fewer number of transition-metallic elements, there are great choices of polycarboxylic acids and *N*-heterocyclic ligands used in the synthesis procedure [4]. To date, many polycarboxylate-based coordination polymers were synthesized and structurally characterized in the auxiliary coordination of *N*-heterocycles such as bipyridine, triazole and tetrazole derivates [5].

Various polycarboxylic acids have been extensively used to assemble coordination polymers, owing to their versatile coordination modes, high structural stability and magnetic-exchange propagating ability [6]. 1,3-Benzenedicarboxylic acid (isophthalic acid, H_2ip) is a valuable V-shape ligand with a 120° angle between two carboxyl groups, which was frequently employed in preparing coordination polymers with diverse structures and properties [7]. Comparing with rigid isophthalic acid, the ether-linked semirigid 5,5′-(1,2-phenylenebis(methoxy))-diisophthalic acid (H_4L, Scheme 1) has more advantages. It contains a central phenyl group and two rigid isophthalic acid arms combined by intervening flexible methoxy groups. The cooperation of four rotating carboxyl groups and two freely twisting methoxy groups would afford a directional control and structural extension along three dimensions [8]. This versatile tetracarboxylic acid can act as a valuable multidentate ligand to prepare porous CPs and MOFs with unique structural motifs and functional properties. Moreover, carboxylic bridge can propagate magnetic interaction between paramagnetic metal ions. Previously, several coordination polymers have been assembled by 1,3- and 1,4-substituted H_4L [9]. In this work, we use a new 1,2-substituted H_4L as primary ligand, successfully synthesized and structurally characterized five 2D and 3D coordination polymers. Their magnetic properties and thermal stabilities are also investigated.

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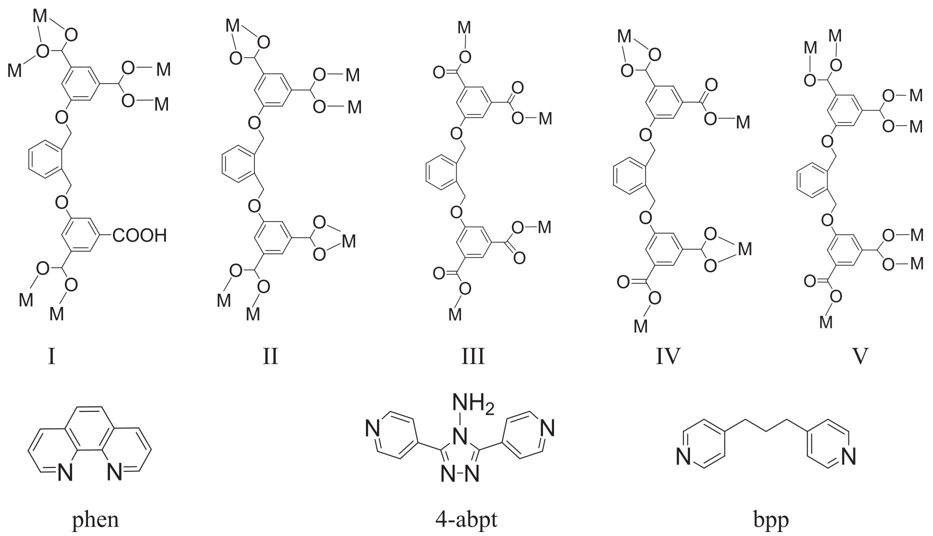

Scheme 1. Schematic description of H_4L coordination modes and *N*-heterocyclic ligands in **1**–**5**.

2. Experimental

2.1. Materials and methods

5,5′-(1,2-phenylenebis(methoxy))diisophthalic acid was purchased from Jinan Henghua Sci. & Tec. Co. Ltd. (China). Other chemicals were of reagent grade and used as received without further purification. Elemental analyses (C, H and N) were determined on a Vario EL III analyzer. Infrared spectra were recorded by a Nicolet A370 FT-IR spectrometer using KBr pellets in 400–4000 cm^{-1} range. Thermogravimetric analyses (TGA) were completed on a Netzsch STA 449C thermal analyzer at a heating rate of 10 °C min^{-1} in air. Powder X-ray diffraction data (PXRD) were recorded on a Rigaku D/MAX-2550 diffractometer at a scanning rate of 5° min^{-1} in the 2θ range of 5–50°. Variable-temperature (2–300 K) magnetic susceptibilities were measured on a Quantum Design MPMS-XL7 SQUID magnetometer at an applied field of 1000 Oe. Diamagnetic corrections were applied by using Pascal's constants.

2.2. Syntheses of complexes

2.2.1. $[Co_3(HL)_2(phen)_2]_n \cdot 2nH_2O$ (**1**)

A mixture of $Co(NO_3)_2 \cdot 6H_2O$ (0.20 mmol), H_4L (0.05 mmol), phen (0.05 mmol), DMF (2 mL) and water (5 mL) was sealed in a 15-mL Teflon-lined reactor and heated at 120 °C for 72 h. Purple crystals were obtained in 43% yield based on H_4L. Anal. calcd for $C_{72}H_{50}N_4O_{22}Co_3$: C, 57.65; H, 3.36; N, 3.74. Found: C, 56.21; H, 3.23; N, 3.67. IR: 3456 w, 3057 w, 2902 w, 1713 m, 1578 s, 1455 w, 1396 s, 1372 s, 1263 s, 1028 m, 764 s, 721 m cm^{-1}.

2.2.2. $[Mn_2L(phen)_2]_n \cdot 2nH_2O$ (**2**)

A mixture of $MnCl_2 \cdot 4H_2O$ (0.20 mmol), H_4L (0.05 mmol), phen (0.05 mmol), DMF (2 mL) and water (5 mL) with three drops of HNO_3 (1.0 mol·L^{-1}) was sealed in a 15-mL Teflon-lined reactor and heated at 160 °C for 72 h. Light yellow crystals were obtained in 40% yield based on H_4L. Anal. calcd for $C_{48}H_{34}N_4O_{12}Mn_2$: C, 59.52; H, 3.54; N, 5.78. Found: C, 60.01; H, 3.76; N, 6.12. IR: 3420 m, 3072 w, 2929 w, 2884 w, 1560 s, 1448 m, 1380 s, 1250 m, 1027 s, 840 m, 781 m, 722 s cm^{-1}.

2.2.3. $[Cu_2L(4\text{-}abpt)_2(H_2O)_2]_n \cdot 2nDMF$ (**3**)

A mixture of $Cu(NO_3)_2 \cdot 3H_2O$ (0.20 mmol), H_4L (0.05 mmol), 4-abpt (0.05 mmol), DMF (4 mL) and water (5 mL) was sealed in a 15-mL Teflon-lined reactor and heated at 100 °C for 72 h. Blue crystals were obtained with 32% yield based on H_4L. Anal. calcd for $C_{54}H_{52}N_{14}O_{14}Cu_2$: C, 51.96; H, 4.20; N, 15.71. Found: C, 51.11; H, 4.27; N, 14.87. IR: 3450 w, 3333 m, 3185 m, 3055 w, 2926 w, 1663 m, 1619 s, 1574 s, 1449 m, 1344 s, 1252 w, 1029 s, 846 m, 780 s, 720 s cm^{-1}.

2.2.4. $[Co_2L(bpp)_2(H_2O)_3]_n \cdot 3nH_2O$ (**4**)

A mixture of $Co(NO_3)_2 \cdot 6H_2O$ (0.20 mmol), H_4L (0.05 mmol), bpp (0.05 mmol), DMF (1 mL) and water (9 mL) was sealed in a 15-mL Teflon-lined reactor and heated at 100 °C for 72 h. Purple crystals were obtained in 46% yield based on H_4L. Anal. calcd for $C_{50}H_{54}N_4O_{16}Co_2$: C, 55.36; H, 5.02; N, 5.16. Found: C, 55.66; H, 5.20; N, 5.16. IR: 3379 m, 2931 w, 1613 m, 1573 s, 1456 w, 1419 w, 1376 s, 1260 w, 1034 s, 809 w, 776 s, 717 s cm^{-1}.

2.2.5. $\{(CH_3)_2NH_2[Co_2L(\mu_3\text{-}OH)(H_2O)_2] \cdot DMF \cdot H_2O\}_n$ (**5**)

A mixture of $CoCl_2 \cdot 6H_2O$ (0.20 mmol), H_4L (0.05 mmol), 4-abpt (0.05 mmol), DMF (2.5 mL) and water (4.5 mL) was sealed in a 15-mL Teflon-lined reactor and heated at 140 °C for 72 h. Purple crystals were obtained with 32% yield based on H_4L. Anal. calcd for $C_{29}H_{36}N_2O_{15}Co_2$: C, 45.21; H, 4.71; N, 3.64. Found: C, 44.96; H, 4.78; N, 3.57. IR: 3426 m, 3300 w, 3082 w, 2798 w, 1635 s, 1578 s, 1362 s, 1265 m, 1100 m, 1040 s, 778 s, 712 s cm^{-1}.

2.3. X-ray crystallography

The well-shaped single crystals of **1**–**5** were selected for X-ray diffraction study. Data collections were performed on a Bruker Smart Apex-II CCD diffractometer with graphite-monochromatic Mo-Kα radiation ($\lambda = 0.71073$ Å) at room temperature. Determinations of the crystal system, orientation matrix and cell dimensions were performed according to established procedures. The structures were solved by the direct methods and refined by full-matrix least-squares on F^2 with SHELXTL program [10]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located and included at their calculated position. Crystallographic data and refinement result are summarized in Table 1. Selected bond distances and angles are listed in Table S1 (Supporting Information).