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Research paper

Syntheses, structures and magnetism of four Ni(II)/Co(II) interpenetrating coordination polymers based on 1,4-bis(4-(imidazole-1-yl)benzyl)piperazine

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ABSTRACT

Four novel interpenetrating coordination polymers have been hydrothermally synthesized based on a long flexible N-donor ligand (bibp) and different polycarboxylates, namely $[Ni(1,3\text{-bdc})(bibp)(H_2O)]\cdot 0.5H_2O$ (**1**), $[Ni(btec)_{0.5}(bibp)_{1.5}]\cdot H_2O$ (**2**), $[Co(btec)_{0.5}(bibp)_{1.5}]\cdot H_2O$ (**3**) and $[Co(oba)(bibp)]\cdot 2H_2O$ (**4**) (bibp = 1,4-bis(4-(imidazole-1-yl)benzyl)piperazine, 1,3-bdc = 1,3-benzenedicarboxylate, btec = 1,2,4,5-benzenetetracarboxylate, oba = 4,4′-oxybisbenzoate). Their structures were determined by single-crystal X-ray diffraction analyses and further characterized by elemental analyses, IR spectra and TG analyses. Compound **1** shows a 2-fold interpenetrating 3D framework with $CdSO_4$ topology. Compounds **2** and **3** exhibit 2-fold interpenetrating **pcu** frameworks. Compound **4** is a 2D → 3D interdigitated network formed from 2D → 2D threefold interpenetrating motifs. In addition, the magnetic properties of compounds **1**–**4** have also been investigated in the temperature range 2–300 K.

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1. Introduction

In the last decade, fascinating structures and diverse topologies of coordination polymers (CPs) have received a great deal of attention [1]. Moreover, CPs have emerged as powerful platforms for exploring potential applications, such as gas adsorption and separation [2], catalysis [3], sensors [4], nonlinear optics [5] and magnetic materials [6]. Among the various coordination polymers, entangled systems have attracted particular attention owing to its intricate framework topologies [7]. Interpenetrating networks, as an important subgroup of entangled systems, have been extensively investigated [8]. There is a common characteristic feature of interpenetrating networks, that is, the individual nets cannot be separated until internal connections are broken [7b,7c]. Currently, the synthesis and the modulation on the molecular level aimed at attaining desirable interpenetrating structures, however, still remain outstanding challenges.

In most cases, the factors, such as templates, the solvent systems, pH value of solution, organic ligands, the metal-ligand ratio, coordination geometry of the metal ions can influence the structures and topologies of products [9]. Among these factors, long flexible linear N-donor ligands, considered as an attractive kind of organic ligands, have successfully built some interpenetrating structures. For example, Ciani and co-workers have synthesized a series of interpenetrating **dia** networks with 1,12-dodecanedinitrile [10]; our group has utilized 1,4-bis(imidazol-1-yl)butane to obtain a 2-fold interpenetrating framework with $CdSO_4$ topology [11]; Fan et al. have reported a threefold interpenetrating 3D framework with a 6-c $\{3^{12}\cdot 4^{28}\cdot 5^5\}$ topology using 1,3-bis(4-pyridyl)propane [12]. It is worthy to be mentioned that long flexible linear N-donor ligands have great potential to fabricate intriguing interpenetrating structures for the followed merits: (i) The flexibility of these ligands whose $-CH_2-$ (alkyl) groups enable to bend and rotate freely leads to different conformation geometries which can easily meet the coordination nature of metal cations. (ii) Usually, long organic ligands will lead to large voids which may thus favor the formation of interpenetrating networks [13]. Therefore, choosing long flexible linear N-donor ligands is regarded as a feasible proposal to construct new interpenetrating networks [14].

During the synthesis course, a long flexible N-containing ligand, named bibp was firstly synthesized, and then reacted with different polycarboxylates and nickel/cobalt acetate. These efforts have led to the isolation of four new interpenetrating coordination polymers, namely $[Ni(1,3\text{-bdc})(bibp)(H_2O)]\cdot 0.5H_2O$ (**1**), $[Ni(btec)_{0.5}(bibp)_{1.5}]\cdot H_2O$ (**2**), $[Co(btec)_{0.5}(bibp)_{1.5}]\cdot H_2O$ (**3**) and $[Co(oba)(bibp)]\cdot 2H_2O$ (**4**) (1,3-bdc = 1,3-benzenedicarboxylate,

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btec = 1,2,4,5-benzenetetracarboxylate, oba = 4,4′-oxybisbenzoate, Scheme 1). The syntheses, crystal structures and the magnetic properties of these compounds will be represented and discussed in this paper.

2. Experimental

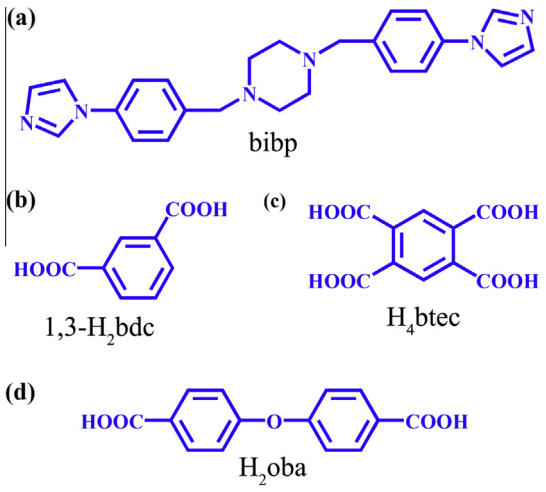
2.1. Materials and general methods

The bibp ligand was synthesized according to the procedures in Electronic Supplementary information. Other reagents and solvents were obtained from commercial suppliers and used without further purification.

Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. Ni and Co were determined by a tps-7000 Plasma-Spec(I) inductively coupled plasma-atomic emission spectrometer (ICP-AES). 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 in flowing N_2 with a heating rate of 10 °C min^{-1}. PXRD 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. All the magnetic susceptibility data were corrected from diamagnetic contributions estimated from Pascal's constants.

2.2. Synthesis of [Ni(1,3-bdc)(bibp)(H_2O)]·0.5H_2O (**1**)

A mixture of $Ni(Ac)_2{\cdot}4H_2O$ (0.050 g, 0.2 mmol), 1,3-H_2bdc (0.017 g, 0.1 mmol), bibp (0.040 g, 0.1 mmol), Et_3N (0.10 mL) and distilled water (10 mL) was stirred about 15 min in air, then transferred and sealed in a 17 mL Teflon-lined autoclave, which was heated at 160 °C for 48 h. After slow cooling to room temperature, green octahedral crystals of **1** were filtered off, washed with distilled water, and dried at ambient temperature (yield: 45% based on Ni). Elemental analysis (%) calcd for $C_{32}H_{33}NiN_6O_{5.5}$: C, 59.28; H, 5.13; N, 12.96; Ni, 9.05%. Found: C, 59.57; H, 4.89; N, 12.79; Ni, 9.31%. FT/IR data (cm^{-1}): 3436(br), 3110(w), 2923(w), 2889 (w), 2840(w), 1602(s), 1546(s), 1522(s), 1479(m), 1446(s), 1383 (s), 1343(w), 1304(s), 1263(m), 1247(w), 1177(w), 1117(m), 1064 (m), 996(m), 962(w), 929(w), 902(w), 847(m), 807(m), 745(m), 719(m), 655(m), 630(w), 571(w), 526(w), 457(w), 431(w).



Scheme 1. Schematic drawing of (a) bibp, (b) 1,3-H_2bdc, (c) H_4btec and (d) H_2oba ligands.

2.3. Synthesis of [Ni($btec)_{0.5}$($bibp)_{1.5}$]·H_2O (**2**)

A mixture of $Ni(Ac)_2{\cdot}4H_2O$ (0.050 g, 0.2 mmol), H_4btec (0.025 g, 0.1 mmol), bibp (0.040 g, 0.1 mmol), Et_3N (0.10 mL) and distilled water (10 mL) was stirred about 15 min in air, then transferred and sealed in a 17 mL Teflon-lined autoclave, which was heated at 160 °C for 72 h. After slow cooling to room temperature, green plank crystals of **2** were filtered off, washed with distilled water, and dried at ambient temperature (yield: 31% based on Ni). Elemental analysis (%) calcd for $C_{41}H_{42}NiN_9O_5$: C, 61.59; H, 5.29; N, 15.77; Ni, 7.34%. Found: C, 61.78; H, 5.15; N, 15.95; Ni, 7.14%. FT/IR data (cm^{-1}): 3418(br), 3167(w), 3132(w), 3044(w), 2932 (w), 2873(w), 2808(m), 2767(m), 1611(s), 1566(s), 1524(s), 1484 (m), 1430(w), 1366(s), 1300(s), 1265(m), 1245(w), 1183(w), 1151 (w), 1129(w), 1066(m), 1006(w), 962(w), 926(w), 850(m), 808 (m), 777(w), 730(w), 653(w), 624(w), 570(w), 527(w), 423(w).

2.4. Synthesis of [Co($btec)_{0.5}$($bibp)_{1.5}$]·H_2O (**3**)

The preparation of **3** was similar to that of **2** except that $Co(Ac)_2{\cdot}4H_2O$ was used instead of $Ni(Ac)_2{\cdot}4H_2O$ and a change in the dosage of Et_3N (0.25 mL). Pink plank crystals of **3** were collected (yield: 21% based on Co). Elemental analysis (%) calcd for $C_{41}H_{42}CoN_9O_5$: C, 61.57; H, 5.29; N, 15.76; Co, 7.37%. Found: C, 61.80; H, 5.09; N, 15.98; Co, 7.12%. FT/IR data (cm^{-1}): 3417(br), 3161(w), 3131(w), 2934(w), 2873(w), 2807(m), 2767(w), 1611(s), 1567(s), 1523(s), 1484(m), 1368(s), 1300(s), 1264(m), 1183(w), 1153(w), 1131(w), 1065(m), 1007(w), 962(w), 927(w), 851(m), 809(m), 774(w), 730(w), 653(w), 623(w), 576(w), 529(w), 423(w).

2.5. Synthesis of [Co(oba)(bibp)]·2H_2O (**4**)

A mixture of $Co(Ac)_2{\cdot}4H_2O$ (0.100 g, 0.4 mmol)·H_2oba (0.104 g, 0.4 mmol), bibp (0.160 g, 0.4 mmol), Et_3N (0.25 mL) and distilled water (10 mL) was stirred about 15 min in air, then transferred and sealed in a 17 mL Teflon-lined autoclave, which was heated at 160 °C for 72 h. After slow cooling to room temperature, purple plank crystals of **4** were filtered off, washed with distilled water, and dried at ambient temperature (yield: 76% based on Co). Elemental analysis (%) calcd for $C_{38}H_{38}CoN_6O_7$: C, 60.88; H, 5.11; N, 11.21; Co, 7.86%. Found: C, 61.10; H, 5.34; N, 10.99; Co, 7.63%. FT/IR data (cm^{-1}): 3402(w), 3118(m), 3069(w), 2937(w), 2817 (m), 2774(w), 1599(s), 1567(s), 1526(s), 1498(w), 1460(w), 1418 (m), 1377(s), 1301(m), 1240(s), 1157(m), 1126(m), 1096(w), 1062(m), 1007(w), 963(w), 938(w), 877(m), 852(m), 807(m), 781 (m), 728(w), 700(w), 657(m), 557(w), 525(w), 464(w), 427(w).

2.6. X-ray crystallography

Single-crystal X-ray diffaction data for **1**–**3** were collected using an Agilent Technologies SuperNova Dual diffractometer with Cu Kα radiation (λ = 1.54184 Å) at 291.08 K. Single-crystal X-ray diffaction data for **4** were collected using a Bruker Smart Apex CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å) at 296.15 K. Using Olex2 [15], the structures of **1**–**3** were solved with the Superflip [16] structure solution program using Charge Flipping and the structure of **4** was solved with the ShelXS [17] structure solution program using Direct Methods. Moreover, the structures of **1**–**4** were refined with the ShelXL [18] refinement package using Least Square minimization. The non-hydrogen atoms were refined anisotropically. The organic hydrogen atoms were generated geometrically. A part of aqua hydrogen atoms in compounds **1** and **4** could not positioned from difference Fourier maps. Other aqua hydrogen atoms were located from difference Fourier maps and refined with isotropic displacement parameters. The detailed crystallographic data and structure refinement parameters for

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