Journal of Solid State Chemistry 261 (2018) 37–42

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Three novel coordination polymers based on tris(*p*-carboxyphenyl) phosphane oxide: Syntheses, structural characterization and magnetic properties

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ARTICLE INFO

Keywords:
Tris(4-carboxylphenyl)phosphine Oxide N-donor linker
Coordination polymers
Structure diversity
Magnetic property

ABSTRACT

Three coordination polymers (CPs), namely, $\{[Co_3(HL)_2(bib)_3\ (H_2O)_7]\cdot 12H_2O\}_n$ (**1**), $\{[Co(HL)(bib)]\cdot H_2O\}_n$ (**2**), and $\{[Co_{1.5}(L)(bibp)_{1.5}\ (H_2O)]\cdot 1.5DMF\cdot 2EtOH\cdot 3H_2O\}_n$ (**3**), have been synthesized from the tripodal ligand of tris(*p*-carboxyphenyl)phosphane oxide (H_3L) with the help of 1,4-bis(imidazol-1-yl)benzene (bib) or 4,4′-bis(imidazol-1-yl)biphenyl (bibp). Structural analyses reveal that complex **1** features a 3D 4-connected $\{6^5 0.8\}$-cds net. **2** displays a 2D 6–connected $\{3^6 0.4^6 0.5^3\}$-hxl sheet based on the binuclear $\{Co_2(COO)_2\}$ SBUs. Complex **3** shows a 3D (3,4,4)-connected net with $\{6\cdot 8^2\}_2\{6\cdot 8^4 0.10\}_2\{6^2 0.8^2 0.10^2\}$ point symbol. Furthermore, the results of the variable-temperature magnetic susceptibilities indicate that complexes **1**–**3** have antiferromagnetic behavior between Co(II) ions.

1. Introduction

Coordination polymers (CPs), as a kind of functional materials, have been paid more and more attention in materials science fields, due to their fascinating structures and potential application in areas of gas adsorption and separation [1–6], luminescent probe [7–10], catalysis [11–14], magnetism [15–20], biological activities [21], and so on [22,23]. However, it is still a serious undertaking for researchers to design and synthesize ideal CPs with distinct architectures and outstanding performance, on account of numerous influence factors such as organic ligands, metal ions, metal-ligand ratio, solvent, pH value, reaction temperature and duration, etc [24–29]. Among them, the rational selection of organic ligands is an efficient approach to construct functional CPs [30,31].

Aromatic multicarboxylate ligands have multiple coordination sites and can form a variety of coordination modes to build a series of CPs with complicated geometric construction and particular functional features under different synthesis systems [32–36]. Furthermore they have delocalized π electrons in large conjugated aromatic linker, which can transmit magnetic couplings in varying degrees when incorporating with paramagnetic transition-metal ions [37]. Besides, N-donor auxiliary ligands act as pillars to take part in the coordination, obtaining an intricate and stable framework [38]. Therefore, we chose an aromatic multicarboxylate ligand of tris(4-carboxylphenyl) phosphine oxide (H_3L) as the main organic ligand. 1,4-bis(imidazol-1-yl) benzene (bib) or 4,4′-bis(imidazol-1-yl)biphenyl (bibp) was used as auxiliary ligand which will possibly enlarge the structural diversities and enrich topologies of CPs.

Under above background, three CPs, $\{[Co_3(HL)_2(bib)_3\ (H_2O)_7]\cdot 12H_2O\}_n$ (**1**), $\{[Co(HL)(bib)]\cdot H_2O\}_n$ (**2**) and $\{[Co_{1.5}(L)(bibp)_{1.5}(H_2O)]\cdot 1.5DMF\cdot 2EtOH\cdot 3H_2O\}_n$ (**3**), have been constructed by H_3L ligand with the help of bib/bibp linker (Scheme 1). In addition, the magnetic properties of complexes **1**–**3** have been researched.

2. Experimental

2.1. Materials and methods

All reagents used in the experiments were commercially available and used without further purification. H_3L, bib and bibp ligands were purchased from Jinan Henhua Sci. & Tec. Co. Ltd. Elemental analyses (EA) (C, H, N) were carried out on a Vario MACRO cube elemental analyzer. IR spectra were recorded on a FTIR-8400S spectrometer within the 4000–500 cm^{-1} range. Powder X-ray diffraction (PXRD) data were obtained by means of a Rigaku D/Max-2500 PC diffractometer with Cu-Kα radiation over the 2θ range of 5–50°. Thermal gravimetric (TG) analyses were characterized on a ZCT-A analyzer in N_2 condition from 25 to 800 ℃ at a heating rate of 10 ℃ min^{-1}. The variable-temperature magnetic susceptibility measurements ware performed on a Quantum Design SQUID MPMS XL-7 instrument.

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https://doi.org/10.1016/j.jssc.2018.02.007
Received 26 December 2017; Received in revised form 6 February 2018; Accepted 9 February 2018
Available online 14 February 2018
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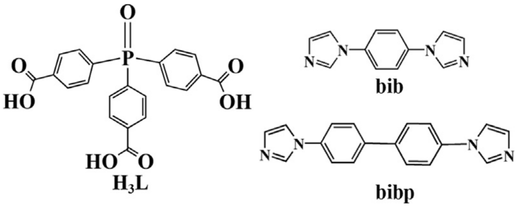

Scheme 1. The H_3L, bib and bibp ligands used.

2.2. Syntheses of complexes 1–3

2.2.1. Synthesis of $\{[Co_3(HL)_2(bib)_3(H_2O)_7]\cdot 12H_2O\}_n$ (1)

A mixture of $Co(NO_3)_2\cdot 6H_2O$ (0.032 mmol, 9.3 mg), H_3L (0.016 mmol, 6.6 mg), bib (0.016 mmol, 3.4 mg) and 4 mL H_2O was sealed in a 25 mL Teflon-lined stainless steel vessel, heated at 160 °C for 2 days, and cooled to 30 °C at the rate of 3 °C h^{-1}. Pink block crystals of **1** were obtained by filtration, washing, and drying (yield: 47%, based on H_3L). Anal. (%) calcd. for $C_{78}H_{92}Co_3N_{12}O_{33}P_2$: C, 47.65; H, 4.68; N, 8.53. Found (%): C, 47.71; H, 4.63; N, 8.49. IR (KBr pellet, cm^{-1}): 3378 (w), 1651 (vw), 1590 (s), 1537 (s), 1494 (vw), 1387 (s), 1308 (w), 1111 (m), 736 (s) (Fig. S1).

2.2.2. Synthesis of $\{[Co(HL)(bib)]\cdot H_2O\}_n$ (2)

The same synthetic process *as* for **1** was used except that 0.025 mL $NH_3\cdot H_2O$ (0.25 mol/L) aqueous solution was added, giving purple crystals of **2** with a yield of 46% (based on H_3L). Anal. (%) calcd. for $C_{33}H_{25}CoN_4O_8P$: C, 56.94; H, 3.59; N, 8.05. Found (%): C, 56.97; H, 3.65; N, 8.01. IR (KBr pellet, cm^{-1}): 3480 (w), 1702 (w), 1630 (m), 1591 (vw), 1526 (s), 1494 (vw), 1412 (s), 1108 (m), 738 (m) (Fig. S1).

2.2.3. Synthesis of $\{[Co_{1.5}(L)(bibp)_{1.5}(H_2O)]\cdot 1.5DMF\cdot 2EtOH\cdot 3H_2O\}_n$ (3)

A mixture of $Co(NO_3)_2\cdot 6H_2O$ (0.008 mmol, 2.3 mg), H_3L (0.004 mmol, 1.6 mg), bibp (.004 mmol, 1.1 mg), 0.025 mL $NH_3\cdot H_2O$ (0.25 mol/L) aqueous solution and 1 mL DMF/EtOH/H_2O (v/v/v = 4/1/5) mixed solution was added to a hard glass tube, pumped to a near-vacuum, heated at 110 °C for 2 days, and cooled to 30 °C at a rate of 1.6 °C h^{-1}. Purple block crystals of **3** were gained with a yield of 38% (based on H_3L). Anal. (%) calcd. for $C_{96}H_{70}Co_3N_{12}O_{16}P_2$: C, 61.07; H, 3.71; N, 8.91. Found (%): C, 61.12; H, 3.68; N, 8.87. IR (KBr pellet, cm^{-1}): 3437 (vw), 1598 (m), 1545 (m), 1516 (s), 1382 (s), 1308 (w), 1108 (m), 1060 (m), 962 (w), 736 (s) (Fig. S1).

2.3. X-ray crystallography

Single crystals of complexes **1**–**3** with appropriate dimensions were characterized on a Bruker Apex II CCD diffractometer, equipped with graphite-monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined anisotropically applying the ShelXL software package. All hydrogen atoms were located in the subsequent difference Fourier maps [39]. Some disordered solvent molecules in void volume can be removed by *PLATON/SQUEEZE* [40]. All crystallographic data and pertinent structure refinement parameters of **1**–**3** are listed in Table S1. Selected bond lengths and angles are summarized in Table S2. Topological analyses for complexes were performed by means of TOPOS [41].

3. Result and discussion

3.1. Structure descriptions

3.1.1. Structure of $\{[Co_3(HL)_2(bib)_3(H_2O)_7]\cdot 12H_2O\}_n$ (1)

Structural analysis reveals that complex **1** crystallizes in the triclinic space group *P*1. The asymmetric unit consists of three Co^{II} ions, two HL^{2-} ligands, three bib ligands, seven coordinated water molecules, and twelve lattice water molecules. As can be seen in the Fig. 1a, Co(1) is six-coordinated by two N atoms from two bib linkers, four O atoms from two different HL^{2-} ligands and two coordinated water molecules, exhibiting a distorted $\{CoN_2O_4\}$ octahedron geometry. Co(2) locates in a similar $\{CoN_3O_3\}$ octahedron coordination environment, completed by three O-atoms from two different HL^{2-} ligands and three N-atoms from three distinct bib linkers. While Co(3) is surrounded by five oxygen atoms from coordinated aqua molecules and one N-atom from bib linker.

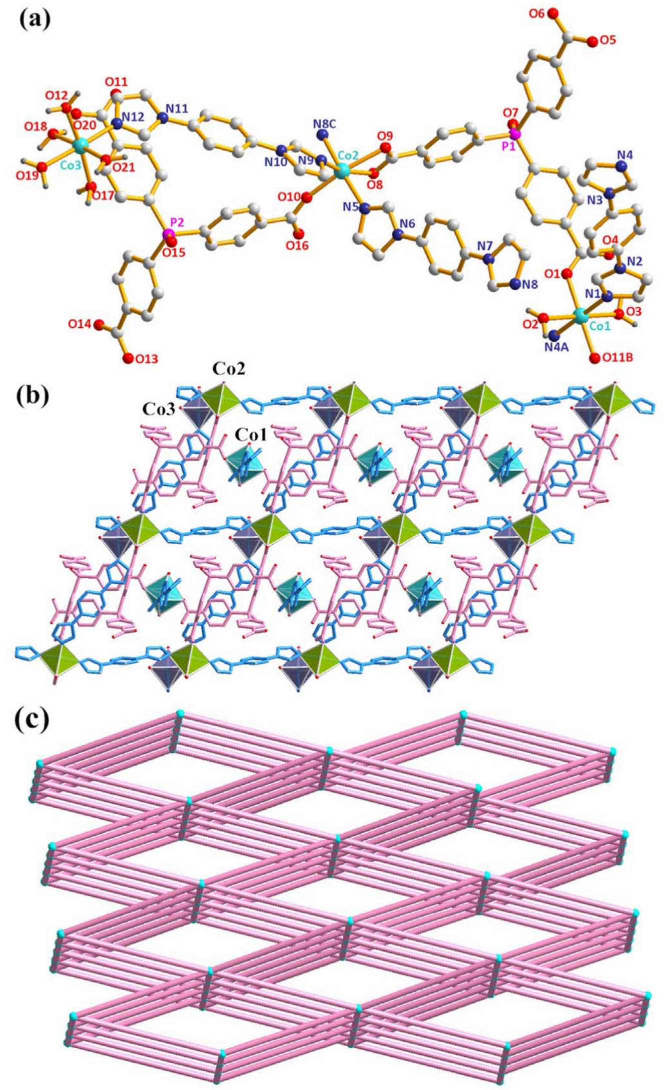

Fig. 1. (a) The asymmetric unit of **1** (Symmetry codes: A: *x*, *y*, −1 + *z*; C: 1 + *x*, *y*, *z*.). (b) Schematic view of the 3D net of **1**. (c) The 3D 4-connected **cds** net with $\{6^5 0.8\}$ point symbol of **1.**

In the formation of **1**, the carboxyl groups of H_3L ligands are partially deprotonated but show two distinct coordination modes: $(\kappa^1\text{-}\kappa^0)\text{-}(\kappa^1\text{-}\kappa^0)\text{-}\mu_2$ mode (Mode I, Scheme 2) and $(\kappa^1\text{-}\kappa^0)\text{-}(\kappa^1\text{-}\kappa^1)\text{-}\mu_2$ mode (Mode II, Scheme 2). Two kinds of HL^{2-} ligands bridge alternately Co(1) and Co(2) ions constructing successfully a 1D wave $[Co_2(L)_2]_n$ chain, in which the nearest Co···Co distances are 12.531(6) Å for Co1···Co2, 11.906(5) Å for Co1···Co2B (Fig. S2a), respectively. Meanwhile, the bib ligands link Co(1) ions to form a 1D $[Co(bib)]_n$ chain with the Co(1)···Co(1) distance being 13.651(2) Å (Fig. S2b). Similarly, the other kind of bib linkers connects Co(2) ions to obtain a 1D $[Co(bib)]_n$ chain with the Co(2)···Co(2) distance being 13.563(2) Å, which are further expanded into a 1D fishbone-like chain with the help of another kind of bib linkers and Co(3) ions, where the Co(2)···Co(3) distance is

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