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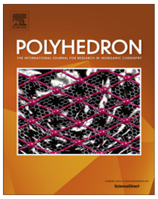

Structural control and magnetic properties of three Co(II) coordination polymers based on 6-(3,5-dicarboxylphenyl)nicotinic acid

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ABSTRACT

Three coordination polymers (CPs) based on 6-(3,5-dicarboxylphenyl)nicotinic acid (H_3DCPN) and N-donor linkers, $\{[Co(HDCPN)(bbib)(H_2O)]\cdot 2H_2O\}_n$ (**1**), $[Co(HDCPN)(bbib)]_n$ (**2**), and $\{[Co(HDCPN)(bpy)_{0.5}(H_2O)]\cdot H_2O\}_n$ (**3**) (bbib = 1,4-bis(benzimidazo-1-ly)benzene, bpy = 4,4′-bipyridine), were synthesized under solvothermal conditions. Single-crystal X-ray diffraction analysis reveals that complexes **1**–**3** are 3D supramolecular structures. Complexes **1** and **2** display 2D 4-connected sql networks, and complex **3** shows a 2D (3,4)-c network, which are all further packed into 3D supramolecular structures by hydrogen bonds. It is noteworthy that the adjacent layers interpenetrate with each other to generate 2D + 2D → 2D network in complex **1**, and complex **3** possesses an intriguing 2D + 2D → 3D parallel polycatenation architecture. The different structures for complexes **1** and **2** can be attributed to temperature-dependent structural variation. Furthermore, the magnetic properties of complexes **2** and **3** have been also investigated, and both of them exhibit weak antiferromagnetic coupling interactions.

1. Introduction

Coordination polymers (CPs), a class of novel functional materials, have attracted numerous investigators and researchers at crystallography in the past few decades, due to the intriguing topologies and the enormous potential applications [1]. CPs can be applied to many kinds of fields, such as gas adsorption and storage, drug delivery, industrial catalysis, electronic device, magnetism, photoluminescence and so on [2–5]. Up to now, chemists and engineers have paid much attention to explore the relationship between excellent properties and unique architectures by appropriate selection of organic ligands and metal ions.

However, the rational and controllable design of CPs with expected architectures is still an important challenge that couldn't be neglected. This is attributed to the fact that there are various uncertain factors, for instance, organic ligands, central metal ions, reaction temperature and time, the counterions, pH value, solvent of the reaction system, etc, which would affect the final structure of targeted compounds [6–10]. Among those above intrinsic and extrinsic factors, the length, rigidity and functional groups of organic ligands take possession of the crucial places. It has been frequently documented that the aromatic multicarboxylate ligands are prominent candidates in the process of constructing appealing CPs [11–13]. To the best of our knowledge, the mixed-ligands strategy, incorporating the multicarboxylate and N-donor ligands, is beneficial to form new CPs and further construct multifunctional materials [14]. Moreover, as a consequence of the interpenetration, CPs may be used as potential super-hard, porous [15], and magnetic materials [16].

Due to its various coordination modes, the supporting role of phenyl rings, and carboxylate groups as the donor or accepter of hydrogen bonds, a nitrogen-containing aromatic multicarboxylate ligand [6-(3,5-dicarboxylphenyl)nicotinic acid (H_3DCPN)] is chosen to constructed CPs, and we have reported three coordination compounds self-assembly by Co^{2+}, Cd^{2+}, Mn^{2+} ions and H_3DCPN. Here, the multicarboxylate ligand H_3DCPN is chosen with two different N-donor co-ligands [1,4-bis(benzimidazo-1-ly)benzene (bbib), 4,4′-bipyridine (bpy)] (shown in Scheme 1) and Co(II) ions [17] to construct three novel coordination polymers, namely, $\{[Co(HDCPN)(bbib)(H_2O)]\cdot 2H_2O\}_n$ (**1**), $[Co(HDCPN)(bbib)]_n$ (**2**), and $\{[Co(HDCPN)(bpy)_{0.5}(H_2O)]\cdot H_2O\}_n$ (**3**). In addition, the magnetic properties of complexes **2** and **3** have been investigated.

2. Experimental

2.1. Materials and physical measurements

H_3DCPN, bbib and bpy ligands were purchased from Jinan Henghua Sci. & Tec. Co. Ltd., and other reagents were commercially

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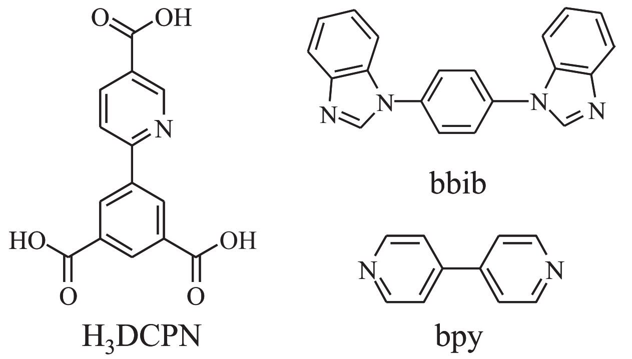

Scheme 1. The organic ligands used in the three complexes.

available. These materials were used as received, without further purification. Elemental analyses of C, H, and N were carried out on a Vario MACRO cube elemental analyzer. IR spectra were recorded with dry KBr pellets by means of a FTIR-8400S spectrometer in the range of 4000–500 cm^{-1}. The samples were measured by thermogravimetric (TG) measurements under N_2 condition on a METTLER TGA analyzer up to 700 °C using a heating rate of 10 $°C{\cdot}min^{-1}$. Powder X-ray diffraction (PXRD) data were characterized on a Rigaku D/Max-2500 PC diffractometer with Mo Kα radiation ($\lambda = 0.710$ Å) over the 2θ range of 5–50° at room temperature. The variable-temperature magnetic susceptibility measurements for polycrystalline complexes **2** and **3** were collected on a Quantum Design MPMS XL-7 SQUID instrument over the temperature range of 2–300 K under an applied field of 1000 Oe.

2.2. Syntheses of the complexes

2.2.1. Synthesis of $\{[Co(HDCPN)(bbib)(H_2O)]{\cdot}2H_2O\}_n$ (**1**)

A mixture of H_3DCPN (0.0075 mmol, 2.2 mg), bbib (0.0075 mmol, 2.3 mg), $Co(NO_3)_2{\cdot}6H_2O$ (0.015 mmol, 4.4 mg) and H_2O/ethanol/DMA (1.0 mL, v/v/v, 2/1/1) was added to a hard glass tube, pumped to a near-vacuum, and heated at 80 °C for 2 days, then cooled to room temperature at a rate of 1 $°C{\cdot}h^{-1}$. Pink block crystals of **1** were obtained by filtration, washing, and drying (yield: 47%, based on Co). *Anal.* Calcd for $C_{34}H_{27}CoN_5O_9$: C, 57.64; H, 3.84; N, 9.88. Found: C, 57.60; H, 3.79; N, 9.94%. IR (KBr pellet, cm^{-1}): 3436 (s), 1702 (m), 1633 (m), 1518 (s), 1455 (m), 1356 (m), 1236 (m), 851 (w), 771 (w), 744 (s) (Fig. S8).

2.2.2. Synthesis of $[Co(HDCPN)(bbib)]_n$ (**2**)

A mixture of H_3DCPN (0.0075 mmol, 2.2 mg), bbib (0.0075 mmol, 2.3 mg), $Co(NO_3)_2{\cdot}6H_2O$ (0.010 mmol, 2.9 mg) and H_2O/ethanol/DMA (1.0 mL, v/v/v, 2/1/1) was added to a hard glass tube, pumped to a near-vacuum, and heated at 100 °C for 3 days, then cooled to room temperature at a rate of 4 $°C{\cdot}h^{-1}$. Dark pink block crystals of **2** were obtained (yield: 51%, based on Co). *Anal.* Calc. for $C_{34}H_{21}CoN_5O_6$: C, 62.40; H, 3.23; N, 10.70. Found (%): C, 62.32; H, 3.30; N, 10.67. IR (KBr pellet, cm^{-1}): 3426 (m), 1710 (m), 1630 (m), 1523 (s), 1454 (m), 1394 (s), 1235 (s), 853 (w), 769 (m), 742 (s) (Fig. S8).

2.2.3. Synthesis of $\{[Co(HDCPN)(bpy)_{0.5}(H_2O)]{\cdot}H_2O\}_n$ (**3**)

A mixture of H_3DCPN (0.015 mmol, 4.3 mg), bpy (0.015 mmol, 2.3 mg), $Co(NO_3)_2{\cdot}6H_2O$ (0.030 mmol, 8.7 mg), aqueous NaOH solution (0.10 mL, 0.25 $mol{\cdot}L^{-1}$) and 3.0 ml H_2O was sealed in a 25 ml Teflon-lined stainless steel vessel, which was heated at 160 °C for 2 days and then cooled to room temperature at a rate of 3 $°C{\cdot}h^{-1}$, giving purple block crystals of **3** in 35% yield based on Co. *Anal.* Calc for $C_{19}H_{15}CoN_2O_8$: C, 49.80; H, 3.30; N, 6.11. Found: C, 49.86; H, 3.27; N, 6.06%. IR (KBr pellet, cm^{-1}): 3419 (m), 1733 (m), 1653 (s), 1551 (s), 1447 (m), 1366 (m), 1276 (m), 815 (m), 769 (m), 728 (m) (Fig. S8).

2.3. X-ray crystallography

Complexes **1**–**3** with appropriate dimensions were chosen under an optical microscope for data collection. Diffraction intensity data of single crystals for the complexes were characterized on a CCD area detector diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 296.15 K. Absorption corrections were applied to the data based on multiple techniques. The structures were solved by using Olex2 and refined with the

Table 1
Crystal data for complexes **1**–**3**.

Complex	1	2	3
Empirical formula	$C_{34}H_{27}CoN_5O_9$	$C_{34}H_{21}CoN_5O_6$	$C_{19}H_{15}CoN_2O_8$
Formula weight	708.53	654.49	458.26
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$C2/c$
a (Å)	10.665(2)	9.907(9)	22.812(10)
b (Å)	12.157(3)	12.441(10)	10.160(5)
c (Å)	13.053(3)	14.153(14)	16.003(7)
α (°)	65.380(2)	88.822(9)	90
β (°)	85.587(2)	71.419(13)	103.916(4)
γ (°)	89.959(2)	72.326(9)	90
V (Å^3)	1533.1(6)	1570(2)	3600(3)
Z	2	2	8
ρ_{calc} ($g{\cdot}cm^{-3}$)	1.535	1.385	1.691
μ (mm^{-1})	0.627	0.600	1.008
$F(000)$	730.0	670.0	1872.0
Index ranges	$-13 \leqslant h \leqslant 13$, $-15 \leqslant k \leqslant 15$, $-16 \leqslant l \leqslant 17$	$-12 \leqslant h \leqslant 12$, $-16 \leqslant k \leqslant 16$, $-18 \leqslant l \leqslant 18$	$-26 \leqslant h \leqslant 29$, $-12 \leqslant k \leqslant 13$, $-20 \leqslant l \leqslant 20$
Reflections collected	20374	17705	11416
Independent reflections	7054 [$R_{int} = 0.0620$]	7242 [$R_{int} = 0.0906$]	4168 [$R_{int} = 0.0544$]
Data/restraints/parameters	7054/27/454	7242/0/416	4168/0/284
R [$I \geqslant 2\sigma(I)$][a]	$R_1 = 0.0673$, $wR_2 = 0.1758$	$R_1 = 0.0658$, $wR_2 = 0.1807$	$R_1 = 0.0472$, $wR_2 = 0.0948$
R [all data][a]	$R_1 = 0.1218$, $wR_2 = 0.2071$	$R_1 = 0.1624$, $wR_2 = 0.2310$	$R_1 = 0.1013$, $wR_2 = 0.1128$
Goodness-of-fit on F^2	1.036	0.922	1.015
Largest diff. peak/hole (e Å^{-3})	2.03/−1.13	0.72/−0.88	0.69/−0.46
CCDC number	1477233	1477234	1477231

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$.

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