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Construction of 3D supramolecular networks based on 1D chains from flexible bis(imidazolyl) and 4-hydroxybenzolate

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ABSTRACT

The reaction of 1,2-bis(imidazol-1′-yl)ethane (bime), 4-hydroxybenzoic acid (HO-HBC) with different metal salts in water/ethanol gave rise to three supramolecular architectures $[M(HO\text{-}BC)_2(H_2O)_2(bime)]_n$ [M = Mn(II), Co(II) and Ni(II)]. Single crystal X-ray diffraction analysis reveals that complexes **1**–**3** are isomorphous and are 3D supramolecular networks. HO-BC serves as a monodentate ligand through one carboxylate oxygen atom coordinating to metal center. The extensive hydrogen bonds from HO-BC and coordination water result in the formation of 3D supramolecular networks. The *gauche*-conformational bime connects the neighboring metal ions into 1D chain, which is located in the large void of the 3D networks. The thermogravimetric analysis reveals that complexes **1**–**3** are stable before 273 °C. Magnetic analysis shows that there are no interactions between neighboring metal ions.

1. Introduction

The rational design and synthesis of metal–organic coordination polymers are currently of great interest owing to their intriguing topological variety and potential application as functional materials [1–3]. With the development of supramolecular chemistry and crystal engineering, it is possible to predictable synthesis of coordination polymers through elaborately controlling assembly of organic ligands and metal ions [4]. The structures and properties of products are mainly dependent upon the functional groups of organic ligands and the coordination preference of metal ions. In the context, much effort has been devoted to the construction of coordination polymers through the concomitant use of nitrogen-containing and carboxylate ligands [4b,5–7]. As well-known, the carboxylate group possesses the diverse coordination modes and can produce various robust architectures. Moreover, its negative charge may compensate the positive charge from the metal ions, which mitigates the counterion effect in the self-assembly process [6]. The coordination of nitrogen-containing ligands to metal ions further satisfies the coordination geometries of metal ions. Thus, the coexistence of carboxylate and multidentate nitrogen-containing ligands generates various frameworks, ranging from discrete oligonuclear species to 1D, 2D and 3D networks [4b,7]. As for metal ions, such as Mn(II), Co(II), Ni(II), Cu(II) and Zn(II), they usually prefer to bind to water to satisfy their preferred octahedral geometries [8], which results in the potential possibility for stabilizing and extending coordination frameworks *via* hydrogen-bonding contacts. Thus, besides coordination bonding interaction, hydrogen bonding, aromatic π-π stacking interactions as well as van der Waals force also play important roles in determining the ultimate architectures [8,9]. These supramolecular interactions not only further increase the stability of the whole frameworks, but also are responsible for most of the reported dynamic nature of coordination polymers owing to their flexible length and angles [10].

In the construction of coordination polymers, bis(imidazolyl) ligands are promising building units owing to their simple synthetic procedure and strong coordination ability to transition metal ions [11–15]. Among them, we are more interested in 1,2-bis(imidazol-1′-yl)ethane (bime) [13], because its *gauche* and *anti* conformations can induce different structural topologies and properties. As reported before, bime usually links metal ions into macrometallocycle or zigzag chain based on its different conformations, further coordination of metal ions by carboxylate ligands generate high-dimensional coordination polymers [14,15]. In our previous work, we have prepared a series of coordination polymers from bime and 5-hydroxylisophthalic acid (H_2ip-OH), in which *anti* and/or *gauche* conformations of bime were displayed [15]. Inspired by the excellent results from ip-OH, we speculated that the replacement of dicarboxylate ip-OH by monocarboxylate 4-hydroxybenzenecarboxylate (HO-BC) may lead to more supramolecular interactions, finally produces much different architectures. Herein, we report the syntheses, structures and magnetic properties of three coordination polymers, $[M(HO\text{-}BC)_2(H_2O)_2(bime)]_n$ [M = Mn(II), Co(II), Ni(II)]. The three complexes are isomorphous and are 3D supramolecular networks consisting of 1D [M(bime)] chains.

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2. Experimental section

2.1. Materials and physical measurements

1,2-bis(imidazol-1′-yl)ethane (bime) was synthesized according to the literature method [13a]. The other reagents and solvents were purchased from commercial supplies and without further purification. The IR spectra (KBr pellets) were recorded on a Magna 750 FT-IR spectrophotometer in the range of 400–4000 cm^{-1}. C, H and N elemental analyses were determined on an EA1110 CHNS-0 CE element analyzer. Powder X-ray diffraction data were recorded on a PANaytical X'pert pro X-ray diffractometer with graphite-monochromatized Cu Kα radiation (λ = 1.542 Å). Thermal stability studies were carried out on a NETSCHZ STA 449C thermoanalyzer at a heating rate of 10 °C/min under N_2 atmosphere. The polycrystalline magnetic susceptibility data were collected on a Quantum Design MPMS model 6000 magnetometer in the temperature range from 2 to 300 K.

2.2. Preparation of $[Mn(HO\text{-}BC)_2(H_2O)_2(bime)]_n$ (**1**)

A mixture of $MnCl_2 \cdot 4H_2O$ (0.023 g, 0.12 mmol), 1,2-bis(imidazol-1′-yl)ethane (0.030 g, 0.17 mmol), 4-hydroxybenzoic acid (0.040 g, 0.29 mmol) in water/ethanol (1:1, 20 mL) was stirred for 2 h at room temperature. The resulting solution was stood in air for 1 day, colorless crystals of **1** were obtained, the crystals were collected by filtering and drying in air. Yield: 0.025 g (40% based on $MnCl_2 \cdot 4H_2O$). Elementary analysis: Calc. for $C_{11}H_{12}Mn_{0.5}N_2O_4$ (263.69): C, 50.10 H, 4.59; N, 10.62. Found: C, 50.25; H, 4.45; N, 10.79%. IR (KBr, cm^{-1}): 3443(vs), 3143(vw), 3117(vw), 1591(w), 1524(w), 1506(vw), 1386(s), 1284 (w), 1242(vw), 1164(vw), 1103(vw), 1087(vw), 931(vw), 846(vw), 796(w), 743(vw), 667(vw).

2.3. Preparation of $[Co(HO\text{-}BC)_2(H_2O)_2(bime)]_n$ (**2**)

A mixture of $Co(CH_3COO)_2 \cdot 4H_2O$ (0.041 g, 0.23 mmol), 1,2-bis(imidazol-1′-yl)ethane (0.025 g, 0.14 mmol), and 4-hydroxybenzoic acid (0.030 g, 0.22 mmol) in water/ethanol (1:1, 20 mL) was stirred for 2 h, the resulting solution was evaporated at room temperature, pink crystals of **2** were given after 1 day, the crystals were collected by filtering and drying in air. Yield: 0.030 g, (52% based on 4-hydroxybenzoic acid). Elementary analysis: Calc. for $C_{11}H_{12}Co_{0.5}N_2O_4$ (265.69): C, 49.73 H, 4.55; N, 10.54. Found: C, 49.80 H, 4.43; N, 10.70%. IR (KBr, cm^{-1}): 3435(vs), 3118(s), 3144(s), 1593(s), 1524(m), 1499(m), 1439(m), 1396(s), 1379(s), 1284(m), 1242(m), 1164(w), 1113(vw), 1087(vw), 941(vw), 856(vw), 796(w), 753(vw), 668 (vw), 650 (vw).

2.4. Preparation of $[Ni(HO\text{-}BC)_2(H_2O)_2(bime)]_n$ (**3**)

A mixture of $Ni(CH_3COO)_2 \cdot 4H_2O$ (0.038 g, 0.15 mmol), 1,2-bis(imidazol-1′-yl)ethane (0.024 g, 0.13 mmol), 4-hydroxybenzoic acid (0.041 g, 0.36 mmol) in water/ethanol (1:1, 20 mL), the resulting solution was evaporated at room temperature, light green crystals were produced after 1 day. The crystals were collected by filtering and drying in air. Yield: 0.025 g, (37% based on 1,2-bis(imidazol-1′-yl)ethane). Elementary analysis: Calc. for $C_{11}H_{12}Ni_{0.5}N_2O_4$ (265.57): C, 49.75; H, 4.55; N, 10.55. Found: C, 49.67; H, 4.63; N, 10.48%. IR (KBr, cm^{-1}): 3436(s), 3118(w), 1593(s), 1525(s), 1491(s), 1448(vw), 1397(vs), 1379(vs), 1277(s), 1243(w), 1165(vw), 1114(vw), 1499(m), 937(vw), 856(vw), 788(w), 763(vw), 660(vw).

2.5. X-ray crystal structural determination

The single crystals of complexes **1**–**3** were mounted on a glass fiber for the X-ray diffraction analysis. Data were collected on a Rigaku AFC7R equipped with a graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) from a rotating generator at 293 K. Intensities were corrected for LP factors and empirical absorption using the ψ scan technique. The structures were solved by direct methods and refined on F^2 with full-matrix least-squares techniques using Siemens *SHELXTL* version 5 package of crystallographic software [16]. All nonhydrogen atoms were refined anisotropically. The positions of H atoms were generated geometrically (C–H bond fixed at 0.96 Å), assigned isotropic thermal parameters, and allowed to ride on their parent carbon atoms before the final cycle of refinement. Crystal data as well as details of data collection and refinement for complexes **1**–**3** are summarized in Table 1. The selected bond distances and bond angles are given in Table 2. Crystallographic data of **1**–**3** have been deposited in the Cambridge Crystallographic Data Center as supplementary publication with CCDC number: 844543–844545.

3. Results and discussion

3.1. Crystal structure of complex **1–3**

Single crystal X-ray diffraction analysis revealed that complexes **1–3** are isomorphous, all of them crystallize in the monoclinic space group *C2/c*. Herein, we only describe the structure of **1** as an example. As shown in Fig. 1, the asymmetric unit consists of one HO-BC, one water, half of Mn(II) and half of bime. Mn(II) is in a slightly distorted octahedral geometry and is coordinated by two carboxylate oxygen atoms from different HO-BC, two water molecules and two imidazolyl nitrogen atoms from different bime. Mn(II) lies at an inversion center. The phenyl ring of HO-BC and imidazolyl ring of bime are approximately perpendicular to each other with the twisting angle between them being 91.3°. The Mn–N distance is 2.2308(16) Å. The Mn–$O_{HO\text{-}BC}$ distance of 2.2302(14) Å is slightly longer than that of Mn—O_{H_2O} [2.1885(14) Å]. These values are in normal range in the Mn(II)

Table 1
Crystal data and structural determination summary for 1–3.

	1	**2**	**3**
Formula	$C_{11}H_{12}Mn_{0.5}N_2O_4$	$C_{11}H_{12}Co_{0.5}N_2O_4$	$C_{11}H_{12}N_2Ni_{0.5}O_4$
Fw	263.70	265.69	265.58
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/c	*C*2/c	*C*2/c
a (Å)	23.897(3)	24.060(3)	24.24(2)
b (Å)	9.4755(8)	9.2656(7)	9.242(7)
c (Å)	11.0351(11)	10.9691(17)	11.034(11)
β (°)	111.060(4)	110.643(8)	110.861(11)
V (Å^3)	2331.8(4)	2288.3(5)	2310(4)
Z	8	8	8
D_c (g/cm^3)	1.502	1.542	1.527
μ (mm^{-1})	0.622	0.807	0.896
F(000)	1092	1100	1104
Reflections collected	8281	8670	9725
Unique reflections	2669	2516	2632
R_{int}	0.0341	0.0215	0.0785
Parameters	172	172	166
GOF	1.094	1.074	1.157
R_1 ($I > 2\sigma(I)$)[a]	0.0418	0.0307	0.0836
$_wR_2$ (all data)[b]	0.0864	0.0715	0.2014
$\Delta\rho_{max}$ and $_{min}$ (e/Å^3)	0.217 and −0.285	0.277 and −0.237	0.463 and −0.592

[a] $R = \sum||F_0| - |F_c||)/\sum|F_0|$.

[b] $_wR = [\sum w(F_0^2 - F_c^2)^2/\sum w(F_0^2)2]^{1/2}$.