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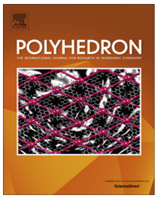

Three metal induced 3D coordination polymers based on H_3BTC and 1,3-BIP as co-ligands: Synthesis, structures and fluorescent properties

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ABSTRACT

Three new 3D coordination polymers, $\{[Co(BTC)_2(H_2O)_2][Co(1,3\text{-}BIP)(H_2O)_4]_2\}_n$ (**1**), $\{[Zn_3(BTC)_2(1,3\text{-}BIP)_3]\cdot 2DMF\}_n$ (**2**) and $\{[Cu_3(BTC)_2(1,3\text{-}BIP)_3]\cdot DMA\}_n$ (**3**), were synthesized under solvothermal conditions and characterized by single crystal X-ray diffraction, powder XRD, FT-IR, TGA and elemental analysis techniques. Although the three MCPs were constructed from the same tricarboxylate and N-donor ligands, their structures are quite different. Complex **1** features a 1D + 2D → 3D framework constructed by 2D $[Co(BTC)_2(H_2O)_2]_n^{4n-}$ layers and 1D $[Co(1,3\text{-}BIP)(H_2O)_4]_n^{2n+}$ chains, in which there exist three kinds of $O\text{–}H\cdots O$ hydrogen bonds, not only among the coordinated water molecules but also among the coordinated water molecules and carboxylate O atoms. Although complexes **2** and **3** have similar chemical formula, their structures are different. Complex **2** exhibits a 3D → 3D twofold interpenetrating framework, while complex **3** shows an interesting 3D framework. Furthermore, the fluorescent properties of the complexes **1** and **2** were also investigated in the solid state at room temperature.

1. Introduction

The crystal engineering of metal coordination polymers (MCPs) is one of the most rapidly developing areas of chemical science owing to their diversity of type and physical–chemical properties [1]. Obviously, it is the important responsibility for chemists to rationally design and synthesize more MCPs with diverse structures. It is well known that the assembly processes and structures of MCPs are influenced by many factors, such as the coordination preferences of the metal ions [2–4], the conformation of the bridging ligands [5], solvent systems [4], counteranion [6] and pH value of the solution [7] can also affect the nature of the coordination networks and the framework formation. As one of the most common factors influencing the assembly of MCPs, the metal ions can be viewed as a family of controllable building blocks. One particular metal element with a given valence normally defines its intrinsic coordination preference and geometry [8]. Therefore, systematic studies of diversified conditions leading to different structures in the formation of coordination polymers are important and of intense interest.

In recent years, the direct use of two types of organic ligands has been found to be an effective method for the synthesis of MCPs. Multicarboxylate ligands are frequently chosen to construct various dimensions of MCPs because of their rich coordination modes, including monodentate, bridging and chelating [9,10]. As an example, 1,3,5-benzenetricarboxylic acid (H_3BTC), with three exo-carboxylic acid groups arranged symmetrically around the benzene ring, is a flat trigonal multicarboxylate ligand which has widely served as a useful building block [11,12]. Meanwhile, bis-(imidazole) ligands bearing alkyl spacers are a good choice for an N-donor ligand. The flexible nature of the spacers allows the ligands to bend and rotate when they coordinate to the metal centers, and this often causes structural diversity. Several imidazole ligands, such as 1,2-bis(imidazole)ethane (1,2-BIE), 1,3-bis(imidazole)propane (1,3-BIP), 1,4-bis(imidazole)butane (1,4-BIB), 1,5-bis(imidazole)pentane (1,5-BIB), 1,6-bis(imidazole)hexane (1,6-BIH) and 1,4-bis(imidazol-1-ylmethyl)benzene, with $-(CH_2)_n-$ ($n \geqslant 2$) spacers as their flexible backbones, have attracted considerable attention. To date, a series of mixed-ligand MCPs have been prepared by assembling Cd(II), Co(II), Zn(II), Ni(II) and Mn(II) with H_3BTC and bis-(imidazole) [13–17]. These MCPs display various 2D and 3D structural patterns, with different coordination geometries of the metal ions, clearly indicating the metal-directed assembly [8,18,19].

Herein, we report the synthesis and crystal structures of three 3D coordination polymers based on 1,3,5-benzenetricarboxylate acid (H_3BTC) and 1,3-bis(imidazole)propane (1,3-BIP) as the mixed

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ligands, namely $\{[Co(BTC)_2(H_2O)_2][Co(1,3\text{-}BIP)(H_2O)_4]_2\}_n$ (**1**), $\{[Zn_3(BTC)_2(1,3\text{-}BIP)_3]\cdot 2DMF\}_n$ (**2**) and $\{[Cu_3(BTC)_2(1,3\text{-}BIP)_3]\cdot DMA\}_n$ (**3**) (DMA = N,N-dimethyl acetamide), in which the structures of complexes **2** and **3** are different, though their chemical formula are similar.

2. Experimental

2.1. Materials and methods

All starting materials were of reagent quality and obtained from commercial sources without further purification. Elemental analysis for C, N and H was performed on a PE 240C elemental analyzer. IR spectra were recorded in the range 400–4000 cm^{-1} on a Nicolet iS10 spectrometer using KBr pellets. Thermogravimetric analyses were performed with a Perkin Elmer Pyris 1 TGA instrument in the range 20–1000 °C under a nitrogen flow at a heating rate of 10 °C min^{-1}. Powder X-ray diffraction (PXRD) data were collected on a Rigaku Ultima IV X-ray diffractometer with Cu Kα radiation ($\lambda = 0.154056$ nm). The luminescent spectra for polycrystalline samples were measured at room temperature on a Perkin Elmer LS 55 fluorescence spectrometer with a xenon arc lamp as the light source.

2.2. Synthesis of $\{[Co(BTC)_2(H_2O)_2][Co(1,3\text{-}BIP)(H_2O)_4]_2\}_n$ (**1**)

A mixture of $Co(NO_3)_2\cdot 6H_2O$ (0.2 mmol, 58.2 mg), 1,3-BIP (0.20 mmol, 35.2 mg), H_3BTC (0.20 mmol, 42.0 mg) and DMA-H_2O (2 mL + 2 mL) was placed in a vial, heated to 100 °C for 3 d and then cooled to room temperature over 24 h. Yellow block crystals of complex **1** were collected, washed with water and air-dried (yield: 69%). Elemental analysis (wt%) calcd for $C_{36}H_{50}Co_3N_8O_{22}$ (*Mr* = 1123.63): C, 38.45; H, 4.44; N, 9.97. Found: C, 38.61; H, 4.74; N, 9.40%. IR (cm^{-1}): 3364 (bs), 3114 (m), 2939 (m), 1618 (s), 1562 (s), 1432 (m), 1374 (s), 1235 (w), 1099 (m), 796 (m).

2.3. Synthesis of $\{[Zn_3(BTC)_2(1,3\text{-}BIP)_3]\cdot 2DMF\}_n$ (**2**)

A mixture of $Zn(NO_3)_2\cdot 6H_2O$ (0.2 mmol, 58.4 mg), 1,3-BIP (0.20 mmol, 35.2 mg), H_3BTC (0.20 mmol, 42.0 mg) and DMF-H_2O (2 mL + 2 mL) was placed in a vial, heated to 100 °C for 3 d and then cooled to room temperature over 24 h. The resulting product was colorless block crystals, which were washed with alcohol to give a pure sample (yield: 57%). Elemental analysis (wt%) calcd for $C_{51}H_{56}N_{14}O_{14}Zn_3$ (*Mr* = 1223.09): C, 48.07; H, 4.16; N, 14.88. Found: C, 47.66; H, 4.35; N, 15.25%. IR (cm^{-1}): 3439 (bs), 3120 (m), 2936 (m), 1624 (s), 1574 (s), 1432 (m), 1374 (s), 1335 (m), 1096 (m), 949 (m).

2.4. Synthesis of $\{[Cu_3(BTC)_2(1,3\text{-}BIP)_3]\cdot DMA\}_n$ (**3**)

Complex **3** was synthesized similar to **1** but using $Cu(NO_3)_2\cdot 3H_2O$ (0.2 mmol, 37.4 mg) in place of $Co(NO_3)_2\cdot 6H_2O$. The resulting product was blue block crystals that were washed with alcohol to give a pure sample (Yield: 39%). Elemental analysis (wt%) calcd for $C_{49}H_{51}N_{13}O_{13}Cu_3$ (*Mr* = 1220.68): C, 48.17; H, 4.17; N, 14.91. Found: C, 48.31; H, 4.14; N, 14.40%. IR (cm^{-1}): 3433 (bs), 3126 (m), 2939 (m), 2362 (w), 1621 (s), 1562 (m), 1402 (w), 1346 (s), 1102 (m), 760 (m).

2.5. Determination of the crystal structures

Suitable single crystals complexes **1**–**3** were carefully selected under an optical microscope and data collection was performed on a CrysAlisPro, Oxford Diffraction Ltd, Version 1.171.34.36 CCD automatic diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) using the ω-scan mode at room temperature. The raw data frames were integrated into SHELX-format reflection files and corrected using the SAINT program. Absorption corrections based on multiscan were obtained using the SADABS program. All the structures were solved with direct methods and refined with full-matrix least-squares on F^2 using SHEXL 97 [20,21]. Hydrogen atoms were located by geometric calculations and their positions and thermal parameters were fixed during the structure refinement. Crystallographic data and experimental details of the structural analyses for the complexes are summarized in Table 1. Selected bond length and angle parameters are listed in Table S1.

3. Results and discussion

3.1. Elemental analyses

All the experimental results are consistent with the calculated values based on the formula given by X-ray single crystal diffraction.

3.2. FT-IR spectra

As shown in Fig. S1, the strong broad band at 3364 cm^{-1} for **1** is the stretching vibration of the O–H group. Meanwhile, the weak bands at 3439 cm^{-1} for **2** and 3433 cm^{-1} for **3** are the stretching mode of O–H, which may be caused by a little surface adsorption water. The strong peaks at 1607 cm^{-1} for **1**, 1612 cm^{-1} for **2** and 1612 cm^{-1} for **3** indicate the presence of deprotonated $-COO^-$ groups. The peaks at (1524, 1386) cm^{-1} for **1**, (1532, 1382) cm^{-1} for **2** and (1585, 1393) cm^{-1} for **3** correspond to the asymmetric and symmetric vibrations of the carboxylate group (COO^-), and the difference in value between the two peaks is less than 200 cm^{-1}, which indicates that the carboxylate groups adopt the chelate coordination mode [22].

Table 1
Crystal data of **1–3**.[a]

Compounds	**1**	**2**	**3**
Formula	$C_{36}H_{50}N_8O_{22}Co_3$	$C_{51}H_{56}N_{14}O_{14}Zn_3$	$C_{49}H_{51}N_{13}O_{13}Cu_3$
fw	1123.63	1285.21	1220.68
T (K)	293(2)	293(2)	293(2)
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a (Å)	11.3384(6)	24.4031(7)	12.7542(5)
b (Å)	16.6100(8)	17.1178(4)	14.2033(5)
c (Å)	11.9430(6)	16.0742(6)	15.4313(6)
α (°)	90	90.00	66.904(4)
β (°)	102.483(5)	94.521(3)	89.991(3)
γ (°)	90	90.00	82.946(3)
V (Å^3)	2196.06(19)	6693.7(4)	2548.36(17)
Z	2	4	2
D_{calc} (g cm^{-3})	1.699	1.275	1.591
$F(000)$	1158	2648	1254
Index ranges	$-13 \leqslant h \leqslant 13$, $-14 \leqslant k \leqslant 19$, $-10 \leqslant l \leqslant 14$	$-29 \leqslant h \leqslant 28$, $-18 \leqslant k \leqslant 20$, $-19 \leqslant l \leqslant 11$	$-15 \leqslant h \leqslant 15$, $-16 \leqslant k \leqslant 16$, $-18 \leqslant l \leqslant 18$
Goodness-of-fit (GOF) on F^2	1.026	1.101	1.022
Reflection/unique	8497/3849	11751/902	8958/7449
R_1, wR_2 [$I > 2(I)$]	0.0237, 0.0637	0.0730, 0.2239	0.0446, 0.1129
R_1, wR_2 (all data)	0.0263, 0.0652	0.1011, 0.2435	0.0554, 0.1186
Largest difference in peak/hole (e Å^{-3})	0.275/−0.379	1.564/−1.674	1.283/−1.000

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