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Polycarboxylate anions effect on the structures of a series of transition metal-based coordination polymers: Syntheses, crystal structures and bioactivities

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ABSTRACT

Five novel transition metal (Zn, Cd, Mn and Co)-based coordination polymers **1**–**5** with a flexible rodlike N,N′-donor ligand (bbi = 1,1′-(1,4-butanediyl)bis(imidazole))and four O-donor polycarboxylate anions (H_2oxa = oxalic acid; H_2fma = fumaric acid; H_2bpdc = 2,2′-biphenyldicarboxylic acid; H_4cit = citric acid) have been successfully synthesized and characterized by elemental analysis, IR spectra, and X-ray diffraction, namely $\{[Zn(bbi)_3(NO_3)]Br\cdot 2H_2O\}_n$ (**1**), $[Zn(oxa)(bbi)]_n$ (**2**), $[Mn(fma)_2(bbi)_2(H_2O)_2]_n$ (**3**), $[Cd_2(bpdc)_2(bbi)_2]_n$ (**4**) and $\{[Co_8(cit)_4(bbi)_6(H_2O)_{10}]\cdot 7H_2O\}_n$ (**5**). Compounds **1**–**5** display various coordination motifs due to different conformations of the bbi ligand, at the same time, owing to diverse coordination modes of the polycarboxylate ligands. And the effect of the polycarboxylate ligands plays important roles in the construction of extended networks. Compounds **1**, **2** and **5** all exhibit 2D layer structures, in which **1** displays a 3-fold interpenetration framework containing 2D networks with (6,3) topology and **2** is a 2D structure with (4,4) topology. Compound **5** contains a 2D 4^4 grid-like layer with $(4^4\cdot 6^2)$ topology composed of octanuclear cobalt clusters. Two high-dimensional compounds (3D) with a microporous network, containing 1D flower-like metal–organic motifs interlinked by bbi ligands for **4** and a 3-fold interpenetrating network with 6^6-dia topology by considering the manganese ion as a four-connected node for **3**, are observed. The biological activities of the title compounds have been studied. The results indicate that **1**–**5** exhibit certain selective antimicrobial activities against *Escherichia coli*, *Staphylococcus aureus* and *Enterobacter aerogenes*, besides, **5** exhibits more obvious radical-scavenging activities than that of bbi ligand. Furthermore, Solid-state properties of thermal stability and the photoluminescence properties at room temperature for these crystalline materials have also been investigated.

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1. Introduction

The design and fabrication of novel multidimensional coordination polymers are of great interest due to not only their fascinating topological structures but also from their promising properties and great potential applications in many different areas [1–29]. According to previous literature, the construction of coordination polymers mainly depends on the nature of the organic ligands (spacers) and metal ions (nodes) [30–38]. It also has been observed that organic ligands play crucial roles for the designed synthesis of some interesting coordination networks, such as the donating type, the flexibility, and the geometry of the organic ligands [34,39–41]. The nitrogen-donor ligands have been intensely investigated for the construction of novel multidimensional coordination polymers because they can satisfy and even mediate the coordination needs of the metal centers and consequently generate more meaningful architectures [42–46]. So far, a number of coordination polymers with diverse topologies have been achieved by using rigid rod-like N-donor ligands such as 4,4′-bipyridine and 4,4′-azobispyridine, which show interesting physical properties [47–52]. In contrast to rigid spacers, flexible ligands, which can adopt various conformations, may induce coordination polymers with novel topologies and properties. Such flexible bridging ligands are of recent interest [4,53–58]. 1,1′-(1,4-Butanediyl)bis(imidazole) (bbi) can be used as flexible divergent ligand to construct coordination polymeric materials. From a structural point of view, it should be pointed out that this ligand, which possesses flexibility owing to the presence of alkyl spacers between bis(imidazole) rings, can freely bend and rotate to meet the steric requirement of coordination geometries of metal ions in the assembly process. Furthermore, as is

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widely known, benzimidazoles have prominent antibacterial activities and radical-scavenging activities. Therefore, the biological activities of the imidazolyl compounds enhance the function of the metal complexes with imidazoles ligands. With this background in mind, we were devoted to the rational design and synthesis of relevant unreported coordination polymers based on flexible bis(imidazole) ligands, and further testing their bioactivity.

Meanwhile, di- and polycarboxylic acids are another kind of good candidates for the construction of novel metal–organic compounds as the carboxyl groups can form C–O–M–O four-membered rings with central metal ions, thereby improving the stability of coordination polymers. Furthermore, not only because of their more coordination sites and various coordination modes to metal ions, resulting from completely or partially deprotonated sites allowing for the large diversity of topologies, but also because of their ability to act as H-bond acceptors and donors to assemble supramolecular structures.

Among various organic ligands, we are particularly interested in the effects of polycarboxylate anions on the architectures of the final compounds. So far, although the effect of anions on the structures of compounds has been studied, systematic investigations on the influence of organic anions such as aromatic polycarboxylate ligands and flexible aliphatic polycarboxylate ligands on their compound structures have been lacking.

In this work, through precise control of organic-acid linker structural features such as dentation and shape, in the absence or presence of polycarboxylate ligands, a remarkable class of compounds containing transition metals and bis(imidazole) ligand with rich architectures has been obtained: $\{[Zn(bbi)_3(NO_3)]Br{\cdot}2H_2O\}_n$ (**1**), $[Zn(oxa)(bbi)]_n$ (**2**), $[Mn(fma)(bbi)(H_2O)_2]_n$ (**3**), $[Cd_2(bpdc)_2(bbi)_2]_n$ (**4**) and $\{[Co_8(cit)_4(bbi)_6(H_2O)_{10}]{\cdot}7H_2O\}_n$ (**5**). On the basis of synthesis and structural characterization, the influence of carboxylate ligands on controlling of the final compound structures is discussed.

2. Experimental

2.1. Materials and general methods

All reagents and solvents employed were commercially available and used as received without further purification. Infrared spectra on KBr pellets were recorded on a Nicolet Nexus 670 FT-IR spectrophotometer in the range 4000–400 cm^{-1}. Elemental analyses were determined with an Elementar Vario EL model instrument. Thermal analyses were performed on a NETZSCH STA 449C microanalyzer with a heating rate of 10 °C min^{-1} under air atmosphere. Luminescence spectrum of the solid sample was recorded with a Hitachi 850 fluorescence spectrophotometer.

2.2. Preparation of the title compounds

2.2.1. Synthesis of $\{[Zn(bbi)_3(NO_3)]\ Br{\cdot}2H_2O\}_n$ (1)

A mixture of Zn $(NO_3)_2$ (60 mg, 0.2 mmol) and bbi (38 mg, 0.2 mmol) in a 1:1 M ratio was stirred in water (10 mL) and the pH of the mixture adjusted to 5.5 with 0.5 M NaOH and 0.2 M HBr solution. It was then sealed in a 25-mL Telfon-lined stainless-steel container, which was heated to 150 °C for 72 h and then cooled to room temperature at a rate of 5 °C h^{-1}. Colorless block crystals were obtained. Yield: 56% (based on Zn). *Anal.* Calc. for $C_{15}H_{23.5}\ Br_{0.5}\ N_7O_{4.5}Zn$: C, 37.56; H, 4.90; N, 20.45. Found: C, 38.98; H, 4.87; N, 20.40%. IR data (KBr, cm^{-1}): 3420 (m), 3098 (m), 2941 (w), 2360 (m), 2342 (m), 1615 (m), 1515 (s), 1464 (s), 1373 (vs), 1292 (vs), 1256 (s), 1199 (s), 1011 (w), 924 (w), 745 (vs), 634 (w), 500 (w), 427 (m).

2.2.2. Synthesis of $[Zn(oxa)(bbi)]_n$ (2)

Compound **2** was obtained by the reaction of $Zn(NO_3)_2$ (3 mg, 0.01 mmol), oxalic acid (1.3 mg, 0.01 mmol) and bbi (1.9 mg, 0.01 mmol) in molar ratio 1:1:1 in water–methanol (1:1) solvent at room temperature in a sealed glass tube of type H. Colorless crystals of **2** were collected in 74% yield (based on Zn). *Anal.* Calc. for $C_{12}H_{14}N_4O_4Zn$: C, 41.98; H 4.08; N, 16.33. Found: C, 42.18; H, 3.91; N, 16.31%. IR data (KBr, cm^{-1}): 3741 (w), 3110 (s), 2858 (w), 1613 (s), 1560 (vs), 1516 (vs), 1358 (m), 1229 (m), 1109 (s), 829 (w), 784 (m), 663 (s), 659 (s), 487 (w).

2.2.3. Synthesis of $[Mn(fma)(bbi)(H_2O)_2]_n$ (3)

$Mn(OAc)_2$ (49 mg, 0.2 mmol), fumaric acid (23.2 mg, 0.2 mmol), and bbi (38 mg, 0.2 mmol) in a 1:1:1 M ratio were stirred in water (9 mL) and methanol (1 mL) and the pH adjusted to 7 with 0.5 M NaOH solution. Telfon-lined stainless-steel container, which was heated to 120 °C for 72 h and then cooled to room temperature at a rate of 5 °C h^{-1}. Colorless block crystals were obtained. Yield: 62% (based on Mn). *Anal.* Calc. for $C_7H_9Mn_{0.5}N_2O_3$: C, 42.72; H, 4.58; N, 14.24. Found: C, 42.74; H, 4.43; N, 14.19%. IR data (KBr, cm^{-1}): 3114 (s), 2949 (w), 1572 (s), 1521 (m), 1452 (w), 1382 (s), 1277 (w), 1242 (w), 1217 (m), 1101(w), 1080 (m), 1031 (w), 983 (w), 931 (w), 839 (m), 742 (m), 703(w), 659 (m).

2.2.4. Synthesis of $[Cd_2(cpds)_2(bbi)_2]_n$ (4)

$Cd(OAc)_2$ (101.2 mg, 0.4 mmol), 2,2′-biphenyldicarboxylic acid (48.4 mg, 0.2 mmol), and bbi (38 mg, 0.2 mmol) in a 1:1:1 M ratio were stirred in water (10 mL) and the pH of the mixture adjusted to 5.5 with a 0.5 M NaOH solution. The hydrothermal synthesis of **4** followed the same procedure as for **1**. Colorless crystals. Yield: 62% (based on Cd). *Anal.* Calc. for $C_{38}H_{30}Cd_2N_4O_7$: C, 51.85; H, 3.41; N, 6.37: Found: C, 51.87; H, 3.44; N, 6.33%. IR data (KBr, cm^{-1}): 3619 (w), 1652 (s), 1626 (s), 1598 (m), 1562 (m), 1516 (s), 1454 (m), 1417 (s), 1358 (s), 1293 (m), 1243 (w), 1109 (w), 842 (w), 666 (m).

2.2.5. Synthesis of $\{[Co_8(cit)_4(bbi)_6(H_2O)_{10}]{\cdot}7H_2O\}n$ (5)

A mixture of $Co(OAc)_2$ (50 mg, 0.2 mmol), citric acid (42 mg, 0.2 mmol), and bbi (38 mg, 0.2 mmol) in a 1:1:1 M ratio was stirred in water (7 mL) and methanol (3 mL) and the pH of the mixture adjusted to 6 with a 0.5 M NaOH solution. The hydrothermal synthesis of **5** followed the same procedure as for **3**. Pink block crystals were obtained. Yield: 60% (based on Co). *Anal.* Calc. for $C_{54}H_{92}Co_8N_{12}O_{45}$: C, 30.84; H, 4.38; N, 8.00. Found: C, 30.87; H, 4.41; N, 7.95%. IR data (KBr, cm^{-1}): 3439 (m), 3053 (w), 2928 (w), 2860 (w), 2361 (m), 1868 (w), 1725 (s), 1608 (s), 1578 (s), 1507 (m), 1449 (s), 1415 (s), 1363 (s), 1292 (w), 1241 (w), 1195 (m), 1131 (m), 1090 (m), 1058 (m), 1017 (m), 826 (s), 765 (s), 719 (w), 626 (w), 545 (s), 506 (m), 464 (m).

2.3. X-ray crystallography study

Single-crystal X-ray diffraction analyses of the five compounds were carried out on a Bruker SMART APEX II CCD diffractometer, equipped with a graphite monochromator using Mo Kα radiation (λ = 0.71073 Å), by using a φ/ω scan technique at room temperature. The structures were solved using direct methods and successive Fourier difference synthesis (SHELXS-97) [59], and they were refined using the full-matrix least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97) [60]. The hydrogen atoms attached to ligands were generated geometrically; the solvent hydrogen atoms were located from difference Fourier maps and fixed isotropic displacement parameters. The crystallographic data and selected bond lengths and angles for **1**, **3**–**5** are listed in Tables 1 and 2.

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