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Anion-controlled assembly of metal 3,5-bis(benzimidazol-1-ylmethyl) benzoate complexes: Synthesis, characterization and property



Hai-Wei Kuai^{a,b}, Gao-Chao Lv^a, Chao Hou^a, Wei-Yin Sun^{a,*}

^a Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing National Laboratory of Microstructures, Nanjing University, Nanjing 210093, China

^b Faculty of Life Science and Chemical Engineering, Huaiyin Institute of Technology, Huaian 223003, China

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ABSTRACT

Hydrothermal reactions of 3,5-bis(benzimidazol-1-ylmethyl)benzoic acid (HL) with Cd(II), Cu(II) and Zn(II) salts provide eight new metal complexes which were characterized by single crystal and powder X-ray diffraction, IR, elemental and thermogravimetric analyses. Two cadmium frameworks [Cd(L)₂]·2H₂O (**1**) and [Cd(L)Cl] (**2**) have 3D structures with (4².6⁵.8³)(4².6) and **rtl** (4.6²)₂(4².6¹⁰.8³) topologies, respectively. Structural diversity of four copper complexes [Cu₃(L)₂]·NO₃·0.5H₂O (**3**), [Cu₂(HL)₂(SO₄)]·3.5H₂O (**4**), [Cu(L)(bdc)_{0.5}]·1.5H₂O (**5**) and [Cu₂(L)(HL)(Hbdc)] (**6**) (H₂bdc=1,4-benzenedicarboxylic acid) is achieved through the alteration of copper salts and addition of auxiliary ligand. As a result, **3** has a 1D ladder structure, **4** is a discrete dinuclear complex, **5** displays a (3,4)-connected 2-nodal 3-fold interpenetrating framework with (4².6.10².12)(4².6) topology, **6** exhibits a 4-connected uninodal 2D **sql** (4⁴.6²) network. Within the zinc series, ZnCl₂ and ZnSO₄ were used for the syntheses of [Zn(L)Cl] (**7**) and [Zn(L)(SO₄)_{0.5}]·2H₂O (**8**), respectively. **7** shows a 3-connected uninodal 2D **hcb** network with (6³) topology and **8** is a (3,6)-connected 2-nodal 3D framework with (4².6)₂(4⁴.6⁸.10) topology. The luminescent properties of the Cd(II) and Zn(II) complexes were investigated.

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1. Introduction

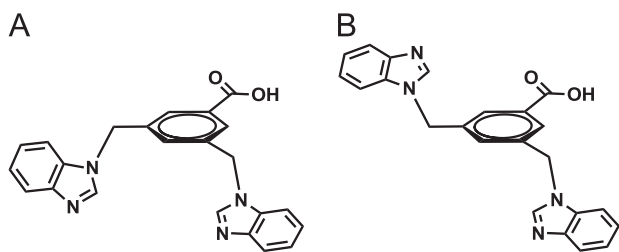
The rational design and synthesis of coordination frameworks have attracted remarkable attention from chemists in view of their diverse structures and topologies as well as potential applications [1]. Up to now, a great number of metal–organic frameworks (MOFs) with various structures and interesting properties have been deliberately prepared and summarized in recent comprehensive reviews [2]. The studies of contemporary chemistry and crystal engineering are mainly focused on the exploration of new crystalline materials with fine functions and possible applications [3]. However, it is known that the functional properties of complexes are largely dependent on their architectures, and thus, the pursuit of structural diversity seems to be important for the exploitation of solid state materials of complexes [4]. Moreover, previous studies have shown that many factors can exert subtle influence on the structure of resultant complexes such as the coordination geometry of metal center, the intrinsic nature of organic ligand, counterion, reaction solvent, and the ratio of metal salt to ligand [5]. Therefore, on one hand it is still a great challenge to design and synthesize complexes with target structure and

function, therefore, comprehending how those complicated influential factors affect the assembling process is at the forefront of dominating coordination arrays, on the other hand, the prospect of tunable architectures and properties of MOFs seems available, which then provides us an impetus to try as more experimental conditions as possible to structurally diversify complexes. It has been documented that the intrinsic nature of organic ligand plays crucial role in determining the resulted structures [6]. Consequently, effort should be devoted to optimize organic building blocks and regulate external conditions for desirably structural motifs.

Based on the above consideration, we focus our attention on the reactions of metal salts with a *N*- and *O*-donor containing ligand 3,5-bis(benzimidazol-1-ylmethyl)benzoic acid (HL). In the previously reported studies, rigid carboxylate-containing ligands such as 1,3- and 1,4-benzenedicarboxylate, and 1,3,5-benzenetricarboxylate, have been extensively studied in the construction of MOFs due to their convincing coordination capacities and varied coordination modes [7], meanwhile, flexible steric-hindered *N*-donor ligands, especially, those with benzimidazolyl groups such as 1,4-bis(benzimidazol-1-ylmethyl)-2,3,5,6-tetramethylbenzene and 1,3,5-tri(benzimidazol-1-ylmethyl)-2,4,6-trimethylbenzene, have also been well employed to assemble MOFs [8]. However, a combination of carboxylate and flexible benzimidazolyl groups within one ligand remains less developed. The *N*- and *O*-mixed

* Corresponding author. Tel.: +86 25 83 59 3485; fax: +86 25 83 31 4502.

E-mail addresses: sunwy@nju.edu.cn, sweiyin@yahoo.com (W.-Y. Sun).



Scheme 1. Different conformations of HL: (A) cis and (B) trans.

donor-containing ligand HL can exhibit several distinctive features in the construction of MOFs. First, the carboxylate group can adopt mutable coordination patterns [9]. Second, HL can have different conformation as illustrated in Scheme 1. Finally, the steric hindrance of benzimidazol groups may engender subtle impact on the formation of MOFs. In this work, we report preparation and structural characterization of a series of metal complexes. The influential factors of synthetic strategy on structures are discussed. In addition, luminescent properties of the complexes were examined.

2. Experimental section

2.1. Materials and measurements

All commercially available chemicals are of reagent grade and were used as received without further purification. A modified experimental procedure was used to prepare the HL ligand [10]. Elemental analyses of C, H, and N were taken on a Perkin-Elmer 240C elemental analyzer at the analysis center of Nanjing University. Infrared spectra (IR) were recorded on a Bruker Vector22 FT-IR spectrophotometer by using KBr pellets. Thermogravimetric analyses (TGA) were performed on a simultaneous SDT 2960 thermal analyzer under nitrogen atmosphere with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. The luminescence spectra for the powdered solid samples were measured on an Aminco Bowman Series 2 spectrofluorometer with a xenon arc lamp as the light source. In the measurements of emission and excitation spectra the pass width is 5 nm, and all the measurements were carried out under the same experimental conditions. Powder X-ray diffraction (PXRD) patterns were measured on a Shimadzu XRD-6000 X-ray diffractometer with $\text{CuK}\alpha$ ($\lambda = 1.5418\text{ \AA}$) radiation at room temperature.

2.2. Syntheses

2.2.1. $[\text{Cd}(\text{L})_2] \cdot 2\text{H}_2\text{O}$ (**1**)

A reaction mixture of $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (26.6 mg, 0.1 mmol), HL (76.4 mg, 0.2 mmol) and NaOH (8.0 mg, 0.2 mmol) in 10 mL H_2O was sealed in a 16 mL Teflon-lined stainless steel container and heated at $180\text{ }^{\circ}\text{C}$ for 3 days. After cooling to the room temperature, colorless block crystals of **1** were collected by filtration and washed by water and ethanol for several times with a yield of 41%. Anal. calcd for $\text{C}_{46}\text{H}_{37}\text{N}_8\text{O}_6\text{Cd}$ (**1**) (%): C, 60.70; H, 4.10; N, 12.31; Found: C, 60.41; H, 3.82; N, 12.60. IR (KBr pellet, cm^{-1}): 3391 (m), 1610 (m), 1566 (s), 1495 (s), 1456 (s), 1399 (s), 1342 (s), 1290 (m), 1258 (s), 1194 (s), 932 (w), 900 (w), 746 (s).

2.2.2. $[\text{Cd}(\text{L})\text{Cl}]$ (**2**)

Complex **2** was obtained by the same procedure as that used for preparation of **1** except using CdCl_2 (18.3 mg, 0.1 mmol) instead of $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$. After cooling to the room temperature, colorless block crystals of **2** were isolated by filtration and washed by water and ethanol several times in 29% yield. Anal. calcd for

$\text{C}_{23}\text{H}_{17}\text{ClN}_4\text{O}_2\text{Cd}$ (**2**) (%): C, 52.19; H, 3.24; N, 10.59; Found: C, 52.46; H, 3.01; N, 10.39. IR (KBr pellet, cm^{-1}): 1613 (m), 1550 (s), 1498 (s), 1459 (m), 1434 (m), 1402 (s), 1376 (s), 1344 (m), 1293 (m), 1260 (m), 1185 (s), 915 (m), 781 (s), 748 (s), 697 (w), 652 (w).

2.2.3. $[\text{Cu}_3(\text{L})_2] \cdot \text{NO}_3 \cdot 0.5\text{H}_2\text{O}$ (**3**)

Complex **3** was also obtained by the procedure as that used for preparation of **1** except using $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (24.1 mg, 0.1 mmol) instead of $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$. After cooling to the room temperature, pale yellow block crystals of **3** were collected by filtration and after washed by water and ethanol several times in 35% yield. Anal. calcd for $\text{C}_{46}\text{H}_{35}\text{N}_9\text{O}_{7.5}\text{Cu}_3$ (**3**) (%): C, 53.93; H, 3.44; N, 12.31; Found: C, 53.66; H, 3.62; N, 12.59. IR (KBr pellet, cm^{-1}): 3420 (m), 1620 (s), 1588 (s), 1511 (s), 1459 (m), 1383 (s), 1351 (s), 1293 (m), 1255 (m), 1190 (m), 1120 (w), 1104 (w), 748 (s), 697 (w), 595 (w).

2.2.4. $[\text{Cu}_2(\text{HL})_2(\text{SO}_4)] \cdot 3.5\text{H}_2\text{O}$ (**4**)

Complex **4** was obtained by the same procedure as that used for preparation of **1** except using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (25.0 mg, 0.1 mmol) instead of $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$. After cooling to the room temperature, pale yellow block crystals of **4** were obtained in 40% yield. Anal. calcd for $\text{C}_{46}\text{H}_{43}\text{N}_8\text{O}_{11.5}\text{SCu}_2$ (**4**) (%): C, 52.57; H, 4.12; N, 10.66; Found: C, 52.29; H, 4.22; N, 10.59. IR (KBr pellet, cm^{-1}): 3432 (m), 1687 (s), 1613 (s), 1511 (s), 1459 (s), 1434 (m), 1383 (s), 1293 (s), 1260 (s), 1229 (s), 1190 (s), 1120 (s), 979 (s), 934 (m), 895 (m), 774 (s), 736 (s), 711 (s), 621 (m).

2.2.5. $[\text{Cu}(\text{L})(\text{bdc})_{0.5}] \cdot 1.5\text{H}_2\text{O}$ (**5**)

Reaction mixture of CuBr_2 (44.6 mg, 0.2 mmol), HL (38.2 mg, 0.1 mmol), H_2bdc (8.3 mg, 0.05 mmol), and NaOH (8.0 mg, 0.2 mmol) in 10 mL H_2O was sealed in a 16 mL Teflon-lined stainless steel container and heated at $180\text{ }^{\circ}\text{C}$ for 3 days. After cooling to the room temperature, blue block crystals of **5** were obtained in 36% yield. Anal. calcd for $\text{C}_{27}\text{H}_{22}\text{N}_4\text{O}_{5.5}\text{Cu}$ (**5**) (%): C, 58.53; H, 4.00; N, 10.11; Found: C, 58.26; H, 3.79; N, 9.89. IR (KBr pellet, cm^{-1}): 3459 (m), 1588 (s), 1562 (s), 1511 (s), 1459 (s), 1402 (s), 1376 (s), 1287 (m), 1255 (m), 1190 (m), 1120 (w), 1011 (w), 883 (m), 825 (m), 774 (m), 748 (s), 697 (w).

2.2.6. $[\text{Cu}_2(\text{L})(\text{HL})(\text{Hbdc})]$ (**6**)

Complex **6** was obtained by hydrothermal procedure as that used for preparation of **5** except using $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (48.2 mg, 0.2 mmol) instead of CuBr_2 . After cooling to the room temperature, pale yellow block crystals of **6** were obtained in 33% yield. Anal. calcd for $\text{C}_{54}\text{H}_{40}\text{N}_8\text{O}_8\text{Cu}_2$ (**6**) (%): C, 61.42; H, 3.82; N, 10.61; Found: C, 61.62; H, 3.55; N, 10.46. IR (KBr pellet, cm^{-1}): 1702 (s), 1600 (s), 1562 (m), 1511 (m), 1459 (m), 1383 (s), 1293 (w), 1235 (s), 1185 (m), 1004 (m), 928 (w), 895 (w), 736 (s), 672 (w), 582 (w).

2.2.7. $[\text{Zn}(\text{L})\text{Cl}]$ (**7**)

Complex **7** was obtained by hydrothermal procedure as that used for preparation of **1** except using ZnCl_2 (13.6 mg, 0.1 mmol) instead of $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$. After cooling to the room temperature, colorless block crystals of **7** were obtained in 52% yield. Anal. calcd for $\text{C}_{23}\text{H}_{17}\text{ClN}_4\text{O}_2\text{Zn}$ (**7**) (%): C, 57.28; H, 3.55; N, 11.62; Found: C, 57.51; H, 3.82; N, 11.89. IR (KBr pellet, cm^{-1}): 1627 (s), 1588 (s), 1511 (s), 1459 (m), 1383 (s), 1293 (m), 1260 (m), 1229 (m), 1197 (m), 1120 (w), 1094 (w), 1011 (w), 915 (w), 744 (m), 743 (s), 678 (w).

2.2.8. $[\text{Zn}(\text{L})(\text{SO}_4)_{0.5}] \cdot 2\text{H}_2\text{O}$ (**8**)

Complex **8** was obtained by hydrothermal procedure as that used for preparation of **1** except using ZnSO_4 (16.1 mg, 0.1 mmol) instead of $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$. After cooling to the room temperature, colorless block crystals of **8** were obtained in 45% yield. Anal. calcd for $\text{C}_{23}\text{H}_{21}\text{N}_4\text{O}_6\text{S}_{0.5}\text{Zn}$ (**8**) (%): C, 52.04; H, 3.99; N, 10.55; Found: C,

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