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Effect of central metals and N-donor ligands on the architectures of a series of coordination polymers based on a bis(sulfanediyl) thiadiazole diacetate

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Five new transition metal coordination polymers, namely, [Co(bbbm)(BSTDA)] (**1**), [Co(bdmbmb)(BSTDA)(H_2O)]·(H_2O) (**2**), [Ni(bbbm)(BSTDA)$(H_2O)_2$] (**3**), $[Ni_2(3\text{-dpyh})_2(BSTDA)_2(H_2O)]$ (**4**) and $[Cd(bbbm)_{1.5}(BSTDA)]$ (**5**) have been synthesized from an S-/thiadiazole-containing dicarboxylate [H_2BSTDA = bis(sulfanediyl) thiadiazole diacetic acid] and different flexible/semi-rigid N-donor ligands [bbbm = 1,1-(1,4-butanediyl) bis-1H-benzimidazole, bdmbmb = 1,4-bis(5,6-dimethylbenzimidazole-1-yl)benzene and 3-dpyh = N,N′-bis(3-pyridinecarboxamide)-1,6-hexane]. Structural analysis indicates that the title complexes present different structures although using the same S-/thiadiazole-containing dicarboxylate. Complex **1** is a 3D framework constructed from 2D (6^3) Co-BSTDA layers and 1D Co-bbbm chains. When the flexible bbbm in **1** was replaced by a semi-rigid bdmbmb ligand, a 2D parallelogram (4,4) network **2** derived from 1D Co-BSTDA and Co-bdmbmb single chains has been obtained. Complex **3**, with Ni^{II} ion as substitute of Co^{II} ion in **1**, exhibited a 2D (4,4) network constructed form 1D Ni-BSTDA and Ni-bbbm single chains. When the bbbm in **3** was replaced by a longer and more flexible N-donor ligand 3-dpyh in **4**, a 2D wave-like (4,4) layer constructed from $[Ni\text{-}BSTDA]_2$ and $[Ni\text{-}(3\text{-dpyh})]_2$ double chains with bimetallic nodes was generated. While the Co^{II} ion in **1** was substituted by Cd^{II} ion in **5**, a 3D framework crossed by 2D (6^3) wave-like Cd-bbbm layers and 1D zigzag Cd-BSTDA chains was obtained. Structural diversity in complexes **1**–**5** demonstrates that the coordination characters of metal ions, the spacer length and flexibility of N-donor ligands have great influence on the final structures of the title complexes. In addition, fluorescence properties of complexes **1**–**5** are also reported in this paper.

1. Introduction

Design and syntheses of coordination polymers (CPs) with transition metals and organic ligands have drawn enormous attentions in the past decade [1–5]. More and more interests have been focused not only on the novel topological structures of these complexes, but also their potential applications in gas storage, luminescence, magnetism and catalysis [6–11]. Although a mass of transition metal CPs with interesting architectures and properties have been successfully obtained, controllable synthetic strategy for target CPs is still a great challenge, owing to the facts that assembly of these complexes can be easily influenced by the properties of metal ions and ligands [12–14].

Among the large numbers of organic ligands used to construct coordination polymers, N-heterocycle derivatives and aromatic polycarboxylic acids have been considered as excellent building blocks with versatile coordination modes and remarkable coordination ability [15–19]. Many transition metal CPs based on flexible or semi-rigid N-heterocycle ligands, which contain twistable spacers, have been successfully synthesized by Bu, Lang, Ma's groups [20–23]. In the recent years, we have reported a series of transition metal CPs based on flexible/semi-rigid N-donor ligands, such as 1,1-(1,4-butanediyl)bis-1H-benzimidazole (bbbm), 1,1-(1,4-butanediyl)bis(5,6-dimethylbenzimidazole) (bbdmbm), N,N′-bis(3-pyridinecarboxamide)-1,2-ethane (3-dpye) and N,N′-bis(3-pyridinecarboxamide)-1,6-hexane (3-dpyh) [24–26].

On the other hand, metal-carboxylate frameworks have received much attention because of their chemical stability and potential applications in gas adsorption, magnetism and luminescence [27,28]. Various kinds of polycarboxylates have been used in the preparation of complicated complexes [29–31]. Here, a bis(sulfanediyl) thiadiazole diacetic acid (H_2BSTDA) is chosen as anionic organic linker based on the following considerations

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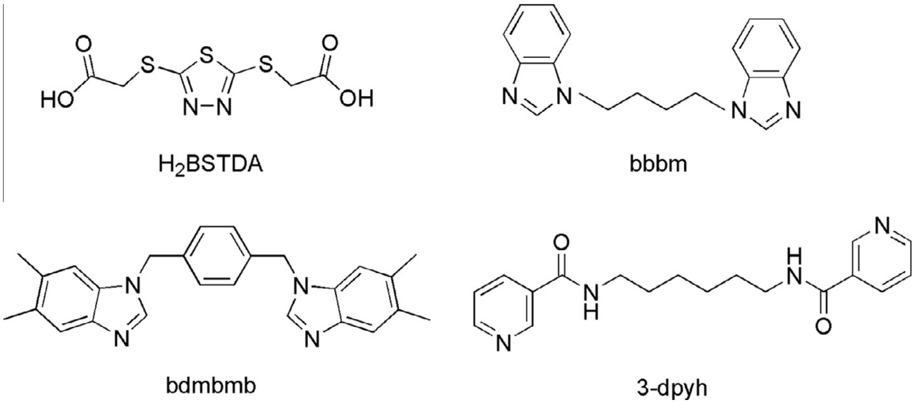

Scheme 1. The ligands used in this paper.

(Scheme 1): (a) The carboxylic groups exhibit different coordination modes and remarkable coordination ability; (b) Sulfur atoms and methylene groups, acting as spacers, can enhance flexibility of the carboxylate, thus leading to the various conformations of BSTDA anions and possible diversification of title complexes. To the best of our knowledge, reports on the complexes constructed from BSTDA anion are very limited up to now [32–35].

In order to investigate the effect of flexibility of N-heterocycle ligands and central metals on the assembly and structures of BSTDA-based complexes, three kinds of N-donor ligands 1,1-(1,4-butanediyl) bis-1H-benzimidazole (bbbm), 1,4-bis(5,6-dimethylbenzimidazole1yl)benzene (bdmbmb), N,N′-bis(3-pyridinecarboxamide)-1,6-hexane (3-dpyh) have been employed as the auxiliary ligands and three transition metals $Co^{II}/Ni^{II}/Cd^{II}$ have been selected as the central atoms. As a result, five new coordination polymers, [Co(bbbm)(BSTDA)] (**1**), $[Co(bdmbmb)(BSTDA)(H_2O)]\cdot(H_2O)$ (**2**), $[Ni(bbbm)(BSTDA)(H_2O)_2]$ (**3**), $[Ni_2(3\text{-}dpyh)_2(BSTDA)_2(H_2O)]$ (**4**) and $[Cd(bbbm)_{1.5}(BSTDA)]$ (**5**) have been obtained under hydrothermal conditions and structurally characterized. In addition, the photoluminescent properties of the complexes have been also reported.

2. Experimental

2.1. Materials and general methods

All chemicals were used as supplied from commercial sources without further purification. The heterocyclic ligands were synthesized by the literature method [35–38]. FT/IR spectra (KBr pellets) were taken on a Magna 560 spectrometer. Elemental analyses were obtained on a Perkin–Elmer 240CHN analyzer. Thermogravimetric analyses (TGA) were performed on a Pyris Diamond TG instrument under a flowing N_2 atmosphere with a heating rate of 10 °C min^{-1}. Powder X-ray diffraction (PXRD) patterns were measured on an Ultima IV with D/teX Ultra diffractometer at 40 kV, 40 mA with Cu Kα (λ = 1.5406 Å) radiation. Luminescence spectra were measured on a Hitachi F-4500 fluorescence spectrophotometer.

2.2. Preparation of complexes **1**–**5**

2.2.1. [Co(bbbm)(BSTDA)] (**1**)

The mixture of $Co(NO_3)_2\cdot 6H_2O$ (0.0582 g, 0.2 mmol), bbbm (0.029 g, 0.1 mmol), H_2BSTDA (0.0266 g, 0.2 mmol), NaOH (3 mL, 0.1 mol/L) and H_2O (7 mL) was sealed in a 25 mL Teflon reactor at 120 °C for 3 days. After slow cooling to room temperature, purple block crystals of **1** were obtained. Yield: 25% based on Co^{II}. *Anal.* Calc. for $C_{24}H_{22}CoN_6O_4S_3$: C, 46.98; H, 3.61; N, 13.70. Found: C, 46.87; H, 3.52; N, 13.79%. IR (KBr, cm^{-1}): 3480s, 3190s, 2880s, 2810s, 1667s, 1641s, 1482s, 1352m, 1228m, 1185m, 1089s, 865s, 770s.

2.2.2. $[Co(bdmbmb)(BSTDA)(H_2O)]\cdot(H_2O)$ (**2**)

Complex **2** was prepared in the same manner as that for **1**, except for using bdmbmb (0.039 g, 0.1 mmol) as the substitute of bbbm. Purple block crystals of **2** were obtained. Yield: 30% based on Co^{II}. *Anal.* Calc. for $C_{32}H_{34}CoN_6O_6S_3$: C, 50.99; H, 4.55; N, 11.15%. Found: C, 51.20; H, 4.41; N, 11.02%. IR (KBr, cm^{-1}): 3480s, 3113w, 1630s, 1589s, 1441s, 1356s, 1205s, 1158s, 782m, 764m, 680m, 645m, 630w.

2.2.3. $[Ni(bbbm)(BSTDA)(H_2O)_2]$ (**3**)

Complex **3** was prepared in the same process as that for **1** but using $Ni(NO_3)_2\cdot 6H_2O$ (0.058 g, 0.2 mmol) in place of $Co(NO_3)_2\cdot 6H_2O$. Green block crystals of 3 were obtained. Yield: 30% based on Ni^{II}. *Anal.* Calc. for $C_{24}H_{26}N_6NiO_6S_3$: C, 44.39; H, 4.04; N, 12.94%. Found: C, 44.47; H, 4.01; N, 12.85%. IR (KBr, cm^{-1}): 3470s, 3120s, 3014s, 2798w, 2389m, 2314m, 1680s, 1210s, 1150m, 785s, 610m.

2.2.4. $[Ni_2(3\text{-}dpyh)_2(BSTDA)_2(H_2O)]$ (**4**)

Complex **4** was prepared in the same method as that for **3** except that 3-dpyh (0.033 g, 0.1 mmol) was used instead of bbbm. Yield: 50% based on Ni^{II}. *Anal.* Calc. for $C_{48}H_{54}N_{12}Ni_2O_{13}S_6$: C, 43.78; H, 4.13; N, 8.91%. Found: C, 43.62; H, 4.09; N, 8.75%. IR (KBr, cm^{-1}): 3458s, 3150s, 1846m, 1650s, 1640m, 1547s, 1520s, 1459m, 1392s, 1170m, 1125s, 846s, 810s.

2.2.5. $[Cd(bbbm)_{1.5}(BSTDA)]$ (**5**)

Complex **5** was prepared in the same way as that for **1** except for $Cd(NO_3)_2\cdot 4H_2O$ (0.062 g, 0.2 mmol) as the substitute of $Co(NO_3)_2\cdot 6H_2O$. Yield: 25% based on Cd^{II}. *Anal.* Calc. for $C_{33}H_{31}CdN_8O_4S_3$: C, 48.80; H, 3.85; N, 13.80%. Found: C, 48.68; H, 3.82; N, 13.92%. IR (KBr, cm^{-1}): 3640w, 3467m, 2882m, 1670s, 1640s, 1506s, 1475s, 1420s, 1372m, 1350s, 1289s, 1210s,1135s, 860m, 790m.

2.3. X-ray crystallography

Diffraction data for complexes **1**–**5** were collected on a Bruker Smart 1000 CCD area detector diffractometer (Mo Kα radiation, graphite monochromator, λ = 0.71073 Å). The crystal structures of **1**–**5** were solved by the direct method and refined on F^2 by full-matrix least-squares technique with the SHELXL-97 software package [39]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms of ligands were placed in geometrically idealized positions and refined isotropically. In the complex **2**, the O2W