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A series of flexible bis(imidazole)-based coordination polymers tuned by central metal ions and dicarboxylates: Diverse structures and properties

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ABSTRACT

Seven new coordination polymers, namely, $[Ni(L)_{1.5}(2\text{-CMSN})(H_2O)]\cdot 2H_2O$ **1**, $[Co_2(L)_2(2\text{-CMSN})_2(H_2O)]\cdot H_2O$ **2**, $[Cd(L)(2\text{-CMSN})(H_2O)]$ **3** $[Zn(L)(2\text{-CMSN})]\cdot 2H_2O$ **4**, $[Cd(ADTZ)(H_2O)]$ **5**, $[Cd(L)(ADTZ)(H_2O)]$ **6**, and $[Zn(L)(ADTZ)]\cdot H_2O$ **7** [where $2\text{-}H_2CMSN$ = 2-carboxymethylsulfanyl nicotinic acid, H_2ADTZ = 2,5-(s-acetic acid) dimercapto-1,3,4-thiadiazole, L = 1,4-bis(imidazol-1-ylmethyl)benzene] have been synthesized under hydrothermal conditions. The complexes were structurally characterized by single crystal X-ray diffraction analyses, infrared spectroscopy (IR), elemental analyses, powder X-ray diffraction (PXRD) and thermogravimetric analyses (TGA). Complex **1** features a 1D ladder-like double chain. Complexes **2** and **3** exhibit the similar 2D networks based on six-nuclear metallic rings. Complex **4** is a 2D sheet. Complex **5** exhibits a 3D (4,6)-connected $(4^3\cdot 5^3)(4^5\cdot 5^3\cdot 6^7)$ topology. Complex **6** shows a 2D undulated network with the Schläfli symbol of $(3\cdot 5^2)(3^2\cdot 5^3\cdot 6^4\cdot 7)$. Complex **7** is a 3D 4-fold interpenetrated **dia** network. Structural comparison of these polymers suggests that different central metals and dicarboxylates play important roles in the construction of **1**–**7**. The luminescent properties of complexes **3**, **4**, **6**, **7** and the electrochemical properties of complexes **1**, **2** have been investigated. Furthermore, the complexes **2**–**4**, **6** and **7** exhibit photocatalytic activities for dye methylene blue degradation under UV light and show good stability toward photocatalysis.

1. Introduction

The design and construction of coordination polymers have attracted increasing attention in the field of crystal engineering due to their novel diverse structures and topologies [1–3], as well as their potential applications in many areas such as catalysis [4,5], gas adsorption [6–8], fluorescence [9,10] and ion exchange [11,12]. It is well-known that the construction of coordination polymers is dependent on many factors, such as coordination geometry of the central metal ions [13], solvents [14], pH values [15–17], reaction temperatures [18,19], organic ligands [20–22]. Among these factors, the N-donor organic ligand, as a kind of excellent building units, is one of the most important factors, because their various flexibility, length, steric effects and angle of coordination atoms will result in diverse structures [23,24]. The multicarboxylate ligands are also excellent building blocks, which can serve as good candidates for building highly connected, self-penetrating, or helical coordination frameworks due to their bent backbones and versatile bridging fashions [25,26]. So far, multicarboxylate ligands have been widely used in the construction of coordination polymers [27,28]. However, to our knowledge, the coordination chemistry of N-heterocycle-S-containing dicarboxylates have received relatively less attention [29].

As a continuous effort of our previous work [30], here we selected a flexible N-donor ligand 1,4-bis(imidazol-1-ylmethyl)benzene (L) and two flexible N/S-containing dicarboxylic acids 2-carboxymethylsulfanyl nicotinic acid ($2\text{-}H_2CMSN$) and 2,5-(s-acetic acid) dimercapto-1,3,4-thiadiazole (H_2ADTZ) (Scheme 1) as the mixed ligands to construct diverse coordination polymers based on the following considerations: (i) The flexible L ligand can rotate to meet the requirement of coordination geometries of metal ions in the assembly process [31]. (ii) $2\text{-}H_2CMSN$ is an interesting flexible ligand due to its potential versatile coordinate behavior, which possesses a pyridyl ring, a rigid carboxyl group (–COOH) and a flexible S-containing carboxyl group ($–SCH_2COOH$) [32]. H_2ADTZ contains two flexible $–SCH_2COOH$ groups and a thiadiazole ring. These two carboxylate ligands have different bending and rotating ability, versatile coordination orientation, may construct various architectures [33]. (iii) In addition, the nitrogen atoms of pyridyl or thiadiazole rings and the sulfur atoms from flexible $–SCH_2COOH$ groups have potential coordinate ability, which may also enrich the coordination modes of the N/S-containing ligands and induce excellent structures.

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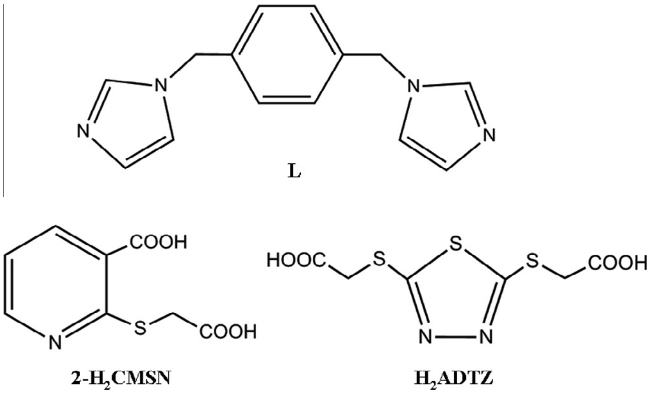

Scheme 1. Structures of N-donor ligand (L) and 2-H_2CMSN/H_2ADTZ used in this work.

As is known, central metals with different coordination environments can also influence the final structures and topologies of the coordination polymers to some extent [34]. In order to investigate the effect of transition metal ions on the structural varieties of the coordination polymers, in this work, we employed different transition metals, including Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+} and Ag^+, to react with L ligand and 2-H_2CMSN or H_2ADTZ under similar reaction conditions. However, we failed in the construction of Cu^{2+} and Ag^+ complexes, and successfully synthesized seven coordination polymers, namely, $[Ni(L)_{1.5}(2\text{-}CMSN)(H_2O)]\cdot 2H_2O$ **1**, $[Co_2(L)_2(2\text{-}CMSN)_2(H_2O)]\cdot H_2O$ **2**, [Cd(L)(2-CMSN)(H_2O)] **3**, [Zn(L)(2-CMSN)]·2H_2O **4**, [Cd(ADTZ)(H_2O)] **5**, [Cd(L)(ADTZ)(H_2O)] **6**, and [Zn(L)(ADTZ)]·H_2O **7**. The luminescent properties of the complexes **3**, **4**, **6** and **7** have been investigated in the solid state. The electrochemical properties of complexes **1** and **2** have also been studied. Furthermore, complexes **2**–**4**, **6** and **7** exhibit good photocatalysis activity for photodegradation of MB under UV irradiation and good stability towards UV photocatalysis.

2. Experimental

2.1. Materials and measurements

All chemicals purchased were of reagent grade, and used without further purification. The 2-H_2CMSN, H_2ADTZ and L ligands were synthesized by the method of the literatures [35–37]. Elemental analyses were performed on a Perkin-Elmer 240C element analyzer. FT-IR spectra were taken on a Varian FT-IR 640 spectrometer (KBr pellets). Powder X-ray diffraction (PXRD) investigations were carried out with a Ultima IV with D/teX Ultra diffractometer at 40 kV, 40 mA with Cu Kα (λ = 1.5406 Å) radiation. Thermogravimetric data for the complexes **1**–**7** were carried out on a Pyris Diamond thermal analyzer. Fluorescence spectra were recorded at room temperature on a Hitachi F-4500 fluorescence/phosphorescence spectrophotometer. A CHI 440 electrochemical workstation connected to a Digital-586 personal computer was used for control of the electrochemical measurements and for data collection. A conventional three-electrode system was used with an SCE as reference electrode, a platinum wire as auxiliary electrode and the modified electrodes as the working electrodes, respectively. UV–Vis absorption spectra were obtained using a SP-1900 UV–Vis spectrophotometer.

2.2. Preparation of the complexes

2.2.1. *[Ni(L)$_{1.5}$(2-CMSN)(H$_2$O)]·2H$_2$O* **1**

A mixture of $Ni(NO_3)_2\cdot 6H_2O$ (0.058 g, 0.20 mmol), **L** (0.024 g, 0.10 mmol), 2-H_2CMSN (0.022 g, 0.10 mmol) and H_2O (8 mL) was placed in a 25 mL Teflon reactor and the pH value was adjusted around 6 by addition of 0.1 M NaOH solution. The mixture was heated at 100 °C for 3 days, and then the autoclave was gradually cooled to room temperature. Green block-shaped crystals of **1** were obtained in 34% yield (based on Ni). Elemental anal. (%) *Anal.* Calc. for $C_{29}H_{32}NiN_7O_7S$: C, 51.12; H, 4.73; N, 14.39. Found: C, 51.03; H, 4.65; N, 14.31%. IR (KBr, cm^{-1}): 3130w, 3035w, 2932w, 2361m, 1591s, 1443m, 1373 s, 1286w, 1238m, 1157w, 1090m, 1030m, 941w, 835w, 735m, 662w.

2.2.2. *[Co$_2$(L)$_2$(2-CMSN)$_2$(H$_2$O)]·H$_2$O* **2**

The same synthetic method as that for **1** was used except that $Ni(NO_3)_2\cdot 6H_2O$ was replaced by $Co(NO_3)_2\cdot 6H_2O$ (0.058 g, 0.20 mmol). Pink block-shaped crystals of **2** were obtained. Yield: 32% (based on Co). Elemental anal. (%) *Anal.* Calc. for $C_{44}H_{42}Co_2N_{10}O_{10}S_2$: C, 50.19; H, 4.02; N, 13.30. Found: C, 50.03; H, 4.15; N, 13.35%. IR (KBr, cm^{-1}): 3125w, 2932w, 2361m, 1595s, 1543m, 1381s, 1271w, 1232m, 1157w, 1109m, 1088m, 941w, 858w, 725m, 660w.

2.2.3. *[Cd(L)(2-CMSN)(H$_2$O)]* **3**

The same synthetic method as that for **1** was used except that $Cd(NO_3)_2\cdot 4H_2O$ (0.062 g, 0.20 mmol) was used instead of $Ni(NO_3)_2\cdot 6H_2O$. Yellow block-shaped crystals of **3** were obtained. Yield: 40% (based on Cd). Elemental anal. (%) *Anal.* Calc. for $C_{22}H_{21}CdN_5O_5S$: C, 45.57; H, 3.65; N, 12.08. Found: C, 45.33; H, 3.69; N, 12.15%. IR (KBr, cm^{-1}): 3126w, 3030w, 2934w, 2361m, 1582s, 1545m, 1377s, 1297w, 1232m, 1155w, 1101m, 1076m, 937w, 832w, 737m, 656w.

2.2.4. *[Zn(L)(2-CMSN)]·2H$_2$O* **4**

The same synthetic method as that for **1** was used except that $Ni(NO_3)_2\cdot 6H_2O$ was replaced by $Zn(NO_3)_2\cdot 6H_2O$ (0.059 g, 0.20 mmol). Yellow block-shaped crystals of **4** were obtained. Yield: 21% (based on Zn). Elemental anal. (%) *Anal.* Calc. for $C_{22}H_{23}ZnN_5O_6S$: C, 47.96; H, 4.21; N, 12.71. Found: C, 47.83; H, 4.29; N, 12.65%. IR (KBr, cm^{-1}): 3130w, 3052w, 2363m, 1604s, 1530m, 1443m, 1383s, 1291w, 1240m, 1153w, 1101m, 1033m, 950w, 849w, 724m, 657w.

2.2.5. *[Cd(ADTZ)(H$_2$O)]* **5**

A mixture containing $Cd(NO_3)_2\cdot 4H_2O$ (0.062 g, 0.20 mmol), H_2ADTZ (0.027 g, 0.10 mmol) and H_2O (8 mL) was placed in a 25 mL Teflon reactor and the pH value was adjusted around 6 by addition of 0.1 M NaOH solution. The mixture was heated at 100 °C for 3 days, and then the autoclave was gradually cooled to room temperature. Yellow block-shaped crystals of **5** were obtained in 23% yield (based on Cd). Elemental anal. (%) *Anal.* Calc. for $C_6H_5CdN_2O_5S_3$: C, 18.30; H, 1.28; N, 7.12. Found: C, 18.38; H, 1.33; N, 7.05%. IR (KBr, cm^{-1}): 3494m, 2938w, 2345w, 1579s, 1410s, 1387s, 1214m, 1616w, 1053m, 930w, 904m, 776m, 682w, 618w, 542m.

2.2.6. *[Cd(L)(ADTZ)(H$_2$O)]* **6**

The preparation of **6** was similar to that of **5** except that **L** (0.024 g, 0.10 mmol) was added to the reaction system of **5**. Yellow block-shaped crystals of **6** were obtained in 39% yield (based on Cd). Elemental anal. (%) *Anal.* Calc. for $C_{20}H_{20}CdN_6O_5S_3$: C, 37.95; H, 3.18; N, 13.28. Found: C, 37.86; H, 3.26; N, 13.15%. IR (KBr, cm^{-1}): 3423w, 3117w, 2347m, 1578s, 1448m, 1380s, 1277w, 1239m, 1114m, 1038m, 955w, 860w, 712m, 618w.

2.2.7. *[Zn(L)(ADTZ)]·H$_2$O* **7**

The same synthetic method as that for **6** was used except that $Cd(NO_3)_2\cdot 4H_2O$ was replaced by $Zn(NO_3)_2\cdot 6H_2O$ (0.059 g, 0.20 mmol). Yellow block-shaped crystals of **7** were obtained. Yield: 19% (based on Zn). Elemental anal. (%) *Anal.* Calc. for $C_{20}H_{20}ZnN_6O_5S_3$: C, 40.99; H, 3.44; N, 14.34. Found: C, 40.87; H, 3.49; N,