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pH–value-controlled assembly of photoluminescent zinc coordination polymers in the mixed-ligand system

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ABSTRACT

Three novel coordination polymers, $[Zn(sdi)_2(NO_3)(H_2O)]\cdot NO_3$ (**1**), $[Zn(sdi)_2(H_2O)_2]\cdot 2NO_3$ (**2**) and $[Zn(sdi)_{0.5}(H_2C_3O_4)(H_2O)]$ (**3**), (sdi = *N*,*N*′-sulfuryldiimidazole) have been synthesized and characterized by elemental analysis, IR spectroscopy, single crystal X-ray diffraction, powder X-ray diffraction and thermogravimetric analyses. These compounds have abundant structural chemistry ranging from zero-dimensional (0D) (**1**), one-dimensional (1D) (**2**), to three-dimensional (3D) (**3**) networks. Compound **1** displays a 0D structure which formed by $[Zn(sdi)_2]_2$ dimers. Compound **2** possesses 1D chain with closed loops. Notably, compound **3** exhibits a 3D (3,4)-connected net with a $(6^3)(6^5\cdot 8)$ topology. Interestingly, compounds **1**–**3** were obtained under similar reaction conditions and the structural diversity of these coordination polymers illustrate the remarkable effect of pH on the self-assembling process. Moreover, the fluorescent properties of these compounds have been investigated.

1. Introduction

Coordination polymers (CPs) architectures are a significant objective for synthetic chemistry as they offer us opportunities to control properties of materials on a molecular scale, such as gas storage, magnetism, fluorescence, ion-exchange, catalysis and so on [1–5]. The principal strategy for constructing CPs depends mostly on the judicious selection of both metal ions and ligands. Currently, *N*-containing heterocyclic ligands are widely used as bridging ligands for the building of CPs [6–10]. In particular, 1H-imidazol-1-yl-containing ligands have been drawing growing attention. They can be utilized as neutral ligands which are required to have an anionic part to balance the charge of metal centers. More importantly, the counterions may have significant implications for the structures as well as the properties of the materials [11–13]. Recently, we reported a V-shaped ligand, *N*,*N*′-sulfuryldiimidazole (sdi) [14]. This semi-rigid imidazole ligand is a good candidate for the construction of CPs with fascinating motifs. As a part of our ongoing studies of synthesizing CPs with semi-rigid V-shaped ligands [15–17], and discussing the factors that could influence the final structures, we selected sdi as organic linker. As far as we know, the researches of CPs based on sdi ligand are still in an initial stage.

It is generally accepted that the self-assembly process of coordination polymers is related with many synthetic factors [18,19], such as solvents, ratio of reactants, temperature, counteranion, etc. Among them, the pH value of the reaction mixture plays a vital role in the crystallization process of CPs [20–33]. For example, Hong and co-workers have reported the formation of four novel cadmium(II) mixed-ligand based CPs controlled by pH value [34]. These structures range from discrete molecules to 3D supramolecular architectures, revealing that the pH value of the reaction has a crucial effect on the assembly and structures of target compounds [35]. From previous research we knew that carboxylic acid exerts different deprotonations under diverse pH conditions and exhibits rich coordination modes to coordinate with metal ions to form distinct CPs [36]. Significantly, the effective mixed ligands strategy consolidating *N*-donor ligands and carboxylates has been demonstrated to construct interesting skelecton [37]. It should also be mentioned that the auxiliary ligand is not involved in coordination in some cases [38,39].

In this paper, we report the synthesis and crystal structures of three novel coordination polymers in various pH conditions: $[Zn(sdi)_2(NO_3)(H_2O)]\cdot NO_3$ (**1**) (0D, pH = 4), $[Zn(sdi)_2(H_2O)_2]\cdot 2NO_3$ (**2**) (1D, pH = 5), $[Zn(sdi)_{0.5}(H_2C_3O_4)H_2O]$ (**3**) (3D, pH = 6). Compared to the previous studies, the diverse pH values could

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control the procedure of the assembly of CPs and then fine tune the structure. The changes in structures between the prior research and the present result will be discussed in detail. In addition, the stability and luminescence properties are also investigated.

2. Experimental

2.1. Materials and physical measurements

The *N*,*N*′-sulfuryldiimidazole ligand (sdi) was prepared according to the literature procedure [14], other reagents were commercially available sources and used without further purification. The FTIR absorption spectra were recorded on a Nicolet Impact 410 FTIR spectrometer in the range of 400–4000 cm^{-1} using the KBr pellets. Element analyses were performed on a Perkin-Elmer 2400 elemental analyzer. Diffraction data collection were performed on a Bruker D8 Advance X-ray diffractometer using Mo-K*a* radiation ($\lambda = 0.71073$ nm), in which the X-ray tube was operated at 150 mA and 40 kV. Thermogravimetric analysis (TGA) experiments were completed from 40 to 800 °C on a Perkin-Elmer TGA-7 thermogravimetric analyzer at a heating rate of 10 °C min^{-1} in N_2 atmosphere. Luminescence spectra were recorded by means of a SHIMAZU VF-320 X-ray fluorescence spectrophotometer at room temperature (25 °C).

2.2. Synthesis of the compounds

2.2.1. Synthesis of $[Zn(sdi)_2(NO_3)(H_2O)]\cdot NO_3$ (1)

$Zn(NO_3)_2\cdot 6H_2O$ (75 mg, 0.25 mmol), sdi (10 mg, 0.05 mmol) and malonic acid (52 mg, 0.05 mmol) were mixed in 5 mL of methanol. The pH of the solution was adjusted to 4.0 by the addition of HNO_3 solution. The mixture was stirred for 30 min at room temperature and filtered into a glass tube. Colorless crystals of **1** were obtained in 5 days and collected by filtration, washed with water, and then dried in air. 85% yield (based on sdi). Anal. calcd (%): C, 23.87; H, 2.32; N, 23.20. Found (%): C, 23.95; H, 2.13; N, 23.11. IR (KBr, cm^{-1}): 3427 (m), 3111 (m), 3010 (m), 1652 (m), 1551 (m), 1453 (m), 1384 (s), 1325 (m), 1207 (m), 1167 (s), 1070 (m), 931 (m), 830 (m), 758 (m), 633 (s), 614 (s), 573 (m).

2.2.2. Synthesis of $[Zn(sdi)_2(H_2O)_2]\cdot 2NO_3$ (2)

$Zn(NO_3)_2\cdot 6H_2O$ (75 mg, 0.25 mmol), sdi (10 mg, 0.05 mmol) and malonic acid (52 mg, 0.05 mmol) were mixed in 5 mL of methanol. The pH of the solution was adjusted to 5.0 by the addition of HNO_3 solution. The mixture was stirred for 30 min at room temperature and filtered into a glass tube. Colorless crystals of **2** were obtained in 5 days and collected by filtration, washed with water, and then dried in air. 89% yield (based on sdi). Anal. calcd (%): C, 23.17; H, 2.57; N, 22.53. Found (%): C, 23.02; H, 2.64; N, 22.39. IR (KBr, cm^{-1}): 3447 (m), 3126 (m), 2426 (w), 1637 (m), 1552 (m), 1456 (m), 1384 (s), 1206 (m), 1165 (m), 1061 (m), 932 (m), 839 (m), 735 (m), 642 (m), 619 (m), 575 (m).

2.2.3. Synthesis of $[Zn(sdi)_{0.5}(H_2C_3O_4)H_2O]$ (3)

$Zn(NO_3)_2\cdot 6H_2O$ (75 mg, 0.25 mmol), sdi (10 mg, 0.05 mmol) and malonic acid (52 mg, 0.05 mmol) were mixed in 5 mL of methanol. The initial pH value of the solution was 6.0. The mixture was stirred for 30 min at room temperature and filtered into a glass tube. Colorless crystals of **3** were obtained in 5 days and collected by filtration, washed with water, and then dried in air. 83% yield (based on sdi). Anal. calcd (%): C, 25.32; H, 2.46; N, 9.85. Found (%): C, 25.22; H, 2.50; N, 9.99. IR (KBr, cm^{-1}): 3442 (m), 3140 (m), 3113 (w), 1654 (m), 1577 (m), 1491 (m), 1384 (m), 1299 (m), 1207 (m), 1170 (m), 1065 (m), 1040 (w), 937 (w), 855 (w), 752 (w), 720 (m), 643 (m), 618 (m), 573 (m).

2.3. X-ray crystallography

The crystallographic diffraction data for **1**–**3** were obtained on a Siemens Smart CCD single-crystal X-ray diffractometer, with a graphite monochromatic Mo-K*a* radiation ($\lambda = 0.71073$ Å) at 293 K. All structures were solved by direct methods using the SHELXS-97 program of the SHELXTL package and refined on F^2 by full-matrix least-squares techniques [40]. All non-hydrogen atoms of three crystal structures were refined with anisotropic thermal parameters. The structures were examined using the Addsym subroutine of PLANTON [41] to assure that no additional symmetry could be applied to models. The crystallographic data and structural refinement parameters of the three CPs are summarized in Table 1 and the selected bond lengths and angles are given in Table S1.

3. Result and discussion

3.1. Structure descriptions

3.1.1. Structure of $[Zn(sdi)_2(NO_3)(H_2O)]\cdot NO_3$ (1)

X-ray single crystal structural analysis indicates that compound **1** crystallizes in the monoclinic space group of $P2_1/c$. The asymmetric unit of **1** has one independent Zn(II) ion, two sdi ligands, two nitrate anions and one coordinated water molecule. Each Zn1 coordinates to three nitrogen atoms (N1A, N4 and N5) from three sdi ligands [Zn1–N1A 2.336(7) Å, Zn1–N4 2.284(7) Å, Zn1–N5 2.304(7) Å] one oxygen atom (O4) from a nitrate anion [Zn1–O4 2.488(7) Å] and one oxygen atom (O3) from a coordinated water molecule [Zn1–O3 2.360(6) Å], respectively (Fig. 1a). The central Zn(II) atom adopts a distorted hexahedron sphere geometry. The coordination angles around the Zn(II) atom are in the range of 79.8(2)-161.0(2)°, as listed in Table S1. The adjacent Zn(II) ions is bridged by two sdi ligands to form a $[Zn(sdi)_2]_2$ unit. The Zn–Zn distance is 8.9223(8) Å and the Zn–S–Zn angle is 28.733(15)°. The neighboring units are essentially non-interacting, and thus develop into a 0D structure (Fig. 1b).

3.1.2. Structure of $[Zn(sdi)_2(H_2O)_2]\cdot 2NO_3$ (2)

Based on the similar synthetic system, **2** can be obtained with the only difference of changing the pH value from 4.0 to 5.0. The X-ray crystallographic study shows that the asymmetric unit of **2** is

Table 1
Crystal data and structure refinements for **1**–**3**.

Compound	1	2	3
Empirical formula	$C_{12}H_{14}N_{10}O_{11}S_2Zn$	$C_{12}H_{16}N_{10}O_{12}S_2Zn$	$C_{12}H_{14}N_4O_{12}SZn_2$
Formula weight	603.82	621.84	569.12
T, K	293	293	293
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	C2/c	Cm
a (Å)	7.1730(2)	10.039(2)	10.016(2)
b (Å)	17.9334(7)	15.079(3)	21.010(4)
c (Å)	17.0516(5)	14.941(3)	6.8857(14)
α (deg)	90	90	90
β (deg)	91.264(3)	100.58(3)	131.69(3)
γ *(deg)*	90	90	90
V (Å^3)	2192.93(13)	2223.4(8)	1082.0(6)
Z	4	4	2
D_c (g/cm^3)	1.829	1.858	1.7467
μ (mm^{-1})	1.391	1.378	2.379
F (0 0 0)	1224.0	1264.0	573.8
R_{int}	0.0327	0.0399	0.0225
R_1[a] [$I > 2\sigma(I)$]	0.0721	0.0368	0.0332
wR_2[b] (all data)	0.2164	0.1097	0.0861
GOF on F^2	1.053	1.041	1.042

[a] $R_1 = \sum||Fo| - |Fc||/\sum|Fo|$.
[b] $wR_2 = \sum[w(Fo^2 - Fc^2)^2]/\sum[w(Fo^2)^2]^{1/2}$.