Crystal Structures, Characterizations and Fluorescence Properties of Two 3D Ca(II)/Sr(II) Coordination Polymers Based on 2-Sulfoterephthalate (Postprint)

Authors: WANG Zhi-Xiang, CAO Jia, Ren Yi-Xia ZHOU Shan-Hong, ZHANG Mei-Li, WANG Ji-Jiang

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Abstract

Two alkaline earth metal coordination polymers [M(2-Hstp)(H2O)] (M = Ca2+ (1) and Sr2+ (2), 2-H3stp = 2-sulfoterephthalate) were synthesized under hydrothermal conditions by the precursor [Mn(2-Hstp)2(4,4 -Hbpy)2] and alkaline earth metal salts. The two alkaline earth complexes are not isomorphic. Complex 1 crystallizes in the monoclinic space group P21/m, while 2 in the monoclinic space group P21/c, despite of their similar formulas. In 1, the Ca2+ ion lies in a seven-coordinated pentagon bipyramidal configuration, coordinated with five 2-Hstp2- anions and one water molecule. However, the Sr2+ ion in 2 is coordinated by nine oxygen atoms to form a single-capped square antiprism polyhedron. Both 1 and 2 exhibit - * emission of the 2-sulfoterephthalate ligand.

Full Text

Preamble

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WANG Zhi-Xiang, CAO Jia, REN Yi-Xia, ZHOU Shan-Hong, ZHANG Mei-Li, WANG Ji-Jiang
(1) College of Chemistry and Chemical Engineering, Shaanxi Key Laboratory of Chemical Reaction Engineering, Yan' an University, Yan' an, Shanxi 716000, China
(2) Yan' an University Affiliated Hospital, Yan' an, Shanxi 716000, China

ABSTRACT

Two alkaline earth metal coordination polymers [M(2-Hstp)(H O)] (M = Ca^{2} (1) and Sr^{2} (2), 2-H stp = 2-sulfoterephthalate) were synthesized under hydrothermal conditions using the precursor [Mn(2-Hstp) (4,4 -Hbpy)] and alkaline earth metal salts. Despite their similar formulas, the two complexes are not isomorphic. Complex 1 crystallizes in the monoclinic space group P2 /m, while complex 2 crystallizes in the monoclinic space group P2 /c. In complex 1, the Ca^{2} ion adopts a seven-coordinated pentagonal bipyramidal configuration, coordinated to five 2-Hstp^{2} anions and one water molecule. In contrast, the Sr^{2} ion in complex 2 is coordinated by nine oxygen atoms to form a single-capped square antiprism polyhedron. Both complexes 1 and 2 exhibit - * emission of the 2-sulfoterephthalate ligand.

Keywords: alkaline earth metal complex; 2-sulfoterephthalate; crystal structure; luminescence property

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Corresponding author. E-mail: renyx2017@163.com

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1. INTRODUCTION

Metal-organic coordination polymers have undergone rapid development in recent decades due to their fascinating structures and topologies, as well as their potential applications in catalysis, magnetism, gas storage, adsorption, luminescence, photoluminescence, and other areas [1-7]. Considerable effort has been devoted to selecting suitable ligands because they play a crucial role in the rational design of structures with specific physical and chemical properties [8]. Organic ligands containing carboxylate groups have received significant attention for their versatile binding modes as bridging linkers between inorganic moieties [9,10]. 2-Sulfoterephthalic acid possesses two carboxylate groups and one sulfonate group that can serve as bridging moieties to form multidimensional coordination networks. Moreover, the adjacent 2-position sulfonate and 1-position carboxylate groups favor stranded and helical structures, and several d-block transition metal complexes have been reported in the literature [11-13]. Based on 2-sulfoterephthalate, we have designed and synthesized numerous metal-organic frameworks, including several lanthanide and transition metal complexes [14-16].

Compared to d- and f-block metal ions, alkaline earth metals have received much less attention [17-19] due to their unpredictable coordination numbers and tendency to form solvated metal centers [20,21]. Nevertheless, some s-block coordination complexes are already commercially important [22]. For instance, Tanay et al. synthesized three new alkaline earth metal (Ca, Sr, Ba) coordination complexes with interesting structural diversity, variable chemical stability, and proton conductivity [23]; Debasis et al. reported a series of s-block coordination polymers as novel lightweight sensing materials [24]; Shunfu Du et al. synthesized two Ba(II)-based and two Ca(II)-based 3D frameworks with high thermal stability and photoluminescent properties under similar reaction conditions and stoichiometry [25]; and Dong Woo Lee et al. successfully synthesized and characterized a novel multifunctional non-centrosymmetric strontium-organic framework material with high thermal stability [26].

Synthesizing alkaline earth metal coordination polymers with attractive structures and applications remains a compelling challenge. Herein, we obtained two 3D microporous complexes [M(2-Hstp)(H O)] (M = Ca and Sr) by ion exchange from the precursor [Mn(2-Hstp) (4,4 -Hbpy)] under hydrothermal conditions, and investigated their crystal structures and luminescence properties.

2. EXPERIMENTAL

2.1 Materials and Methods

All chemicals and solvents were commercially available and used without further purification. Elemental analyses for C, H, and N were performed using a Vario EL elemental analyzer. FT-IR spectra were recorded from KBr pellets in the range of 4000–400 cm^{1} on a Nicolet Avatar 360 FT-IR spectrometer. Powder X-ray diffraction (PXRD) patterns were measured with a PANalytical X' Pert PRO MPD diffractometer (CuK , = 1.5406 Å). Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA/DSC thermogravimetric analyzer (Switzerland) at a heating rate of 10 °C · min^{1} from room temperature to 900 °C in air. Fluorescence measurements were carried out using an F4500 spectrofluorophotometer.

2.2 Synthesis

Preparation of the precursor [Mn(Hstp) (4,4 -Hbpy)]: The precursor complex was prepared according to the literature method [14].

[Ca(2-Hstp)(H O)] (1): A mixture containing the precursor [Mn(Hstp) (4,4 -Hbpy)] (0.0085 g), CaCl (0.0020 g), isopropyl alcohol (0.5 mL), and H O (0.5 mL) was sealed in a 15 mL Teflon-lined autoclave and heated under autogenous pressure to 140 °C for 96 h, then cooled to room temperature naturally. After filtration, colorless crystals were collected, washed with ethanol, and dried in air (yield 49.5% based on Ca). Anal. Calcd. for C H CaO S (302.27): C, 31.76; H, 1.98%. Found: C, 31.55; H, 2.14%. FT-IR (cm^{1}): 3426 (s), 2908 (m), 2359 (w), 1690 (m), 1560 (m), 1422 (w), 1235 (s), 1100 (m), 767 (w), 664 (w), 618 (m), 533 (w).

[Sr(2-Hstp)(H O)] (2): This compound was obtained analogously to compound 1 using SrCl ·6H O instead of CaCl (yield 51.2% based on Sr). Anal. Calcd. for C H SrO S (349.81): C, 27.43; H, 1.72%. Found: C, 27.05; H, 2.08%. FT-IR (cm ^{1}): 3422 (s), 2927 (w), 2359 (w), 1705 (m), 1578 (s), 1420 (m), 1185 (s), 1073 (m), 1024 (m), 771 (w), 655 (w), 610 (m), 526 (w), 457 (w).

2.3 Crystal Structure Determination

Single-crystal X-ray diffraction analyses of [M(2-Hstp)(H O)] (M = Ca^{2} and Sr^{2}) were performed using a Bruker SMART APEX CCD diffractometer equipped with graphite-monochromated MoK radiation (= 0.71073 Å). Raw data were integrated using the SAINT program [27]. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELX-97 program package [28,29]. An empirical absorption correction was applied using the SADABS program. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined using a riding model. Crystallographic details for both complexes are provided in Table 1 , and selected bond distances are listed in Tables 2 and 3 .

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3. RESULTS AND DISCUSSION

3.1 Crystal Structures

Single-crystal X-ray diffraction analysis reveals that both complexes 1 and 2 exhibit 3D frameworks. The coordination modes of 2-sulfoterephthalate are shown in Scheme 1. Complex 1 crystallizes in the monoclinic space group P2 /m, while complex 2 crystallizes in the monoclinic space group P2 /c. IR spectra of the two complexes show absorption peaks at 3426 cm ^{1} (for 1) and 3422 cm ^{1} (for 2) due to the presence of water molecules. Peaks at 1560 and 1422 cm ^{1} for 1, and 1578 and 1420 cm ^{1} for 2 can be assigned to the asymmetric and symmetric stretching vibrations of the carboxylate group in 2-sulfoterephthalate. The red shifts compared to the free ligand indicate that the carboxylate oxygen atoms participate in coordination, consistent with the structural analysis results.

The asymmetric unit of complex 1 consists of one calcium(II) ion, one 2-Hstp^{2} ligand, and one water molecule. As shown in Fig. 1 [Figure 1: see original paper], the calcium(II) ion adopts a seven-coordinated, slightly distorted pentagonal bipyramidal configuration, with O(1w) and O(5) as the axial atoms and the remaining oxygen atoms forming the equatorial plane (Fig. 1a). Three oxygen atoms (O(4c), O(4d), and O(5)) are from the sulfonate group, two (O(3a) and O(3b)) from the 1-site carboxylate group, one (O(2)) from the 4-site carboxylate group of the 2-Hstp ligand, and one (O(1w)) from a water molecule. In complex 1, the 2-Hstp^{2} ligand adopts the coordination mode ^{1}: ^{1}: ^{1}: ^{1}: ^{1}: ^{1}: , linking five Ca(II) ions, in which the 1-site carboxylate group is chelating, the 2-site sulfonate group is tridentate, and the 4-site protonated carboxylate group is monodentate (Scheme 1a). The Ca–O bond lengths range from 2.270(2) to 2.470(2) Å, and the O–Ca–O angles range from 74.20(6)° to 166.47(8)°, which are consistent with those found in other Ca(II) complexes [25]. The sulfonate group of the 2-Hstp^2 ligand connects three calcium ions, forming a 1D ladder-like chain along the b axis. The 1-site carboxylate group adopts a chelating coordination mode and further extends the adjacent 1D ladder-like chains into a 2D network (Fig. 2a [Figure 2: see original paper]). The 4- and 1-site carboxylate groups of the 2-Hstp^2 ligands play a crucial role in constructing the 3D framework (Fig. 2b).

In complex 2, the asymmetric unit comprises one strontium(II) ion, one 2-Hstp^2 anion, and one coordinated water molecule. Each Sr(II) is coordinated by nine oxygen atoms, eight from five 2-Hstp^2 ligands and one from a water molecule (Sr–O bond lengths 2.523(2)–2.728(2) Å). Four oxygen atoms (O(4), O(4a), O(5a), and O(5c)) belong to the 1-site carboxylate groups, three (O(1), O(2a), and O(3b)) are from the 2-site sulfonate groups, and O(7d) is from the 4-site carboxylate group. The O–Sr–O angles range from 66.62(7)° to 147.53(7)°. As illustrated in Fig. 3 Figure 3: see original paper, the Sr(II) ion adopts a distorted single-capped square antiprism geometry, in which O(3b) is the capping atom, and two groups of O(1w), O(2a), O(5c), O(7d) and O(1), O(4), O(4a), O(5) form two square planes, respectively. The 2-Hstp^2 anion adopts an ^{2}: ^{2}: ^{1}: ^{1}: ^{1}: ^{1}: coordination mode (Scheme 1b), in which the 1-site carboxylate group links two adjacent Sr(II) ions to form one-dimensional chains along the b axis. These adjacent chains are further joined and extended into a 2D network via the 2-site sulfonate groups of the 2-Hstp^2 ligand in the ab plane (Fig. 4a [Figure 4: see original paper]). These planes are assembled into a 3D architecture by the 4-site carboxylate groups of the ligands (Fig. 4b).

3.2 TGA Analysis

Thermogravimetric analyses (TGA) of complexes 1 and 2 were carried out in the temperature range of 25–900 °C in air with a heating rate of 10 °C · min ^{1} (Fig. 5 [Figure 5: see original paper]). For complex 1, the first weight loss of 5.90% from 305 to 432 °C can be attributed to the release of one water molecule (calcd. 5.95%). A subsequent major weight loss from 432 to 812 °C corresponds to framework decomposition, with a final residue weight of 40.12%, which might be CaO (calcd. 18.55% based on CaO) and other residues. The TG curve for complex 2 shows two steps: the first weight loss of 5.75% (from 294 to 393 °C) corresponds to the loss of one water molecule (calcd. 5.15%), followed by weight loss from 394 to 760 °C indicating collapse of the entire skeleton of 2, leaving a residue of 32.80% (calcd. 29.62% based on SrO).

3.3 Powder X-ray Diffraction

As shown in Fig. 6 [Figure 6: see original paper], the peak positions of the simulated and experimental powder X-ray diffraction (PXRD) patterns are in good agreement, indicating high purity of these coordination compounds. The relative intensity deviation between the theoretically simulated and experimental patterns may be due to preferred orientation of the crystalline powder samples.

3.4 Fluorescent Properties

The fluorescence spectra of complexes 1 and 2 were measured in the solid state at room temperature (Fig. 7 [Figure 7: see original paper]); the free ligand was previously studied [14]. Complex 1 shows emission peaks at 405 nm (strong) and 540 nm (weak) upon excitation at 328 nm, reflecting emission from the 2-Hstp^2 ligand. Complex 2 exhibits a similar spectral profile, with maximum emissions at 384 nm and 505 nm upon excitation at 340 nm. For main group element complexes, the emission associated with electronic transitions is predominantly located in the organic portion of the molecule [16].

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4. CONCLUSION

In summary, a precursor approach enabled us to obtain two new alkaline earth metal (Ca and Sr) coordination polymers based on the 2-sulfoterephthalate ligand. Although they possess similar chemical formulas, different metal ions lead to distinct structures. The Ca^2 ion in complex 1 is seven-coordinated, while the Sr^2 ion in complex 2 resides in a nine-coordinated environment. The 2-sulfoterephthalate ligand adopts different coordination modes— ^{1}: ^{1}: ^{1}: ^{1}: ^{1}: ^{1}: in 1 and ^{2}: ^{2}: ^{1}: ^{1}: ^{1}: ^{1}: in 2—when constructing the 3D frameworks. Luminescence analysis reveals that complexes 1 and 2 exhibit fluorescence in the solid state at room temperature and may serve as potential fluorescent materials.

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