Synthesis, Crystal Structure, Theoretical Calculations, and Photoluminescent Property of a Mn(II) Complex Assembled by 5-Amino-isophthalic Acid and Phen Ligands Postprint

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Abstract

A coordination polymer [Mn2(ctpt)2(aic)2]n (1, ctpt = 2-(4-chloro-phenyl)-1H-1,3,7,8- tetraaza-cyclopenta[l]phenanthrene, H2aic = 5-amino-isophthalic acid) was hydrothermally designed and synthesized. The complex was characterized by elemental analysis, IR spectroscopy, single-crystal X-ray diffraction, and thermogravimetric analysis (TGA). Each Mn(II) atom is linked by the aic ligands with neighbor Mn(II) atoms, forming an infinite one-dimensional (1D) double-chain structure. Complex 1 crystallizes in monoclinic, space group C2/c, with a = 18.23(1), b = 17.27(1), c = 16.69(1) Å, V = 4814.0(7) Å3, C27H16ClMnN5O4, Mr = 564.84, Dc = 1.559 g/cm3, (MoK) = 0.706 mm-1, F(000) = 2296, Z = 8, the final R = 0.0487 and wR = 0.1269 (I > 2 (I)). The 1D chain structure of complex 1 is stable below 458 ℃. In addition, to elucidate the essential electronic characters of this complex, theoretical calculation analysis of 1 was performed by the PBE0/LANL2DZ method in Gaussian 03 Program.

Full Text

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ABSTRACT

A coordination polymer [Mn (ctpt) (aic)] (1, ctpt = 2-(4-chloro-phenyl)-1H-1,3,7,8-tetraaza-cyclopenta[l]phenanthrene, H aic = 5-amino-isophthalic acid) was hydrothermally designed and synthesized. The complex was characterized

by elemental analysis, IR spectroscopy, single-crystal X-ray diffraction, and thermogravimetric analysis (TGA). Each Mn(II) atom is linked by the aic ligands with neighboring Mn(II) atoms, forming an infinite one-dimensional (1D) double-chain structure. Complex 1 crystallizes in the monoclinic space group C2/c, with a = 18.23(1), b = 17.27(1), c = 16.69(1) Å, V = 4814.0(7) Å^3, C H ClMnN O , M = 564.84, Dc = 1.559 g/cm^3, (MoK) = 0.706 mm ^{1}, F(000) = 2296, Z = 8, the final R = 0.0487 and wR = 0.1269 (I > 2 (I)). The 1D chain structure of complex 1 is stable below 458 °C. In addition, to elucidate the essential electronic characters of this complex, theoretical calculation analysis of 1 was performed by the PBE0/LANL2DZ method in Gaussian 03 Program.

Keywords: Mn(II) complex; crystal structure; fluorescence; 5-aminoisophthalic acid; theoretical calculation

1 INTRODUCTION

Coordination polymers with bridged transition metals have received intense interest and attention for their fascinating architectures and potential applications as materials in optical, electronic, and magnetic fields, as well as in gas storage, catalysis, and so on [1-5]. Consequently, numerous new complexes can be specially designed by the careful selection of metal centers with preferred coordination geometries [6-9]. It has been observed that organic ligands play crucial roles in the preparation of interesting coordination networks, particularly regarding their flexibility, donating type, and geometry [10-11]. Among various organic ligands, aromatic carboxylates have been extensively used because of their extension ability in both covalent bonding and supramolecular interactions (H-bonding and aromatic stacking). For example, 1,3-benzenedicarboxylate, 1,4-benzenedicarboxylate, 1,2-benzenedicarboxylate, 1,3,5-benzenetricarboxylate, and 1,2,3,5-benzenetetracarboxylate are well utilized in the construction of MOFs due to their structural rigidity, chemical stability, and appropriate connectivity. Meanwhile, polycyclic aromatic bidentate ligands like 2,2-bipyridine and 1,10-phenanthroline are frequently used in combination with polycarboxylates, leading to many novel architectures. Building on previous work, here we synthesized the ligand 2-(4-chloro-phenyl)-1H-1,3,7,8-tetraaza-cyclopenta[l]phenanthrene (ctpt), based on which, together with aic, a novel 1D complex [Mn (ctpt) (aic)] (1) has been synthesized. Furthermore, the thermal stability and luminescent properties of 1 have also been investigated.

2 EXPERIMENTAL

2.1 General Materials and Methods

With the exception of ligand ctpt, all other chemicals were commercially available and used as purchased. IR spectra were recorded on a Perkin-Elmer Spectrum One FTIR spectrometer. Elemental analyses of C, H, and N were performed on a PE-2400 elemental analyzer. Thermogravimetric analysis (TG) was performed using a Perkin-Elmer TG-7 analyzer in nitrogen atmosphere.

Crystal structure determination was carried out on a Bruker SMART APEX II CCD X-ray diffractometer. The emission spectra were recorded on an FLSP 920 Edinburgh fluorescence spectrometer.

2.2 Synthesis of Complex 1

Complex 1 was prepared as follows: ctpt (0.099 g, 0.3 mmol), MnSO ·H O (0.051 g, 0.3 mmol), and aic (1.000 g, 0.6 mmol) were dissolved in distilled water (15 mL), and NaOH was added until the pH value of the system was adjusted to about 8.0. The resulting solution was stirred for about 0.5 h at room temperature, sealed in a 30-mL Teflon-lined stainless-steel autoclave, and heated at 170 °C for three days, then cooled to room temperature at a rate of 5 °C/h. Yellow crystals of 1 were collected in 78% yield based on Mn.

C H ClMnN O : calcd. C, 57.36; H, 2.83; N, 12.39%. Found: C, 57.38; H, 2.81; N, 12.51%. IR (KBr, cm ¹): 3435(s), 1620(s), 1556(vs), 1344(vs), 1205(s), 1074(s), 779(s), 714(s).

2.3 X-ray Structure Determination

A selected yellow crystal with approximate dimensions of 0.45 mm × 0.38 mm × 0.33 mm was mounted on a glass fiber. The diffraction data were collected on a Bruker SMART APEX II CCD diffractometer equipped with graphite-monochromated MoK radiation (= 0.71073 Å) at 293(2) K in the range of 1.70 25.03°. A total of 13736 reflections were collected, of which 4244 were independent with R_int = 0.0657. The data were corrected for Lp factors. The crystal structure was solved by direct methods with SHELXS-97 [12] and refined with SHELXL-97 [13] by full-matrix least-squares techniques on F^2. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms isotropically. All hydrogen atoms attached to carbon were generated geometrically.

3 RESULTS AND DISCUSSION

3.1 Description of the Structure

Single-crystal X-ray diffraction analysis reveals that the title complex crystallizes in the C2/c space group. Selected bond distances and bond angles are presented in Table 1 . The analysis shows that complex 1 is a 1D double-chain structure. As shown in Fig. 1 [Figure 1: see original paper], the coordination environment of the Mn atom can be described as a distorted tetragonal pyramid geometry. Each Mn(II) atom in 1 is coordinated by three carboxylate oxygen atoms from three distinct aic ligands and two nitrogen donor atoms from one chelating ctpt ligand. The Mn–O bond distances in 1 range from 2.041(3) to 2.102(3) Å, while the Mn–N bond distances fall in the 2.247(4)–2.278(4) Å range. The O(N)–Mn–N(O) angles range from 88.42(1) to 156.80(1)°. The Mn–O/N bond lengths are all consistent with corresponding values found in the literature [14-18].

Notably, the aic ligand coordinates to three Mn ions through three carboxylic oxygen atoms in a mono-bridging fashion, which gives rise to a 1D double-chain structure (Fig. 2 [Figure 2: see original paper]). It should be mentioned that in the unit of 1, two types of rings are formed: an 8-membered ring (the O(3)-Mn(1)-O(4) angle is 97.727°, and the Mn · · · Mn distance is 3.849 Å) and a 16-membered ring (the O(1)-Mn(1)-O(3) angle is 91.756°, and the Mn · · · Mn distance is 7.953 Å).

Strong N-H · · · O hydrogen bonding interactions are observed in complex 1, which play an important role in stabilizing the network structure and forming a higher-dimensional architecture. As illustrated in Fig. 3 [Figure 3: see original paper], the existence of N-H · · · O hydrogen bonds (H(3A) · · · O(4) = 1.86 Å, N(3) · · · O(4) = 2.702 Å, and N(3)-H(3A) · · · O(4) = 165°) leads to the construction of a 3D supramolecular network.

3.2 Thermal Analysis

To characterize the thermal stability of complex 1, TG curves were obtained from crystalline samples in flowing nitrogen atmosphere at a heating rate of 10 °C/min (Fig. 4 [Figure 4: see original paper]). As expected, complex 1 exhibits two steps of weight loss. The first step corresponds to the removal of aic ligand (30.10% observed, 31.75% calculated) from 458 to 479 °C, and the second step is due to the departure of ctpt ligand (58.90% observed, 58.50% calculated) in the temperature range of 479-804 °C. The final product is presumably MnO. The thermal analysis results indicate that the one-dimensional chain structure of anhydrous complex 1 is stable below 458 °C.

3.3 Photoluminescent Properties

Luminescence properties are very important in photochemistry and photophysics. Therefore, in this study, we investigated the luminescence of 1, as well as that of the free ligands (Fig. 5 [Figure 5: see original paper]). Complex 1 shows one strong emission band at 514 nm (excitation at 320 nm). To further analyze the nature of these emission bands, the emission properties of aic and ctpt ligands were also investigated under the same experimental conditions. The free ligand ctpt exhibits an emission band at 495 nm, while aic shows an emission band at 438 nm (excitation at 320 nm). The emission of complex 1 is red-shifted by 19 nm relative to the ctpt ligand and by 76 nm relative to aic. The emission bands for the free ligands are probably attributable to *-n transitions. Complex 1 may be a good candidate for potential photoluminescence materials because it is highly thermally stable and insoluble in water and common organic solvents.

3.4 Theoretical Calculations

To elucidate the essential electronic characteristics of this complex, theoretical calculations were performed using density functional theory (DFT) [19] with the

Gaussian 09 program [20], employing the LANL2DZ basis set for the Mn atom and the 6-31g(d) basis set for all other atoms. The geometric parameters from X-ray diffraction analysis were used as the starting point, with no symmetry constraints imposed on the complex. The density diagrams of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the Mn complex in the ground state were calculated and are shown in Fig. 6 [Figure 6: see original paper].

For complex 1, both HOMO and LUMO reside primarily on the aniline ligands. The HOMO distribution includes only 0.5% contribution from the d orbital of each Mn atom, whereas the d orbitals of Mn atoms make virtually no contribution to the LUMO. The attached phenanthroline derivative ligands with electron-rich properties facilitate electron transport. Therefore, the HOMO is distributed mainly over one phenanthroline derivative ligand, while the LUMO is localized mainly on another phenanthroline derivative ligand. Each phenanthroline derivative ligand contributes up to 98% to either the HOMO or LUMO.

4 CONCLUSION

In conclusion, a new complex has been hydrothermally synthesized and structurally characterized by elemental analysis, IR spectroscopy, TG, and single-crystal X-ray diffraction. Complex 1 exhibits high thermal stability and is worthy of further study as a candidate for potential photoluminescence materials.

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Table 1. Selected Bond Lengths (Å) and Bond Angles (°) for 1

Bond/Angle	Value
Mn(1)-O(1)	2.102(3)
Mn(1)-O(3)	2.041(3)
Mn(1)-O(2)ii	2.050(3)
Mn(1)-N(1)	2.278(4)
Mn(1)-N(2)	2.247(4)
O(3)-Mn(1)-O(2)ii	111.70(1)
O(3)-Mn(1)-O(1)	91.77(1)
O(3)-Mn(1)-N(2)	107.94(1)
O(2)ii-Mn(1)-N(2)	139.53(1)
O(1)-Mn(1)-N(2)	88.81(1)
O(3)-Mn(1)-N(1)	106.76(1)
O(2)ii-Mn(1)-N(1)	88.42(1)
O(1)-Mn(1)-N(1)	156.80(1)

Symmetry code: ii: -x, y, -z+3/2

Fig. 1. Coordination environment of the Mn ions with H atoms and ctpt omitted for clarity (i: -x, -y, 1-z; ii: -x, y, -z+3/2)

Fig. 2. One-dimensional chain structure of complex 1 (Hydrogen atoms were omitted)

Fig. 3. 3D framework structure of complex 1 in the ac plane (Hydrogen atoms were omitted)

Fig. 4. TG plot of complex 1

Fig. 5. Luminescent spectrum of the ligand and complex 1 in solid state at room temperature

Fig. 6. Frontier molecular orbital of complex 1

Note: Figure translations are in progress. See original paper for figures.