Research paper

Investigation on luminescence and gas adsorption properties of cadmium complex

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Abstract

A bifunctional cadmium complex with luminescence and gas storage, namely [Cd₃(pcppta)₂·4H₂O]ₙ·2H₂O has been synthesized by hydrothermal reaction based on polyacid ligand, 2-(4-carboxyphenoxy)terephthalic acid (H₃pcpta). The fluorescent test results show that the complex has excellent fluorescence properties, and can emit bright blue light under the irradiation of the ultraviolet lamp at 365 nm. The adsorption test results show that the complex has good adsorption effect on carbon dioxide.

1. Introduction

The investigation on the structure and properties of metal organic complex is a hot research topic in the past twenty years [1–5]. Many meaningful results have been developed with the researcher’s efforts in luminescence, electrochemical, magnetism, gas storage, catalysis and so on [6–10]. However, most of those studies on the properties of the complexes are only limited to the single function. The current research frontier of chemistry is to realize the multifunctional material [11–12]. Metal cadmium has good fluorescence property, and a series of cadmium complexes with good optical properties are reported by researchers [13–14]. Carboxylic acid ligands have a good coordination effect, and can form multi-functional complexes with many kinds of metals [15–16]. We report herein our success in building of bifunctional cadmium complex 1 (CCDC: 1470378) with luminescence and gas storage based on a polyacid ligand (H₃pcpta).

2. Experimental

2.1. Materials and methods

All the starting materials for synthesis were of commercially available and used as received.

Elemental analyses (C and H) were performed using a Perkin-Elmer 2400 element analyzer. IR spectra were recorded in the range 400–4000 cm⁻¹ using a VECTOR-22 spectrometer using KBr discs. Fluorescence spectra were recorded on a FLS980 spectrophotometer. N₂ and CO₂ adsorption measurements (up to 1 bar) were performed on an Autosorb-3.0 (Quantachrome) volumetric analyzer.

2.2. Synthesis of complex [Cd₃(pcppta)₂·4H₂O]ₙ·2H₂O

A mixture of H₃pcpta (0.25 mmol), Cd(NO₃)₂·4H₂O (1.0 mmol), NaOH (0.75 mmol) and distilled H₂O (10 mL) was sealed in a 25 mL Teflon-lined autoclave and heated to 120 °C at 10.8 °C h⁻¹. After maintained for 72 h, the reaction vessel was cooled to 10 °C at a rate of 5 °C h⁻¹. Colorless crystals were collected with ca. 45% yield based on H₃pcpta. Elemental Anal. Calc. for Cd₃C₃₀H₂₆O₂₀: C, 34.52; H, 2.51. Found: C, 34.29; H, 2.16%. FT-IR (KBr pellets, cm⁻¹): 3400, 1604, 1535, 1394, 1304, 1240, 1166, 1086, 956, 866, 815, 772, 742, 696, 633, 538.

2.3. X-ray crystallography

Single-crystal X-ray diffraction measurements for complex 1 was collected on a Bruker SMART APEX-II CCD diffractometer equipped with a graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 296(2) K using an ω-θ scan mode. Absorption correction was applied by using the SADABS [17]. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F₂ with SHELX-97 package [18]. The detailed crystallographic data and structure refinement parameters of complex are summarized in Table S1.
2.4. Gas adsorption measurement

Before gas adsorption measurements, the sample was collected by decanting and dried in air. The dry sample was loaded in a sample tube and further activated under high vacuum at an optimized temperature of 150 °C for 8 h. Finally, 79 mg of degassed sample was used for gas sorption measurements. The gas adsorption isotherm measurements were preceded at 77 K for N\textsubscript{2} in a liquid nitrogen bath, at 273 K for CO\textsubscript{2} in an ice-water bath.

3. Results and discussion

3.1. Structural description

The result of X-ray diffraction analysis revealed that complex 1 with a formula of Cd\textsubscript{3}C\textsubscript{30}H\textsubscript{26}O\textsubscript{20} crystallizes in monoclinic system, space group \textit{C2/m}. The asymmetric unit consists of three Cd atom, one pcpta ligand and four crystal water (O6, O7, O8, and O9) in the lattice. As depicted in Fig. 1(a), Cd atoms have two coordination modes: Cd1 atom is surrounded by eight O atoms (O1, O1A, O1B, O1C, O3F, O3G, O3H and O3I) from pcpta ligand, and the coordination geometry can be described as a distorted dodecahedron. Cd2 atom is surrounded by four O atoms (O4, O5, O1D, and O1E) from pcpta ligand and two atoms (O6 and O7) from water, and the coordination geometry can be described as a distorted octahedron. The O-Cd-O angles between adjacent Cd-O bond angles are in the range of 52.18(15)–102.02(12)°. The Cd–O bond lengths are in the range of 2.240(6)–2.471(3) Å, bond lengths are within the normal range.

All carboxylic acids of ligand are distributed on the benzene ring, two carboxyl groups on one benzene ring in the para position allocation, so as to enlarge the distance between the horizontal coordination groups. The two benzene rings are connected by oxygen bridge, this increase in vertical distance between coordination groups. So, after the formation of complex, the adjacent coordination atoms have a certain distance in both longitudinal and transverse directions. Finally, a three-dimensional network structure is formed in the direction of b axis (Fig. 1(b)). Furthermore, in the space filling graph of the complex it can be seen that the complex structure contains larger pores along the b axis (Fig. 1(c)), and the total accessible volume of the fully desolvated complex 1 is ca. 32.2% (1872.5 Å\textsuperscript{3} per unit cell vol), calculated using the PLATON program [19], which provides the possibility of adsorbing the gas. In addition, pcpta ligand acts as three-connection nodes, connecting three Cd(II) ion; Cd1(II) ion acts as four-connection nodes connecting four pcpta ligand; Cd2(II) ion acts as five-connection nodes connecting three pcpta ligand and two water. The TOPOS analysis of this network can be described as a (3, 4, 5)-connected with stoichiometry \{4\textsuperscript{3}·6\textsuperscript{2}\·4\textsuperscript{3}·8\textsuperscript{4}\·4\textsuperscript{3}·6\textsuperscript{8}\·5\textsuperscript{2}\ topology (Fig. 1(d)).

3.2. Thermogravimetric and PXRD analysis

Before fluorescence test and gas adsorption properties analysis, powder diffraction experiments and thermogravimetric experiments of the complex was carried out. Thermogravimetric analysis of complex revealed three steps of decomposition with the 83.17 wt% total weight loss during 68–750 °C as shown in Fig. 2(a).
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