



Research paper

Syntheses, structures, photoluminescence and semiconductor properties of two novel mercury-lanthanide complexes with a three-dimensional open framework

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ABSTRACT

Two novel mercury-lanthanide complexes $[\text{Hg}_3\text{Cl}_6(u\text{-IA})_3\text{Ln}(\text{H}_2\text{O})_2]_n$ (IA = isonicotinic acid anion; Ln = Pr (1) and Sm (2)) have been synthesized under hydrothermal conditions and structurally determined by single crystal X-ray diffraction. Complexes 1 and 2 are isostructure and feature a three-dimensional (3-D) open framework with two types of one-dimensional (1-D) chains. Based on the condensed 3-D open framework, there is a large void space being 1010.3 \AA^3 and 1018.1 \AA^3 which occupy 27.2% and 27.4% of the unit-cell volume for complexes 1 and 2, respectively. Solid-state UV/Vis diffuse reflectance spectroscopy reveals that there is a wide optical band gap of 3.51 eV and 3.54 eV for complexes 1 and 2, respectively. Photoluminescence measurements using solid-state samples discover that both complexes display red light emission. The emission bands can be ascribed to the characteristic emission of the 4f electron intrashell transitions of the Ln³⁺ ions, i.e. $^1D_2 \rightarrow ^3H_4$ and $^3P_0 \rightarrow ^3F_3$ transitions for complex 1, as well as $^4G_{5/2} \rightarrow ^6H_{5/2}$, $^4G_{5/2} \rightarrow ^6H_{7/2}$ and $^4G_{5/2} \rightarrow ^6H_{9/2}$ transitions for complex 2.

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1. Introduction

In recent years, lanthanide complexes have attracted more and more interest for their useful properties, which endow them potential applications in the fields of electrochemical displays, light-emitting diodes (LEDs), magnetic materials, luminescent probes, and so on [1,2]. People have thus far fulfilled a lot of investigations on the properties of lanthanide complexes. Amongst these properties, photoluminescence is especially attractive for us. The interesting photoluminescence properties of lanthanide complexes mainly originate from the rich 4f-orbital electron configurations of the lanthanide elements [3,4]. To our knowledge, lanthanide complexes (except for La and Lu) can usually show strong photoluminescence emissions as long as the 4f electron transitions of the lanthanide ions can efficiently happen. Up to date many researchers devote themselves to the design, preparation and characterization of novel lanthanide photoluminescence materials.

However, the semiconductor properties of lanthanide complexes have been rarely investigated in comparison with the large numbers of studies on the photoluminescence properties. Semiconductor materials are actually attractive because they are potential photocatalysts for treating with the crisis of environmental pollution and energy scarcity in the future [5,6]. Amongst semiconductor materials, organic semiconductor is less researched but it has attracted increasing attention [7–9]. Several lanthanide organic semiconductor complexes have thus far been documented, such as, $[\text{Pc}(\text{OPh})_8]\text{Eu}[\text{Pc}(\text{OPh})_8]\text{Eu}[\text{TP}(\text{C}\equiv\text{CCOOH})\text{PP}]$ [10], $(\text{Pc})\text{Eu}\{\text{Pc}[(\text{OC}_2\text{H}_4)_3\text{OCH}_3]_8\}\text{Eu}\{\text{Pc}[(\text{OC}_2\text{H}_4)_3\text{OCH}_3]_8\}$ [11], $\text{Eu}_2[\text{Pc}(\beta\text{-OBu})_8]_2(\text{TCIPP})$ [12] and $\text{Eu}_2[\text{Pc}(\text{OCH}_2\text{CF}_3)_4]_3$ [13]. However, these are europium organic semiconductors. As a result other lanthanide organic semiconductor complexes are still needed to be explored.

In order to synthesize lanthanide complexes, it is crucial to select appropriate organic ligands, because organic ligands can decide the crystal structures and functions of the lanthanide complexes. A great deal of organic ligands such as aromatic sulfonic acids, aromatic carboxylic acids and heterocyclic derivatives, have been used to prepare lanthanide complexes. Isonicotinic acid is a useful organic ligand to synthesize lanthanide complexes because it possesses three coordinating sites, i.e. one nitrogen atom at one end and two oxygen atoms of its carboxylic group at the

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opposite end. These coordinating atoms enable isonicotinic acid to bind to several metal ions and achieve extended structures.

Our recent research interest is mainly focused on the lanthanide complexes which possess attractive structures and properties like photoluminescence and semiconductor properties. We report herein the preparation, crystal structures and properties of two novel mercury-lanthanide complexes $[\text{Hg}_3\text{Cl}_6(\text{u-IA})_3\text{Ln}(\text{H}_2\text{O})_2]_n$ (IA = isonicotinic acid anion; Ln = Pr (**1**) and Sm (**2**)). Both complexes were synthesized through hydrothermal reactions and feature a condensed 3-D open framework.

2. Experimental

2.1. Materials and instrumentation

All chemicals and reactants were obtained commercially and directly used without further purification. Elemental microanalysis of carbon, hydrogen and nitrogen was conducted on an Elementar Vario EL elemental analyzer. The photoluminescence study with solid state samples was performed on a FX-97XP fluorescence spectroscopy instrument under room temperature. The solid state UV/Vis diffuse reflectance spectroscopy was carried out at room temperature on a computer-controlled TU-1901 UV/Vis spectrometer equipped with an integrating sphere in the wavelength range of 190–900 nm. BaSO_4 powder was used as a reference (100% reflectance), on which the finely ground powder sample was coated.

2.2. Synthesis of $[\text{Hg}_3\text{Cl}_6(\text{u-IA})_3\text{Pr}(\text{H}_2\text{O})_2]_n$ (**1**)

This compound was prepared by mixing $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (1 mmol, 436 mg), HgCl_2 (3 mmol, 813 mg), isonicotinic acid (3 mmol, 369 mg) and 10 mL distilled water in a 25 mL Teflon-lined stainless steel autoclave. The mixture was heated to 433 K and kept at this temperature for 10 days. When the mixture was cooled slowly down to room temperature, green crystals suitable for X-ray analysis were washed and collected. The yield was 40% (based on praseodymium). $\text{C}_{18}\text{H}_{16}\text{Cl}_6\text{Hg}_3\text{N}_3\text{O}_8\text{Pr}$: calc. C, 15.91; H, 1.18; N, 3.09; Found C, 16.05; H, 1.26; N, 3.17.

2.3. Synthesis of $[\text{Hg}_3\text{Cl}_6(\text{u-IA})_3\text{Sm}(\text{H}_2\text{O})_2]_n$ (**2**)

This compound was prepared by using the same procedure but using $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (1 mmol, 446 mg) instead of $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. The yield was 43% (based on samarium). $\text{C}_{18}\text{H}_{16}\text{Cl}_6\text{Hg}_3\text{N}_3\text{O}_8\text{Sm}$: calc. C, 15.80; H, 1.17; N, 3.07; Found C, 15.96; H, 1.24; N, 3.13.

2.4. Crystal structure determination

The single crystal X-ray diffraction data of the title complexes were collected on a SuperNova CCD X-ray diffractometer with graphite monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) by means of a ω scan method. The data reduction and empirical absorption corrections were performed with CrystalClear software [14]. The structures for both complexes were solved by the direct methods with the Siemens SHELXTL™ Version 5 package of crystallographic software [15]. All non-hydrogen atoms were located on the difference Fourier maps of the atomic positions, but the hydrogen atoms were theoretically added and allowed to ride on their parent atoms. Non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the structure factor calculations with assigned isotropic thermal parameters. The structures were refined by using a full-matrix least-squares refinement on F^2 . A summary of the crystallographic data and structure analysis is

Table 1
Crystal data and structure refinement details for complexes **1** and **2**.

Complex	1	2
Formula	$\text{C}_{18}\text{H}_{16}\text{Cl}_6\text{Hg}_3\text{N}_3\text{O}_8\text{Pr}$	$\text{C}_{18}\text{H}_{16}\text{Cl}_6\text{Hg}_3\text{N}_3\text{O}_8\text{Sm}$
Fw	1357.72	1367.16
Color	green	colorless
Crystal size/mm ³	0.10 0.05 0.04	0.15 0.08 0.06
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	11.7463(5)	11.8579(6)
b (Å)	9.5829(5)	9.5430(5)
c (Å)	33.1409(11)	32.8916(13)
β (°)	94.677(4)	94.316(4)
V (Å ³)	3718.0(3)	3711.5(3)
Z	4	4
$2\theta_{\text{max}}$ (°)	50	50
Reflections collected	11,344	17,945
Independent, observed reflections (R_{int})	3743, 3029 (0.1124)	3536, 3174 (0.0913)
d_{calc} . (g/cm ³)	2.426	2.447
μ (mm ⁻¹)	14.105	14.399
T (K)	293(2)	293(2)
F(0 0 0)	2440	2452
R1, wR2	0.0792, 0.1675	0.0619, 0.1380
S	1.017	1.002
Largest and Mean Δ/σ	0.001, 0	0.001, 0
$\Delta\rho$ (max, min) (e/Å ³)	1.292, -1.123	1.251, -1.091

shown in Table 1, while selected bond lengths and bond angles are presented in Table 2.

3. Results and discussion

Single crystal X-ray diffraction analysis reveals that complexes **1** and **2** are isostructure. Therefore, complex **1** is selected as an example to describe the crystal structures for both complexes. Complex **1** is characterized by a 3-D motif. The crystal structure of complex **1** is shown in Fig. 1. Complex **1** is comprised of neutral $[\text{Hg}_3\text{Cl}_6(\text{u-IA})_3\text{Pr}(\text{H}_2\text{O})_2]_n$ molecules and crystallized in the $P2_1/n$ space group of the monoclinic system. The Pr^{3+} ion is coordinated by eight oxygen atoms, of which two are from two coordination water molecules and six come from six isonicotinic acid ligands, to form a slightly distorted square anti-prismatic geometry. The top plane of the square anti-prism is defined by O1W, O3(-x + 3, -y + 2, -z), O2W and O4, while the bottom plane is defined by O6(x + 1/2, -y + 5/2, z + 1/2), O1(-x + 7/2, y + 1/2, -z - 1/2), O5(-x + 5/2, y + 1/2, -z - 1/2) and O2(x - 1/2, -y + 5/2, z + 1/2). The bond distances of Pr-O_{IA} are in the range of 2.292(8) Å–2.714(8) Å, while those of Pr-O_{water} are 2.257(9) Å and 2.740(10) Å. The bond distances of Pr-O are normal and comparable with those existing in the references [16–18]. The bond angles of O-Pr-O are in a broad range of 64.4(3)°–155.1(3)°. The neighboring Pr^{3+} ions are interlinked by four or two μ_2 -IA groups to yield an infinite -Pr-(IA)₄-Pr-(IA)₂-Pr-(IA)₄-Pr- chain with the Pr···Pr distances being of 4.3989(2) Å and 5.2155(3) Å, as shown in Fig. 2a.

There are three crystallographically independent mercury ions in different coordination environment. Hg1 is coordinated by one nitrogen atom, one terminal chlorine atom and two μ_2 -bridging chlorine atoms to yield a distorted tetrahedron. Differently, Hg2 is surrounded by two nitrogen atoms and three μ_2 -bridging chlorine atoms to form a square pyramid with the bottom plane defined by N2, N3, Cl1, Cl4 and the apex occupied by Cl3. Hg3 is bound by two terminal chlorine atoms and two μ_2 -bridging chlorine atoms to yield a distorted tetrahedron. The bond distances of Hg-N are in the range of 2.069(7) Å–2.248(10) Å, which are normal and comparable with those found in the references [19–21]. The bond distances of Hg-Cl are in the range of 2.243(3) Å–3.084(3) Å, which are also normal and comparable with those

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