J. Chem. Thermodynamics 123 (2018) 99–106

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Lanthanide complexes with 2-bromo-5-methoxybenzoic acid and 5,5′-dimethyl-2,2′-bipyridine: Crystal structures, thermodynamic properties and luminescence behaviors

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ARTICLE INFO

Article history:
Received 25 January 2018
Received in revised form 26 March 2018
Accepted 2 April 2018
Available online 3 April 2018

Keywords:
Lanthanide complexes
Crystal structure
Luminescence spectrum
Thermodynamic properties
Heat capacity
2-Bromo-5-methoxybenzoic acid

ABSTRACT

Two ternary lanthanide complexes [Ln(2-Br-5-MOBA)$_3$(5,5′-DM-2,2′-DIPY)]$_2$ (Ln = Sm(1), Eu(2); 2-Br-5-MOBA = 2-bromo-5-methoxybenzoate; 5,5′-DM-2,2′-DIPY = 5,5′-dimethyl-2,2′-bipyridine) with 2-bromo-5-methoxybenzoic acid and 5,5′-dimethyl-2,2′-bipyridine have been synthesized and characterized. The Single-crystal X-ray diffraction date show that complexes **1** and **2** are isostructural in the triclinic system, space group P$\bar{1}$. Infrared spectra (IR) and X-ray powder diffraction (PXRD) further confirm that complexes **1** and **2** are isostructural. The basic structural unit forms a 1D chain through the weak C—H···Br hydrogen bond interaction along the b-axis, and forms a 2D sheet through the π–π stacking interactions along the a-axis. The 2D sheets are further interconnected by the C—H···O hydrogen bond interaction to assembled into a 3D supramolecular network along the c-axis. In addition, the simultaneous thermal analysis (TG, DTG and DSC) of the complexes and the FTIR spectra of the escaped gas were measured. The heat capacities of the complexes were determined by DSC in the temperature region of 258.15–393.15 K. Furthermore, the luminescence spectrum of the complexes **1** and **2** and luminescence lifetime of complex **2** were also measured.

1. Introduction

Due to the special electronic structure, lanthanide ions are easy to coordinate with organic ligands containing oxygen and nitrogen atoms [1–3]. The aromatic carboxylic acid ligands coordinate with lanthanide ions in various coordinated modes, such as chelating bidentate, bridging bidentate, bridging tridentate and monodentate, so the structures of the complexes are diversified [4]. The lanthanide complexes have various potential applications, such as luminescent materials [5,6], medicine [7–9], catalysts [10,11], magnetic materials [12,13] and thermochemical sciences [14]. The luminescence of lanthanide complex is generated by 4f orbital transition of central lanthanide ions, but the f-f transition of lanthanide ions is parity-banned [15–17]. The coordination of organic ligands with lanthanide ions can increase luminescence intensity of lanthanide ions because organic ligands can absorb and transfer energy to lanthanide ions [18–21]. Therefore, the selection of appropriate ligands is very important. In addition, the thermodynamic properties of the complexes are also studied, because they can describe the thermal processes in details. The determination of the molar heat capacities can better calculate some other thermodynamic properties such as enthalpy, entropy, and gibbs free energy.

In this paper, two complexes [Ln(2-Br-5-MOBA)$_3$(5,5′-DM-2,2′-DIPY)]$_2$ (Ln = Sm(1), Eu(2); 2-Br-5-MOBA = 2-bromo-5-methoxybenzoate; 5,5′-DM-2,2′-DIPY = 5,5′-dimethyl-2,2′-bipyridine) were synthesized and characterized by elemental analysis, IR, single crystal X-ray diffraction and powder X-ray diffraction. TG-DTG-DSC/FTIR technique was used to determine the thermal decomposition of the complexes. DSC technique was used to determine the heat capacity of the complexes, and the polynomial equation was fitted by the least square method. According to the thermodynamic equations and the polynomial equations, the smoothed heat capacities and the thermodynamic function value at different temperatures were calculated. At the same time, the

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https://doi.org/10.1016/j.jct.2018.04.002
0021-9614/

luminescence spectrum of the complexes and luminescence lifetime of the complex **2** were also measured.

2. Experimental section

2.1. Materials and chemicals

$Ln(NO_3)_3 \cdot 6H_2O$ was purchased, and analytically pure chemicals were purchased and used without further purification. The main chemicals are listed in Table 1.

2.2. Experimental equipment and conditions

Single-crystal diffractometer with Bruker CCD area detector type was used to collect single crystal diffraction data of complexes **1** and **2**, using Cu (0.154178 nm) and Mo (0.071073 nm) as radiation source, respectively. The data were collected using SHELXL-97 program with full matrix least squares method to refine F^2. The X-ray powder diffraction of the complexes was measured using a Bruker D8ADVANCE diffractometer at a scan rate of 0.2 °/s. Elemental analysis (C, H and N) were obtained on Elementar Vario-EL II elemental analyzer and the content of lanthanide in the complexes was measured by EDTA complexometric titration method. The IR spectra were determined by a Bruker TENSOR 27 model Fourier transform infrared spectrometer (KBr compression method). The TG, DTG, DSC and the escape gas of the complexes were measured by simultaneous thermal analysis (NETZSCH STA 449 F3)-infrared spectroscopy (TENSOR 27) at a heating rate of $10\ K\ min^{-1}$ in a simulated air atmosphere. The heat capacities of the complexes were measured on a NETZSCH DSC 200 F3 using indirect measurement. The linear heating rate was $10\ K\ min^{-1}$ under a nitrogen atmosphere. Under the same conditions, the molar heat capacity of the standard sample (α-Al_2O_3) was firstly measured. The relative standard deviation of the measured standard sample Al_2O_3 was compared with the recommended values (National Institute of Standards and Technology), and the relative deviation is within ±3 %. The heat capacity of the complexes (19 mg) and the standard sample (sapphire: 25.14 mg) were then determined. The luminescence spectrum of the complexes and luminescence lifetime of the complex **2** were measured on a Edinburgh instruments FS5 spectrofluorophotometer.

2.3. Synthesis

The synthesis of complexes **1** and **2** have similar procedure. A mixture of 2-Br-5-MOHBA (0.6 mmol) and 5,5′-DM-2,2′-DIPY (0.2 mmol) was dissolved in 8 mL ethanol solution (95 %). The pH of the mixture was adjusted to 6–7 with $1\ mol\ L^{-1}$ NaOH solution. Then the mixture was dropwise added into 3 mL aqueous solution of $Ln(NO_3)_3 \cdot 6H_2O$ (0.2 mmol) under stirring. After continually stirring for 6.5 h and sting for 12 h, the precipitate was collected by filtration and dry. The crystals were obtained by slowly evaporating mother liquor at room temperature after two weeks. Element analysis for complex **1**, calcd for $C_{72}H_{60}Br_6N_4O_{18}Sm_2$(%) C, 42.20; H, 2.95; N, 2.73; Sm, 14.67. Found: C, 42.16; H, 2.87; N, 2.71; Sm, 14.63. Complex **2**, Calcd for $C_{72}H_{60}Br_6N_4O_{18}Eu_2$(%) C, 42.13; H, 2.95; N, 2.73; Eu, 14.81. Found: C, 42.10; H, 2.93; N, 2.67; Eu, 14.76.

Table 1
The source and purity of the materials in the experiment.

Complexes	Source	Purification method	Massfraction (purity)
$Ln(NO_3)_3 \cdot 6H_2O$	Alfa Aesar	–	>0.999
2-Br-5-MOHBA	Alfa Aesar	–	>0.98
5,5′-DM-2,2′-DIPY	TianJin fine chemicals institute	–	>0.995
Complex **1**	Synthesis	Solvent washing	0.993[a]
Complex **2**	Synthesis	Solvent washing	0.991[a]

[a] Evaluated by averaging based on the measured contents of C, H, N and metals (Sm, Eu).

3. Results and discussion

3.1. Infrared spectra

The IR spectrum of the complexes **1** and **2** and two ligands have been measured in the range of $4000–400\ cm^{-1}$. The spectrum of crystals and complexes are fully identical, indicating that the two complexes have similar coordination environment. The main characteristic absorption bands of the ligands and complexes are summarized in Table 2. The strong absorption band of the carboxylate group ($\nu_{C=O}$) of 2-Br-5-MOHBA at $1704\ cm^{-1}$, and new bands arise from the asymmetric ($\nu_{as\ (COO^-)}$) and symmetric ($\nu_{s\ (COO^-)}$) stretching vibration of COO^- at 1626 and $1408\ cm^{-1}$ for complex **1**, and 1628 and $1409\ cm^{-1}$ for complex **2**. The absorption peaks can be observed at 422 and $420\ cm^{-1}$ corresponding to the vibrations of Ln—O. These changes suggest that the coordinate bonds are formed between the oxygen atoms of the carboxylate groups and the Ln^{3+} ions [22]. The stretching vibration peaks of C=N of 5,5′-DM-2,2′-DIPY at $1467\ cm^{-1}$ shift to $1430\ cm^{-1}$ (complexes **1** and **2**), which indicates that the coordination bonds are formed between nitrogen atoms and Ln^{3+} ions [23].

3.2. Description of crystal structures

The most important crystallographic data for the two complexes are summarized in Table 3. The single-crystal X-ray diffraction analysis reveals that complexes **1** and **2** are isostructural and crystallize in the triclinic system, space group $P\bar{1}$. Therefore, the crystal structure of complex **2** will be illustrated in detail.

Complex **2** is binuclear molecule. The two Eu^{3+} ions have the same coordination environment, and each asymmetric unit is composed of one Eu^{3+} ion, three 2-Br-5-MOBA ligands and one 5,5′-DM-2,2′-DIPY ligand (Fig. 1a). The center Eu^{3+} ion is nine-coordinated, surrounded by seven oxygen atoms and two nitrogen atoms, among three oxygens (O1, O2# and O2) from two bridging tridentate 2-Br-5-MOBA ligands, two oxygen atoms (O4 and O5) from two bridging bidentate 2-Br-5-MOBA ligands, two oxygen atoms (O7 and O8) from one chelating bidentate 2-Br-5-MOBA ligand and two nitrogen atoms (N1 and N2) from the chelating bidentate 5,5′-DM-2,2′-DIPY ligand. The coordination geometry of Eu^{3+} ion is a distorted monocapped square anti-prismatic (Fig. 1b) [24,25]. The distances between Eu—O is in the range of 0.2326(10) to 0.2832(10) nm, and the Eu—N distances are 0.2614 (13) nm for N1 and 0.2617(12) nm for N2. Except for the lengths of Eu—N and Eu—O bonds (Table 4), another important band is the Eu···Eu in the binuclear unit with a distance of 0.4111(15) nm. The average bond lengths of Eu-N and Eu-O are about 0.2616 and 0.2472 nm, respectively. The average distance of the Eu-O bond is shorter than that of the Eu-N bond, which leads to the first breaking of the Eu-N bond during the thermal decomposition, that is, the 5,5′-DM-2,2′-DIPY ligand begins to lose in the first decomposition. The binuclear molecular units are assembled into a 1D chain (Fig. 2a) along the b-axis direction via weaker C-H···Br hydrogen bonding interactions [17] between two 2-Br-5-MOBA ligands. The carbon atom from 2-Br-5-MOBA ligand of bridging bidentate and the bromine atoms from the other chelating bidentate 2-Br-5-MOBA ligand unit with the distance of 0.3766 nm. Two