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Synthesis, thermodynamic properties and antibacterial activities of lanthanide complexes with 3,5-dimethoxybenzoic acid and 1,10-phenanthroline

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ABSTRACT

Four lanthanide complexes with a general formula $[Ln(3,5\text{-}DmeoxBA)_3(phen)]_2$ (Ln = Tb(1), Dy(2), Er(3), Yb(4); 3,5-DmeoxBA = 3,5-dimethoxybenzoic acid; phen = 1,10-phenanthroline) were synthesized and characterized by elemental analysis, infrared spectra (IR), and thermogravimetric, differential scanning calorimetry techniques, combined with Fourier transform infrared (TG/DSC–FTIR) technology. The thermal decomposition processes of the four complexes were investigated by TG/DSC–FTIR techniques. Heat capacities were measured by DSC. The values of the experimental heat capacities were fitted to a polynomial equation with the least-squares method. Based on the fitted polynomial, the smoothed heat capacities and thermodynamic functions $(H_T - H_{298.15\,K})$, $(S_T - S_{298.15\,K})$, and $(G_T - G_{298.15\,K})$ were calculated. The antibacterial action of the four complexes on bacteria and fungus such as *Escherichia coli*, *Staphylococcus aureus* and *Candida albicans* were studied by filter paper approach. The luminescent properties of the complexes 1 and 2 were also studied.

1. Introduction

As we know, lanthanide complexes have attracted widespread interest due to the wide variety of potential applications in magnetic materials, catalysts, photoelectric conversion material and so on [1–9]. Comparatively less is known [10–12] about the biological properties of lanthanide complexes. Some rare-earth ions may participate in various physicochemical processes of living systems [13]. In particular, some lanthanide complexes with anti-microbial activities can be used as antibacterial and antiphlogistic agents, etc. [14–16]. In the present paper, we synthesized and characterized four lanthanide carboxylate complexes ($[Ln(3,5\text{-}DmeoxBA)_3(phen)]_2$ (Ln = Tb(1), Dy(2), Er(3), Yb(4)). The antibacterial action of the four complexes on bacteria and fungus such as *Escherichia coli*, *Staphylococcus aureus* and *Candida albicans* were studied by filter paper approach. The thermal decomposition process of the four complexes and the evolved gases were discussed. The heat capacity is measured over the temperature range from 263.15 to 475.65 K. The luminescent properties of the complexes 1 and 2 were also studied.

2. Experimental

2.1. Preparation of the title complexes

3,5-DmeoxBA (0.6 mmol) and phen (0.2 mmol) were dissolved in 95% ethanol solution together, and the pH of the solution was controlled in the range of 5–7 by addition of NaOH solution (1 mol L^{-1}). Then the mixture ligands was added dropwise into the $LnCl_3 \cdot 6H_2O$ (Ln = Tb(1), Dy(2), Er(3), Yb(4); 0.2 mmol) aqueous solution. Stirred continuously at room temperature for about 8 h and deposited for 12 h. Subsequently, the precipitates were filtered out and dried. Calc. for 1: C, 53.07; H, 4.00; N, 3.17; Tb, 18.01%. Found: C, 52.50; H, 4.07; N, 3.10; Tb, 17.87%. Calc. for 2: C, 52.86; H, 3.98; N, 3.16; Dy, 18.34%. Found: C, 52.72; H, 4.00; N, 3.19; Dy, 18.38%. Calc. for 3:C, 52.57; H, 3.96; N, 3.14; Er, 18.77%. Found: C, 52.00; H, 3.95; N, 3.13; Er, 18.57%. Calc. for 4: C, 52.24; H, 3.93; N, 3.12; Yb, 19.30%. Found: C, 52.08; H, 3.95; N, 3.00; Yb, 18.87%.

According to the elemental analysis and related literature [17], it can be concluded that the formula of complexes is $[Ln(3,5\text{-}DmeoxBA)_3(phen)]_2$(Ln = Tb(1), Dy (2), Er (3), Yb(4)).

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2.2. Chemicals

All the reagents were of analytical grade and used without further purification as commercially obtained. $LnCl_3{\cdot}6H_2O$ (Ln = Tb, Dy, Er, Yb) were prepared by dissolving Ln_2O_3 in hydrochloric acid and then evaporating liquid by water-bath heating.

2.3. Apparatus

The Ln content was determined by EDTA titration using xylenol orange as an indicator. Elemental analyses of C, H, and N were determined using a Vario-EL III elemental analyzer. IR spectra were measured on a Bruker TENSOR27 spectrometer in the range of 4000–400 cm^{-1} using the conventional KBr discs technique at room temperature. Fluorescence spectra were measured on an F-4600 Hitachi Spectrophotometer with slit width 2.5 nm.

The thermogravimetric (TG), differential thermogravimetric (DTG), differential scanning calorimetric (DSC), and Fourier transform infrared (FTIR) analyses were conducted using a TG/DSC–FTIR system, which was a Netzsch STA 449 F3 Instrument with a Bruker TENSOR27 Fourier transform infrared spectrometer, under the simulated air atmosphere, with the rate of 10 K min^{-1} from 300 to 1250 K. The Netzsch STA 449 F3 instrument was linked to the heated gas cell of the FTIR instrument by means of a heated transfer line, and the temperatures of the cell and the transfer line were kept at 473 K. The sample masses were about 6 mg.

Heat capacity of the complexes were determined using a NETZSCH DSC 200 F3 in the temperature range of 263.15–475.65 K under the linear heating rate of 10 K min^{-1} using an indirect measurement method. The atmosphere was nitrogen gas and the flow rate was 20 mL min^{-1}. To verify the reliability of the heat capacity measurement method by DSC, the heat capacity of the reference standard material sapphire was measured and the relative deviations of our experimental results were within ± 0.50% compared with the recommended values by NIST [18]. The baseline, reference and sample measurements were carried out under the same conditions. The sample masses were about 10 mg and the reference standard substance sapphire mass used was12.74 mg. The apparatus has an automatic data processing program from which we can obtain the $C_{p,m}$ curves of the sample by an indirect measurement method.

The antibacterial activity was tested by the disk diffusion method using the Mueller–Hinton agar medium. The test compounds were dissolved in DMSO. The test concentrations are 0.008 mol L^{-1}, 0.016 mol L^{-1} and 0.032 mol L^{-1}, respectively. Sterile filter paper discs (5 cm in diameter) were soaked in 5 μl solutions and tested against *E. coli*, *S. aureus* and *C. albicans*. The antibacterial effects for *E. coli and S. aureus* were investigated after 24–38 h incubation at 37 °C, and the *C. albicans* were investigated after 48 h incubation at 30 °C.

3. Results and discussion

3.1. Infrared spectra

The IR spectra of the four complexes are similar and the important absorption peaks are listed in Table 1 (see supplementary data). The $\nu_{C=O}$ (—COOH) of the free ligand at 1690 cm^{-1} completely disappears in the IR spectrum of the complexes, whereas the characteristic peaks of $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ are observed at 1591–1593 and 1385 cm^{-1},respectively. Meanwhile, the band at 419–421 cm^{-1} is assigned to ν(Ln—O) .These changes indicate that the oxygen atoms from the 3,5-DmeoxBA groups are chelated to Ln^{3+}ion [19,20]. Besides, the absorption peaks of $\nu_{C=N}$ and δ_{C-H} exhibit red shifts compared with the free phen ligand, thus indicating that two nitrogen atoms in phen take part in coordination to Ln^{3+}ion [21,22].

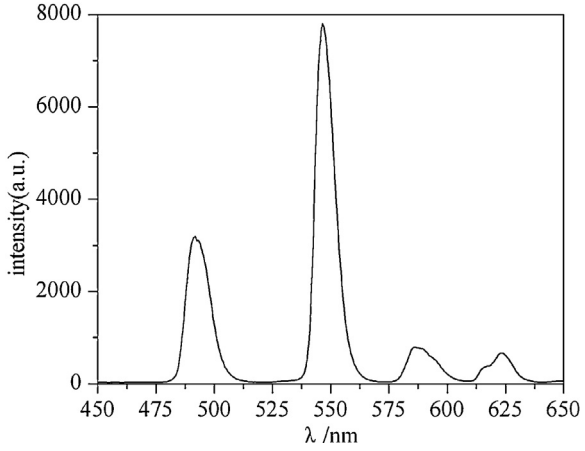

Fig. 1. Emission spectrum of complex 1 (λ_{ex} = 341 nm).

3.2. Fluorescence spectra

The luminescent properties of complexes 1 (Fig. 1) and 2 (Fig. 2) in the solid state were investigated at room temperature. The emission spectrum of complex 1 was recorded upon the excitation at 341 nm. Four emission bands are at 492, 546, 588 and 623 nm, which are attributed to $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$, and $^5D_4 \rightarrow {}^7F_3$ transitions of Tb(III) ion, respectively. The preferred transition ($^5D_4 \rightarrow {}^7F_5$) is the most intense emission band [23,24]. The fluorescent spectrum of complex 2 was observed in the range of 450–650 nm by selective excitation wavelength at 330 nm. In Fig. 2, Dy^{3+}ion gives rise to the typical emission bands at 482 and 577 nm corresponding to the characteristic emission $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transitions. The luminescence of complex 1 is stronger than complex 2 due to the difference in energy between the excited energy level of the ligands and Tb (III) and Dy (III) ions, respectively [25].

3.3. Thermal decomposition process of the title complexes

The TG, DTG and DSC curves were obtained with the rate of 10 K min^{-1} from 300 K to 1250 K. The thermal analytical data for the four complexes are summarized in Table 1. The enthalpies and peak temperatures from DSC analysis are listed in Table 2. The TG–DTG and DSC curves of complexes 1–4 are shown in Fig. 3, respectively.

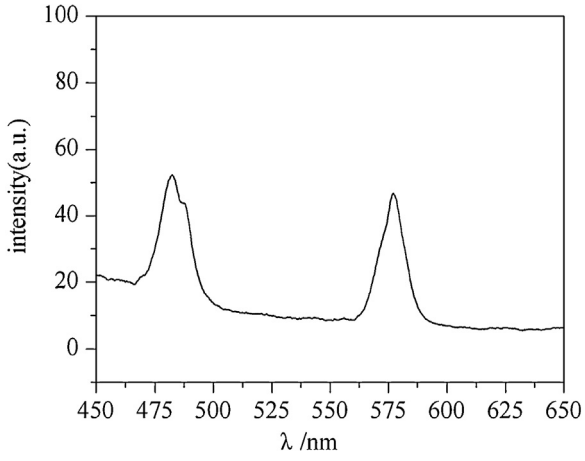

Fig. 2. Emission spectrum of complex 2 (λ_{ex} = 330 nm).