Synthesis and luminescent properties of terbium complex with 2-amino-4-chlorobenzoic acid

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Abstract: A novel complex [Tb(L)$_2$(H$_2$O)$_3$·H$_2$O] (where L=2-amino-4-chlorobenzoic acid) was synthesized and characterized by a series of analysis. The molecular formula of complex was confirmed by Fourier transform infrared (FT-IR) spectroscopy and thermogravimetric/differential thermogravimetric (TG-DTG) measurements. The optical properties of complex was measured by ultraviolet spectroscopy (UV) and fluorescence spectroscopy (FS). The results indicated that Tb^{3+} in the complex was coordinated by ligand, and the complex emitted bright yellow-green luminescence with main peak at 548.8 nm with excitation at 369.4 nm.

Keywords: rare earth complex; 2-amino-4-chlorobenzoic acid; solvothermal synthesis; luminescent properties; rare earths

In the last decades, many lanthanide complexes were noted for their interesting photophysical properties arising from f-f transition[1–4] and their wide range of potential applications in fields as diverse as sensor system, biology[5], material chemistry, medicine, and so forth[6,7]. Up to now, many lanthanide complexes with β-diketone, aromatic carboxylic acid and heterocyclic ligand which show good fluorescence properties have been synthesized[8–10]. All of these investigations on the fluorescence intensity were dependent on the structure of the ligands, and this phenomenon had been explained by the intramolecular energy transfer mechanism. And the intramolecular energy transfer efficiency depends chiefly on the energy difference between the triplet level of the ligands and the resonant emissive energy of Ln^{3+} (ΔE(Tr-Ln^{3+})). While according to Dexter's resonant exchange interaction and thermal deactivation mechanism, ΔE(Tr-Ln^{3+}) can be assumed to have an optimal value around (3000±500 cm^{-1})[11,12]. Among a host of organic ligands, the aromatic carboxylates are good choices since they exhibit a variety of coordination modes and can chelate effectively to lanthanide cation via anionic carboxylate groups. What's more, they can absorb UV light strongly and transfer energy to lanthanide metal center efficiently. For example, the terbium complexes of aminobenzoates[13–15], and halogenated benzoic acid[16–18] exhibit strong luminescence due to efficient energy transfer from the triplet state of the ligand to the rare earth metal ion[12,19]. Sivakumar et al.[20] employed three new 4-benzyloxy benzoic acid derivatives as ligands to synthesize lanthanide coordination compounds with the aim of testing the influence of electron releasing and electron

drawing substituents on the photophysical properties, whose research results indicate that the incorporation of an electro-releasing group in ligands enchances the π-electronic density of the ligand and consequently decreases the energy of the triplet level, while the electro-withdrawing group is on the contrary.

On the basis of the aforementioned theory, we were prompted to prepare new terbium complex by 2-amino-4-chlorobenzoic acid which contains two kinds of substituent groups. The position of the triplet level of the ligand could slightly tuned, compared with the triplet level of o-aminobenzoate (24100 cm^{-1})[21] and the triplet level of p-chlorbenzoic acid (22925 cm^{-1})[22], owing to the effect of two kinds of substituent groups and the ligand may match well with Tb^{3+}. Consequently, it is anticipated that the luminescent properties of the complex should be enhanced obviously. The molecular formula and luminescent properties of the synthesized complex were presented in this article.

1 Experimental

1.1 Materials and apparatus

Terbium oxide (Tb$_4$O$_7$) of over 99.9% purity and 2-amino-4-chlorobenzoic acid of over 98% purity were purchased from Sinopharm Chemical Reagent Co., Ltd., and solvents were used as received. Terbium nitrate Tb(NO$_3$)$_3$·6H$_2$O was prepared by dissolving Tb$_4$O$_7$ in nitric acid (6 mol/L) together with some peroxide followed by successive evaporating excess acid.

The pH measurements were performed with a PHSJ-5

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acidity meter (Shanghai Jingke factory, China). Fourier transform infrared (FT-IR) spectra were recorded on a NEXUS-470 FT-IR spectrophotometer by using KBr pellet in the range of 4000–400 cm^{-1}. Measurement of thermogravimetry-differential thermal gravimetry (TG-DTG) curves were conducted on a METTLER TOLEDO thermal analyzer in the range of 25–1000 ºC at a heating rate of 10 ºC/min under a flowing nitrogen atmosphere. Ultraviolet (UV) spectra were recorded on a SHIMA-DZU 2550-UV-vis spectrophotometer with ethanol as reference solution and solvent. The fluorescence spectra (FS) were measured on a Hitachi F-4600 spectropho-tometer at room temperature. The CIE (Commission Internationale de I'E clairage) chromaticity coordinates (x, y) were obtained through a PMS-50 PLUS UV-Vis-near IR spectrophotocalorimeter.

1.2　Synthesis of $Tb(L)_2(H_2O)_3{\cdot}H_2O$ complex

The terbium complex was prepared by solvothermal method. The pH value of the ethanol solution of ligand and the ethanol solution of terbium nitrate were adjusted to about 6–7 and 5 by adding NaOH aqueous solution, respectively. Then the ethanol solution of terbium nitrate was dropped into ethanol solution of ligand under stirring (the molar ratio of L:Tb^{3+} was 3:1). The mixture was sealed in a 25 mL Teflon-lined stainless steel autoclave and heated at 140 ºC for 12 h and then cooled to room temperature at a rate of 10 ºC/h. The raw product was fil-trated and washed thoroughly with anhydrous ethanol and water in turn, and then dried at 70 ºC overnight. Eventually, pale-yellow powders were obtained.

Whether the unreacted ligand L exists in products or not was detected by thin layer chromatography (TLC) analysis and a 16.5:2.5 PE-EA (petroleum ether and ethyl acetate) mixed solvent as mobile phase and silica gel GF254 as stationary phase. By TLC analysis, it was con-firmed that there is no unreacted ligand in washed com-plex.

2　Results and discussion

2.1　IR spectra of the complex

The main absorption frequencies data for IR spectra of complex and ligand and their IR absorption spectra are shown in Fig. 1.

As can be seen from Fig. 1, it is observed that the characteristic absorption bands of the complex are dif-ferent from that of free ligand. For complex, compared with the stretching vibration of –NH_2 (3436 cm^{-1} as v_{as}(–NH_2), 3317 cm^{-1} as v_s(–NH_2)) in free L^-, there are two types of amino group, coordinated –NH_2 (3493 cm^{-1} as v_{as}(–NH_2), 3370 cm^{-1} as v_s(–NH_2)) and free –NH_2 (3421 cm^{-1} as v_{as}(–NH_2), 3307 cm^{-1} as v_s(–NH_2)). Com-pared with v_{as}(–COO^-) absorption (1606 cm^{-1}) in free L^-
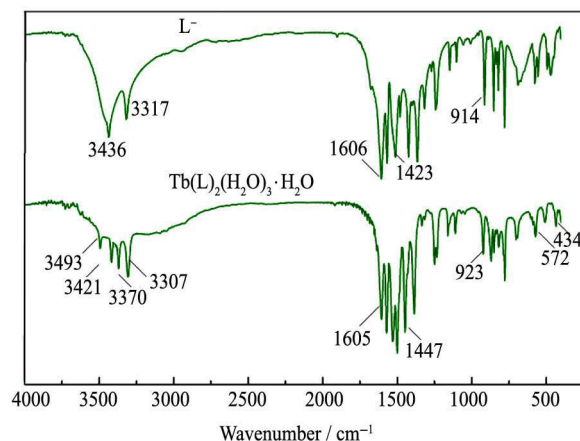

Fig. 1 FT-IR spectra of the complex and ligand

ion, the v_{as}(–COO^-) absorption shift (1605 cm^{-1}) in com-plex is negligible. The v_s(–COO^-) absorption (1447 cm^{-1}) in complex has a red shift (value is 24 cm^{-1}) compared with the v_s(–COO^-) absorption (1423 cm^{-1}) in free L^- ion. The difference of v_{as}(–COO^-) absorption (1605 cm^{-1}) and v_s(–COO^-) absorption (1447 cm^{-1}) in complex is 158 cm^{-1}, according to Manhass[23] theory, a conclusion can be drawn that carboxylate coordinated with central ion Tb^{3+} in the form of bidentate or chelating. Furthermore, the appearance of an absorption band at 434 cm^{-1} is attrib-uted to the symmetric stretching vibration of the Tb–O bond. The above observations confirm that the coordina-tion bonds were formed between Tb^{3+} and L^-, and com-plex was synthesized.

It is worthy noting that abroad stretching vibration ab-sorption of H_2O appears in the range of 3500–3300 cm^{-1}. In addition, the out-of-plane bending vibration of crystal water molecule and the in-plane swing vibration of coor-dinated water molecules are discovered at 916 and 578 cm^{-1}, respectively[24], verifying that there exist both co-ordinated water molecules and crystal water molecules in the complex.

2.2　Thermal decomposition process of the complex

To investigate the thermal stability and the decompo-sition process of the complex, thermogravimet-ric/differential thermogravimetric (TG-DTG) measure-ments of complex were carried out and the TG-DTG curves of complex are shown in Fig. 2.

As seen from the DTG curve, the thermal decomposi-tion process of complex presents four stages. The mass loss in first stage between 132 and 166 ºC is 2.97%, cor-responding to the loss of 1 mol of crystal H_2O, which coincides well with the theoretical value 3.15%. The sec-ond stage ranges from 305 to 522 ºC, with a mass loss of 27.17%, which corresponds to the loss of 3 mol of coor-dinated H_2O, 2 mol of –NH_2 and 2 mol of –Cl (theoreti-cal mass loss is 27.44%). The third step, from 522 to 685 ºC, 2 mol of –C_6H_3 group is eliminated from complex, with a mass loss of 26.19%, which roughly coincides with the