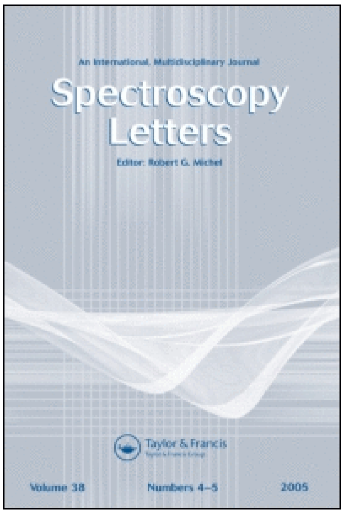

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Spectroscopic and Thermal Properties of Europium *O*-Sulphobenzimide Complexes

Yugen Zhang[a]
[a] Department of Chemistry, University of Science and Technology of China, Anhui, P.R.China

To cite this Article Zhang, Yugen(1998) 'Spectroscopic and Thermal Properties of Europium *O*-Sulphobenzimide Complexes', Spectroscopy Letters, 31: 8, 1609 — 1617
To link to this Article: DOI: 10.1080/00387019808007438
URL: http://dx.doi.org/10.1080/00387019808007438

SPECTROSCOPY LETTERS, 31(8), 1609-1617 (1998)

SPECTROSCOPIC AND THERMAL PROPERTIES OF EUROPIUM *O*-SULPHOBENZIMIDE COMPLEXES

Key words: europium complexes, photoacoustic spectrum, IR, TGA.

Yugen Zhang

Department of Chemistry, University of Science and Technology of China,
Hefei, Anhui 230026, P.R.China

ABSTRACT

A new rare earth *o*-sulphobenzimide ($C_6H_4CONSO_2$) complex $Eu_2(C_6H_4CONSO_2)_3(NO_3)_3 \bullet 12H_2O$ **(I)** was synthesized and characterized. Three decomposition steps of **(I)** were proposed based on its TGA behaviors. The photoacoustic (PA) spectra of europium acetates **(II)** and this *o*-sulphobenzimide complex **(I)** were recorded at room temperature. All PA absorptions were assigned and well explained. The relaxation processes of energy levels $^5D_3$, $^5D_2$, $^5D_1$, $^5D_0$ were mostly through radiative channel indicating their fluorescent characters. The f → f transition absorptions of Eu^{3+} were observed at the range of 350-450 nm in the PA spectra of both **(I)** and **(II)**. And, the L→f transition between conjugate π orbital and Eu^{3+} ion of complex **(I)** was also observed in the range of 300-350 nm.

INTRODUCTION

There has been increased interest in the general chemistry, structural properties and reactivity of metal complexes of *o*-sulphobenzimide in recent years owing to the suspected carcinogenic nature of this sweetening agent (saccharin).[1,3] *o*-sulphobenzimide, as a ligand, is also interesting for its variable coordination characters.[4] Although d electron transition metal/*o*-sulphobenzimide complexes had been widely investigated,[5,6] study of its rare earth complexes was still limited. [4] In this work, we report synthesis and spectroscopic properties of one new *o*-sulphobenzimide lanthanide complex $Eu_2(C_6H_4CONSO_2)_3(NO_3)_3 \cdot 12H_2O$. As comparing, properties of europium acetate complex are also studied.

Recently, the photoacoustic (PA) measurement have been widely used to investigate the chemical and physical properties of many kinds of samples.[7,8] The PA spectroscopy enables to obtain spectra on any type of solid, whether it is crystalline, powder or gel, and it is the method that energy gap and nonradiative relaxation channel can be monitored directly, the complement of absorption and photoluminescence spectroscopic techniques.[9,10] Here, the PA spectra of europium complexes are studied. And the properties of fluorescence excited states and the C-T transitions are also discussed.

MATERIALS AND METHODS

Synthesis:

Complex (I) $Eu_2(C_6H_4CONSO_2)_3(NO_3)_3 \cdot 12H_2O$ was prepared by the reaction of $Eu(NO_3)_3$ and *o*-sulphobenzimide sodium. Dissolving Eu_2O_3 (352 mg, 1 mmol) in HNO_3 solution, and then *o*-sulphobenzimide sodium (615 mg, 3 mmol) was added with stirring. Slowly evaporated at room temperature, colorless crystals were isolated in several days. Elemental analysis of this crystal complex was found: C, 20.43; H, 2.94; N, 6.81; calc. for $Eu_2(C_6H_4CONSO_2)_3(NO_3)_3 \cdot 12H_2O$: C, 20.13; H, 2.87; N, 6.72%.

Complex **(II)** $Eu(Ac)_3 \cdot 4H_2O$ was synthesized from the Eu_2O_3-glacial acetate acid solution system.[11] Results of elemental analysis was found: C, 16.60; H, 4.40; calc. for $Eu(Ac)_3 \cdot 4H_2O$: C, 17.18; H, 4.53%.

Characterization

IR spectra were recorded on a Sakara-440 spectrometer at a frequency range from 4000 to 400 cm^{-1}. The samples were studied as powders dispersal in KBr pellets.

TGA experiments were performed on a WRT-3 thermal analyzer under an 80 ml/min N_2 flow. The temperature ranged from 50 ℃ to 800 ℃with a heating rate 10 ℃/min.

In PA spectra experiment, the excitation source was a 500 W xenon lamp and the optical system was a CT-30F monochrometor. The excitation light modulated by a mechanical chopper at a frequency of 12 Hz. The acoustic signal was detected with the sample placed in a locally built photoacoustic cell fitted with an EMR 10 electret microphone. After the preamplification, output of the microphone was fed to a lock-in-amplifier to whom a reference signal was input from the chopper. The output signal was normalized for changes in lamp intensity using carbon-black.[12]

RESULTS AND DISCUSSIONS

Infrared Spectra

The IR spectra of $Eu_2(C_6H_4CONSO_2)_3(NO_3)_3 \cdot 12H_2O$ (a) and $C_6H_4CONHSO_2$ (b) were shown in Fig. 1. The characteristic IR bands of coordinated *o*-sulphobenzimide molecule and $-NO_3$ groups were observed in the chart of Eu(III) complex **(I)**. Positions of the IR absorptions and their assignments were listed in Table 1. The

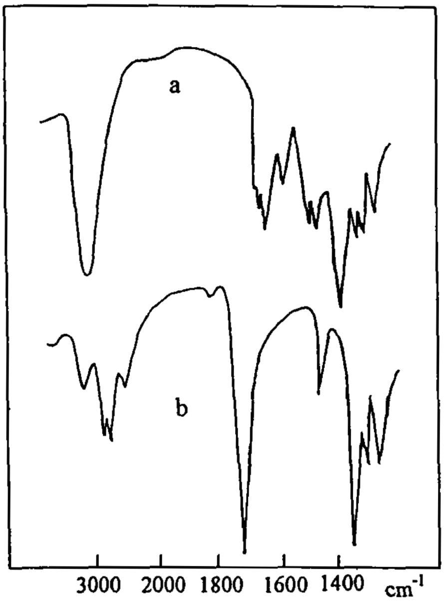

FIG. 1. IR spectra of $Eu_2(C_6H_4CONSO_2)_3(NO_3)_3 \cdot 12H_2O$ (a) and $C_6H_4CONHSO_2$ (b).

TABLE 1.

IR Bands and Their Assignments of $Eu_2(C_6H_4CONSO_2)_3(NO_3)_3 \cdot 12H_2O$ and *o*-Sulphobenzimide (Hsac) Molecules (cm^{-1})

Hsac	$Eu_2(C_6H_4CONSO_2)_3(NO_3)_3 \cdot 12H_2O$	assignment
	3350	υ_{OH}
3120, 2980	3150	υ_{CH}
2720	2400	υ_{NH}
1713	1660, 1620	$\upsilon_{C=O}$
1600, 1464	1587, 1480, 1460	$\upsilon_{ben\text{-}ring}$
	1382	υ_{NO3}
1392, 1342	1335	$\upsilon_{as\ SO2}$
1302	1300	υ_{CN}
1263	1262	δ_{CO}
1183, 1170	1158	$\upsilon_{s\ SO2}$
1145, 1126	1120	δ_{CH}

absorption peak observed at 3350 cm^{-1} in complex **(I)** was due to the υ_{OH} vibration originating from the coordinated water molecules. The $\upsilon_{C=O}$ vibration of –CON- group of free *o*-sulphobenzimide ligand occurred at 1713 cm^{-1}. In complex **(I)**, it shifted to 1660 and 1620 cm^{-1}. This was the most apparent difference between the IR spectra of coordinated and free *o*-sulphobenzimide molecules. Here, the IR band of $\upsilon_{C=O}$ took a small split ($\delta\upsilon$ = 40 cm^{-1}). It was explained by different coordination models among the three *o*-sulphobenzimide molecules in complex **(I)**.[4] The absorption bands of SO_2 group of coordinated *o*-sulphobenzimide in complex **(I)** could not be observed because they were overlapped by strong and broad absorptions of NO_3 groups.

Thermal Properties

The TGA weight loss curve of $Eu_2(C_6H_4CONSO_2)_3(NO_3)_3 \cdot 12H_2O$ was shown in Fig. 2. It was seen that the decomposition process of this compound could be divided into three stages. The coordination water molecules were lost at 121.2 °C in stage one and the lost weight was about 16%. In stage II, coordinated *o*-sulphobenzimide molecules were decomposed at the temperature range 270-500 °C. The detailed decomposition process was beyond to be quantitatively explained for the complex coordination models,. In stage three, final residue Eu_2O_3 was formed at 623.2 °C. The lost weight in stage III was about 20%. This weight loss presumed that the residue after stage II should be a mixture of oxycarbonate and nitrate. So, the decomposition process of this compound was suggested as:

$$\mathrm{Eu_2(C_6H_4CONSO_2)_3(NO_3)_3 \cdot 12H_2O \rightarrow Eu_2(C_6H_4CONSO_2)_3(NO_3)_3} \qquad \mathrm{I}$$

$$\mathrm{2\,Eu_2(C_6H_4CONSO_2)_3(NO_3)_3 \rightarrow Eu_2O_2(CO_3)Eu_2(NO_3)_6 + 20\,CO_2 + 3\,NO + 3\,SO_2} \qquad \mathrm{II}$$

$$\mathrm{Eu_2O_2(CO_3)Eu_2(NO_3)_6 \rightarrow Eu_2O_3 + 6\,NO + CO_2 + O_2} \qquad \mathrm{III}$$

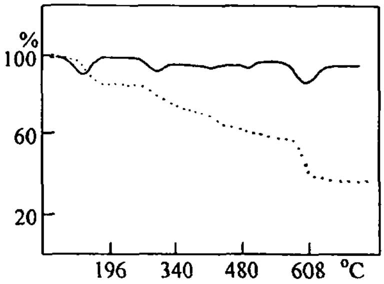

FIG. 2. TGA curves of $Eu_2(C_6H_4CONSO_2)_3(NO_3)_3 \cdot 12H_2O$ complex.

Photoacoustic (PA) spectra

The PA spectra of complex (I) $Eu_2(C_6H_4CONSO_2)_3(NO_3)_3 \cdot 12H_2O$ and $Eu(Ac)_3 \cdot 4H_2O$ (II) were shown in Fig. 3. It is well known that electrons in excited states relax through two kinds of channels: radiative and non-radiative processes. And PA spectrum is the technique that selectively responds to non-radiative relaxation process. For this reason, the PA signal of fluorescent relaxation process will be very weak or vanished.[13] The PA absorption bands and their assignments of complex (I) and (II) were presented in Table 2. Among the energy levels of Eu^{3+} ion, $^5D_0$ was a strong fluorescent state possessing the longest lifetime (about 9.67 ms). Electrons in excited state $^5D_0$ will dominantly choose non-radiative relaxation process. As seeing in Fig. 4, when electrons were excited to $^5D_3$, $^5D_2$, $^5D_1$, usually they would be firstly relaxed to $^5D_0$ by non-radiative transition, and then relaxed by radiation process (fluorescent process) to ground state. It meant that relaxation process of energy levels $^5D_3$, $^5D_2$, $^5D_1$, $^5D_0$ were mostly through radiative channel. As the result, their PA absorption intensities were very weak. As seeing in Fig. 3, the PA signal of $^5D_0$ state could not be observed. Although the excited state $^5D_2$ was the super-sensitive state of

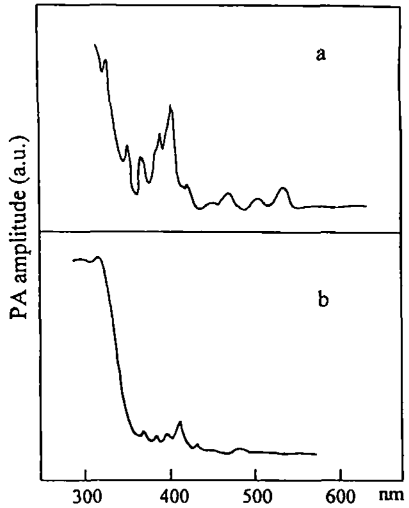

FIG. 3. PA spectra of $Eu(Ac)_3 \bullet 4H_2O$ (a) and $Eu_2(C_6H_4CONSO_2)_3(NO_3)_3 \bullet 12H_2O$ (b) complexes.

TABLE 2.

PA Bands and Their Assignment of $Eu(Ac)_3 \bullet 4H_2O$ and $Eu_2(C_6H_4CONSO_2)_3(NO_3)_3 \bullet 12H_2O$ Complexes (nm).

Assignment[a]	$Eu(Ac)_3 \bullet 4H_2O$	$Eu_2(C_6H_4CONSO_2)_3(NO_3)_3 \bullet 12H_2O$
L → L*		300
L → f		320
E	324.5	
D	332.1	
C	368.9	360
B	385.7	384.5
A	390.6	390.4
$^7F_0 \rightarrow {}^5L_6$	405.6	404.6
$^7F_0 \rightarrow {}^5D_3$	424.6	425.7
$^5F_0 \rightarrow {}^5D_2$	453.1	very weak
$^5F_1 \rightarrow {}^5D_2$	476.0	473.5
$^5F_0 \rightarrow {}^5D_1$	512.8	very weak
$^5F_1 \rightarrow {}^5D_1$	543.4	very weak

[a] A, B, C, D, E belong to f-f transitions, the excited states are very complex and difficult to be distinguished.

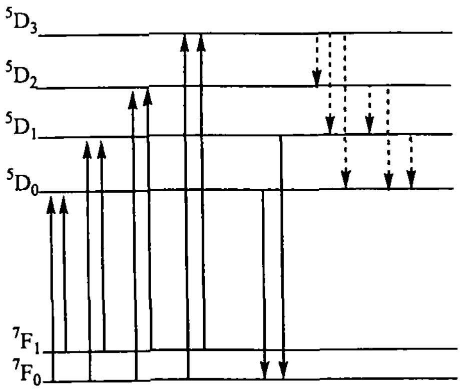

FIG. 4. The energy levels and relaxation processes Eu^{3+} ion.
——→ radiative process; – –→ nonradiative process.

Eu^{3+} ion, its PA signal was quite weak. In other words, this excited state was insensitive to PA technique.

The f-f transition absorptions of Eu^{3+} were observed at range of 350-450 nm in PA spectra of complexes $Eu(Ac)_3 \cdot 4H_2O$ and $Eu_2(C_6H_4CONSO_2)_3(NO_3)_3 \cdot 12H_2O$. In the PAS of complex **(I)**, strong absorption bands in the range of 300-350 nm were observed and they were apparently different from that of europium acetate complex **(II)**. We know that trivalent europium cation is easy to be photoreduced. For this reason, the charge-transfer spectrum of Eu^{3+} complex could be observed in near-uv or visible region. The conjugate π system of *o*-sulphobenzimide molecule also induced to produce charge-transfer ($L \rightarrow f$) absorption in lower energy range. As the experimental result, the $L \rightarrow f$ transition between conjugate π orbital and Eu^{3+} ion of complex **(I)** was observed in the range of 300-350 nm.

ACKNOWLEDGEMENT

We thank the University of Science and Technology of China; Chinese Academy of Science for financial support.

REFERENCES

1. Munro, J. C., Modie, C. A., Krewski, D., Grise, H. C. *Toxicol. Appl. Pharmacol.* 1975; 32: 513
2. Cohen-Addad, N., Chaterjee, M., Bekersky, J., Blumenthal, H. P. *Cancer Lett.* 1986; 32: 151.
3. West, R. W., Sheldon, W. G., Gaylor, D. W., Haskin, M. G., Delongchamp, R. R., Kadlubar, F. F., *Fundam. Appl. Toxicol.* 1986; 7: 585.
4. Zhang, Y. *Trans. Met. Chem.* 1994; 19: 446.
5. Haider, S. Z., Malik, K. M. A., Ahmed, K. J., Hess, H., Riffel, H., Hursthouse, M. S. *Inorg. Chim. Acta* 1983; 72: 21.
6. Zhang, Y., Li, J., Lin, W., Liu, S., Huang, J. *J. Cryst. Spec. Res.* 1992; 22: 433.
7. Sunandana, C. S. *Phys. Stat. Sol. (a)* 1988; 105: 1.
8. Zhang, Y. *Phys. Rev. B* 1995; 51: 14849.
9. Ikari, T. *Jpn. J. of Appl. Phys.* 1990; 20: 887.
10. Zhang, Y. *Chem. Phys.* 1997; 219: 353.
11. Zhang, Y. *Spectroscopy Lett.* 1993; 26: 1479.
12. Zhang, Y., Li, J., Su, Q., Zhao, G. *Spectrochim. Acta* 1992; 48A: 175.
13. Rosencwaig, A. *Photoacoustics and Photoacoustic Spectroscopy*, New York, John Wiley & Sons, 1980.

Date Received: March 30, 1998
Date Accepted: July 23, 1998