

Synthesis of Eu(III) and Tb(III) Complexes with Two New Amide Type Podands and Their Luminescence Properties

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Two new amide type podands L_1 and L_2 ($L_1 = 1,1,1$ -tris{[(2-benzylaminoformyl)phenoxy]methyl}propane, $L_2 = 1,3,5$ -trimethyl-2,4,6-tris{[(2-benzylaminoformyl)phenoxy]methyl}benzene) and their europium and terbium nitrates complexes were synthesized. The luminescence properties of these complexes were also studied.

Keywords amide type podands, europium and terbium nitrates, luminescence spectra

Introduction

Lanthanide complexes have attracted much attention because of their important applications.¹ In particular Eu(III) and Tb(III) can be characterized by long-lived (ms timescale) and strong luminescent electronically excited states, which makes them important in analytical chemistry.² To achieve strong luminescence, some important features such as inclusion, protection, energy transfer from the ligand, *etc.* should be incorporated.³ Encapsulating cryptands and podands have been prepared for these purposes.⁴ It is expected that amide-type podands, which are flexible in structure and have 'terminal-group effects',⁵ will shield the encapsulated ion from interaction with the surroundings effectively. We are interested in this kind of ligands and herein report the synthesis of two amide type podands and their complexes with $\text{Eu}(\text{NO}_3)_3$ and $\text{Tb}(\text{NO}_3)_3$. At the same time, the luminescence properties of the complexes were studied and compared.

Experimental

Materials

N-benzylsalicylamide (**3**),⁶ 1,1,1-tris-(*p*-tosyloxymethyl)-propane (**5**)⁷ and 1,3,5-tribromo-methyl-2,4,6-trimethylbenzene (**7**)⁸ were prepared according to the reported methods. Other chemicals were obtained from commercial sources and used without further purification.

Preparation of podands L_1 and L_2

The synthetic routes for the podands are shown in Scheme 1. A mixture of *N*-benzylsalicylamide (0.58 g, 2.57 mmol), potassium carbonate (0.5 g, 3.6 mmol) and DMF (10 mL) was warmed to *ca.* 80 °C and 1,1,1-tris-(*p*-tosyloxymethyl)-propane (0.5 g, 0.85 mmol) was added. The reaction mixture was stirred at 80—90 °C for three days. After cooling down, the mixture was poured into water (100 mL). The resulted solid was treated with column chromatography on silica gel [petroleum ether-ethylacetate (3:1)] to get 0.19 g of podand L_1 , yield 30%. m. p. 66—68 °C; UV-vis (MeOH) λ_{max} : 209, 280 nm; ¹H NMR (CDCl_3 , 300 MHz) δ : 0.57 (t, $J = 7.2$ Hz, 3H), 0.90 (q, $J = 7.2$ Hz, 2H), 3.61 (s, 6H), 4.49 (d, $J = 5.4$ Hz, 6H), 6.55—8.14 (m, ArH, 27H), $\text{H}_{(\text{N}-\text{H})}$ not detected; IR (KBr) ν : 3410, 1652, 1600, 1530, 1486, 1450, 1295, 1223, 753, 699 cm^{-1} . Anal. calcd for $\text{C}_{48}\text{H}_{47}\text{N}_3\text{O}_6$: C 75.69, H 6.18, N 5.52; found C 75.43, H 6.33, N 5.88.

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L_2 was prepared according to the same procedure as L_1 . But the reaction time was 5 h, yield 65%. m. p. 74–76 °C; UV-vis (DMF) λ_{\max} : 280 nm; ^1H NMR (CDCl_3 , 300 MHz) δ : 2.17 (s, 9H), 4.34 (d, $J = 6$ Hz, 6H), 4.94 (s, 6H), 6.90–8.31 (m, 27H), $\text{H}_{(\text{N}-\text{H})}$ not detected; IR (KBr) ν : 3390, 1652, 1530, 1478, 1293, 1217, 754 cm^{-1} . Anal. calcd for $\text{C}_{54}\text{H}_{51}\text{N}_3\text{O}_6$: C 76.33, H 6.01, N 4.95; found C 76.19, H 5.92, N 4.94.

Preparation of the complexes

A solution of 0.1 mmol L_1 or L_2 in 10 mL of ethyl acetate was added dropwise to a solution of 0.1 mmol europium or terbium nitrate in 10 mL of ethyl acetate. The mixture was stirred at room temperature for 4 h. The pre-

cipitated solid complex was filtered, washed with ethyl acetate and dried *in vacuo* over P_4O_{10} for 48 h and submitted for elemental analysis. Analytical data and molar conductance values of the complexes are given in Table 1.

Physical measurements

The Ln(III) ion was determined by EDTA titration using xylenol orange as an indicator. C, H and N were determined using a Vario-EL elemental analyzer. Conductivity was determined using a DDS-11 conductivity bridge with $10^{-3} \text{ mol} \cdot \text{L}^{-3}$ in suitable solvents. The UV spectroscopy in solutions was performed on a Shimadzu UV-240 recording spectrophotometer in the range of 190–900 nm. ^1H NMR spectra were measured on a Vavian Mercury 300 spectrometer in CDCl_3 solution, with TMS as internal standard. Infrared spectra were recorded in the range of

Scheme 1

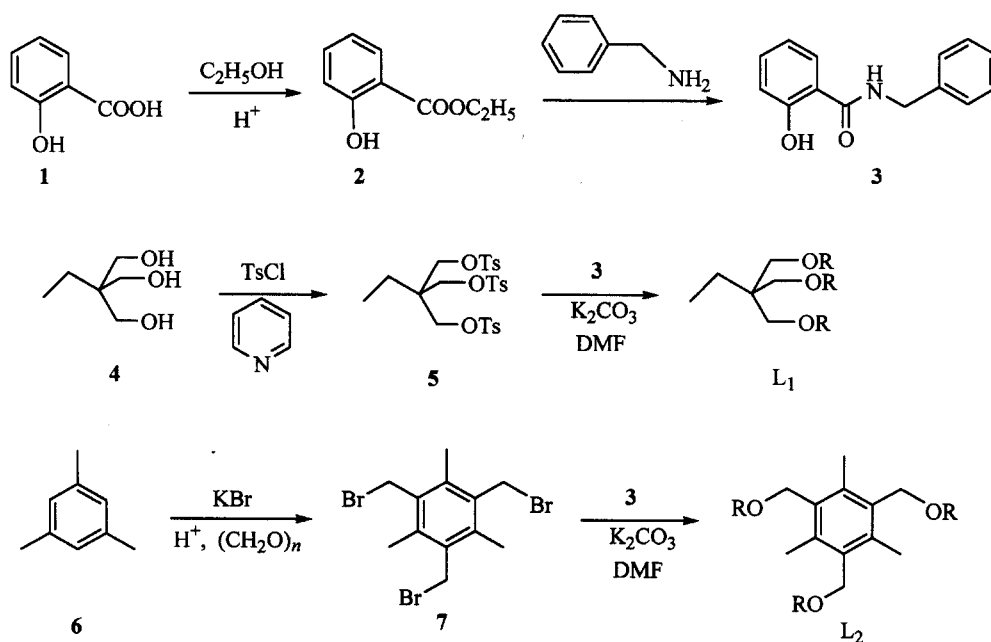


Table 1 Analytical data for the complexes

Complex	Anal. (found) (%) ^a			Ln	Δ_m ($\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$)
	C	H	N		
$\text{Eu}(\text{NO}_3)_3\text{L}_1 \cdot \text{H}_2\text{O}$	51.33 (51.57)	3.89 (4.42)	7.79 (7.52)	13.28 (13.59)	7.0 ^b
$\text{Tb}(\text{NO}_3)_3\text{L}_1 \cdot \text{H}_2\text{O}$	51.37 (51.25)	4.59 (4.39)	7.47 (7.47)	14.20 (14.14)	6.4 ^b
$\text{Eu}(\text{NO}_3)_3\text{L}_2 \cdot 2\text{H}_2\text{O}$	53.65 (53.51)	4.37 (4.57)	7.24 (6.93)	12.38 (12.54)	137.7 ^c
$\text{Tb}(\text{NO}_3)_3\text{L}_2 \cdot 2\text{H}_2\text{O}$	53.23 (53.47)	4.19 (4.37)	7.17 (6.89)	13.01 (13.04)	134.0 ^c

^a Calculated values in parentheses. ^b Measured in CH_3COCH_3 . ^c Measured in DMF.

400—4000 cm^{-1} on a Nicolet spectrometer by using pressed KBr plates. Fluorescence spectra were obtained on a Hitachi M-850 fluorescence spectrophotometer.

Results and discussion

Analytical data for the complexes (Table 1) confirm to a 1 : 1 metal-to-ligand stoichiometry, $\text{Ln}(\text{NO}_3)_3\text{L}$. Complexes of L_1 are soluble in polar organic solvents, such as DMSO, DMF, acetone, methanol, *etc.*, and complexes of L_2 are soluble in DMSO and DMF only.

Infrared spectra

The "free" ligands L_1 and L_2 both exhibit two absorption bands at 1652 cm^{-1} and 1100 cm^{-1} which are assigned to C = O and C—O—C. The complexes also exhibit these two bands. In the complexes, the low-energy band remains unchanged, but the high-energy band red shifts to about 1607 cm^{-1} ($\Delta\nu_{\text{L}_1} = 45 \text{ cm}^{-1}$) and 1610 cm^{-1} ($\Delta\nu_{\text{L}_2} = 42 \text{ cm}^{-1}$) as compared to its counterpart for the "free" ligand, indicating that only the oxygen atom of C = O takes part in coordination to the metal ions. In addition, the metal-oxygen bonds in the complexes of L_1 are stronger than those in complexes of ligand L_2 ($\Delta\nu_{\text{L}_1} > \Delta\nu_{\text{L}_2}$). The possible molecular structure of the complexes is showed in Fig. 1.

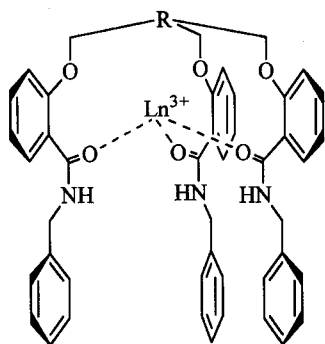


Fig. 1 Possible molecular structure of the complexes.

For all the lanthanide complexes, broad bands at about 3450 cm^{-1} occur from the O—H stretching vibrations of water, and the absence of bands of $\rho_r(\text{H}_2\text{O})$ at *ca.* 590 cm^{-1} shows that the water molecules in complexes are not coordinated water. Additionally, no band at 1380, 820 and 720 cm^{-1} in the spectra of complexes indicates that free nitrate groups (D_{3h}) are absent, but

two intense absorptions associated with the asymmetric stretching in the range of 1290—1310 cm^{-1} (ν_4) and 1485—1495 cm^{-1} (ν_1) appear, clearly establishing that the NO_3^- groups (C_{2v}) are coordinated.⁹ The separation of the two bands is *ca.* 190 cm^{-1} , it is suggested that the NO_3^- groups in the complexes are bidentate ligands.¹⁰

Conductivity studies in solution

The conductivity of complexes of L_1 was measured in CH_3COCH_3 . The molar conductivity is very small, indicating that complexes are non-electrolytes and remain intact in acetone, which is consistent with IR spectra. For complexes $\text{LnL}_2(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$, the molar conductivity was measured in DMF and lies in the range of 2 : 1 (130—170) electrolytes. This discrepancy with IR spectra is because that there is likely competition between the solvent and the ligand (including nitrates) for the lanthanide ion. In the strongly polar DMF the complexes tend to decompose to form solvated Ln^{3+} species.¹¹ It can be concluded from the molar conductivity that one or two nitrates in complexes of L_2 dissociate in DMF.

Luminescence properties of the complexes

Excitations in the ligand-based cause the structural emission of lanthanide complexes while the ligand luminescence is completely quenched, showing that ligand-to-metal energy transfer occurs.¹² The ability to transfer energy from ligand to metal is important in the design of lanthanide(III) supramolecular photonic devices.^{1,11} The luminescence spectra of the ligands and their Eu^{3+} and Tb^{3+} complexes in solid state were recorded at room temperature. The emission spectra of the complexes are shown in Fig. 2.

Excited by the absorption band at 320 nm, the "free" ligand exhibits broad emission bands ($\lambda_{\text{max}} = 450 \text{ nm}$). It is shown in Fig. 2 that all the complexes show the characteristic emissions of Eu^{3+} or Tb^{3+} . This indicates that both podand L_1 and L_2 are good organic chelates to absorb energy and transfer them to metal ions. The stronger and better resolved spectrum of the Tb^{3+} complexes showed the expected sequence of $^5D_4 \rightarrow ^7F_J$ transitions ($J = 6, 5, 4$ or 3). Due to the limitation of the equipment, no further splitting is appeared. In the two

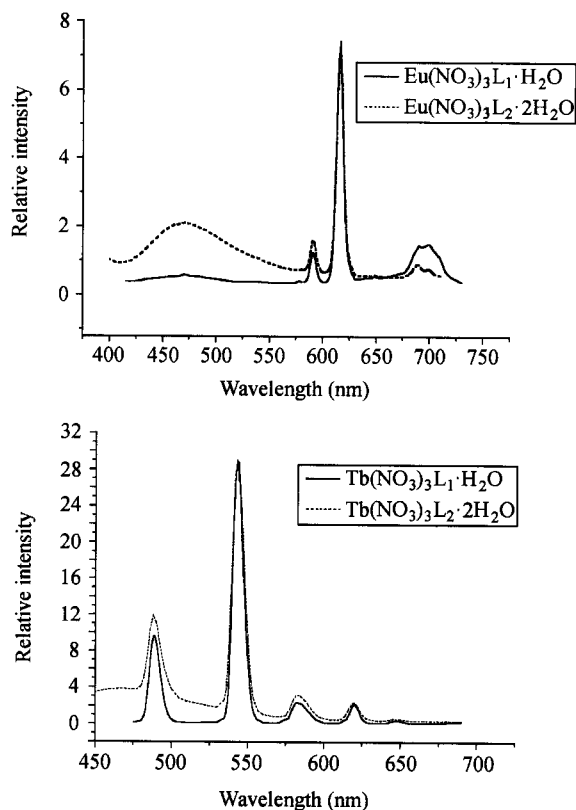


Fig. 2 Emission spectra of complexes in solid state (excited at 320 nm).

spectra of Eu^{3+} complexes, the relative intensity of ${}^5D_0 \rightarrow {}^7F_2$ is more intense than that of ${}^5D_0 \rightarrow {}^7F_1$, showing that the $\text{Eu}(\text{III})$ ion does not lie in a centro-symmetric coordination site.¹⁴ In addition, the complexes of ligands L_1 show no emission bands in *ca.* 450 nm, but the emission bands in the complexes of ligand L_2 are still visible, indicating that the energy transfer in the complexes of L_1 is more effective. An intramolecular energy transfer from the triplet state of the ligand to the resonance level of the $\text{Ln}(\text{III})$ ion is one of the most important processes having influence on the $\text{Ln}(\text{III})$ luminescence quantum yields of $\text{Ln}(\text{III})$ chelates.¹⁵ The energy difference between the triplet state level of the ligand and the lowest excited state level of $\text{Ln}(\text{III})$ can not be too large or too small. So considering the emission spectra of complexes of two podands, it can be concluded that the triplet energy of L_1 is in an appropriate level, which makes the energy transition from the ligand to $\text{Eu}(\text{III})$ and $\text{Tb}(\text{III})$ more easily.

Conclusion

In this paper, the synthesis of $\text{Eu}(\text{III})$ and $\text{Tb}(\text{III})$ complexes with two new amide type podands and their luminescence properties were reported. Comparing the luminescence spectra of the complexes, it could be found that podand L_1 is more effective in energy-transfer than podand L_2 . This result might be attributed to the suitable lowest triplet energy of L_1 in $\text{Ln}L_1(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$. Further study of luminescence and crystal structure of the complexes is in progress.

References

- (a) Aime, S.; Botta, M.; Fasano, M.; Terreno, E. *Chem. Soc. Rev.* **1998**, 27, 19.
(b) Caro, P. *Basic and Applied Aspects of Rare Earths*. Ed. Saez, P. R., Springer, New York, **1997**.
- Sabbatini, N.; Guardigli, M.; Lehn, J.-M. *Coord. Chem. Rev.* **1993**, 123, 201.
- Alexander, V. *Chem. Rev.* **1995**, 95, 273.
- (a) Balzani, V.; Lehn, J.-M.; Vande Loosdrecht, J.; Mecati, A.; Sabbatini, N.; Ziessel, K. *Angew. Chem., Int. Ed. Engl.* **1991**, 30, 190.
(b) Lehn, J.-M.; Roth, C. O. *Helv. Chim. Acta* **1991**, 74, 572.
- Tümmler, B.; Maass, G.; Vögtle, F. *J. Am. Chem. Soc.* **1979**, 101, 2588.
- Michio, K. *Bull. Chem. Soc. Jpn.* **1976**, 49, 2679.
- Farber, S.; Conley, R. *Synth. Commun.* **1974**, 4, 243.
- Jiri, Z.; Magdalena, P.; Petr, H.; Miloš, T. *Synthesis* **1994**, 110, 1132.
- Canall, W.; Siegel, S.; Ferrano, J.; Tani, B. Gebert, E. *Inorg. Chem.* **1973**, 12, 560.
- Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd Edn, John Wiley, New York, **1978**, p. 227.
- Dagdigiam, J. V.; Mckee, V.; Reed, C. H. *Inorg. Chem.* **1982**, 21, 1332.
- Piguet, C.; Hopfgartner, G.; Williams, A.; Bünzli, J.-C. *J. Chem. Soc., Chem. Commun.* **1995**, 491.
- Horrocks, W.; Sudnick, D. *Acc. Chem. Res.* **1981**, 14, 384.
- Su, C.-Y.; Kang, B.-S.; Mu, X.-Q.; Sun, J.; Tong, Y.-X.; Chen, Z.-N. *Aust. J. Chem.* **1998**, 51, 565.
- Latva, M.; Takalo, H.; Mukkala, V.-M.; Marachescu, C.; Rodriguez-Ubis, J.-C.; Kankare, J. *J. Lumin.* **1997**, 75, 149.