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Luminescent properties of solvent effect for europium and terbium nitrate complexes with 3,3,7,7-tetra[*N*-benzyl-*N*-phenyl(acetamide)-2-oxymethyl]-5-oxanonane

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Abstract

The multipodal ligand 3,3,7,7-tetra[*N*-benzyl-*N*-phenyl(acetamide)-2-oxymethyl]-5-oxanonane (L) and its europium and terbium nitrate complexes were synthesized. The complexes were characterized by elemental analysis, IR, fluorescence spectroscopy and conductivity. The lanthanide atoms are coordinated by 0 atoms from C=O, C-O-C. With the difference of the solvent, the fluorescence properties of solvent effect for the complexes were investigated. Some factors that influencing the fluorescent intensity were discussed. © 2006 Elsevier B.V. All rights reserved.

Keywords: Ether-amide type multipodal ligand; Lanthanide; Fluorescence; Solvent effect

1. Introduction

Luminescent lanthanide complexes [1–4] are finding use as labels and sensors for natural and medical science [5,6], which is attributable to their large Stokes shifts, narrow emission profiles, etc. [7]. They have attracted more and more chemists to design the organized molecular architectures containing trivalent lanthanide ions [Eu(III) and Tb(III)] working as efficient light conversion devices [1,8].

Amide-based crown ethers offer many advantages in extraction and analysis of the rare earth ions [9,10] because of their ring-like coordination structure and terminal group effects. The open-chain crown ethers containing amide groups possess suitable molecular structure: a chain with inflexible terminal groups. Therefore, they are excellent reagents for activating ion-selective electrodes and extracts of rare earth ions [11]. However, luminescent properties on open-chain crown ethers with lanthanide complexes have been rarely reported [12]. So we have designed a series of multifunctional ligands having both selective ability to enhance luminescence of lanthanide complexes by providing some of proper conjugate absorption groups suitable for

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energy transfer, i.e. the coordinating groups with cavities for lanthanide ions and amide-based crown ethers. With several suitably designed arms, the multipodal ligands could shield the encapsulated lanthanide ions from interaction with the surroundings, and by deliberate incorporation of appropriate multiple absorption groups suitable for energy transfer, they could be used to develop strong luminescent lanthanide complexes.

In this work, we obtained a open-chain crown ether ligand 3,3,7,7-tetra[*N*-benzyl-*N*-phenyl(acetamide)-2-oxymethyl]-5-oxanonane (L) (Scheme 1) and its lanthanide nitrate [Ln = Eu(III) and Tb(III)] complexes. The solvent effects on fluorescence properties of the complexes were investigated.

2. Experimental

2.1. Materials

All commercially available chemicals were of A.R. grade and all solvents used were purified by standard methods.

2.2. Methods

The metal ions were determined by EDTA titration using xylenal orange as indicator. C, H and N were determined using an Elementar Vario EL. Conductivity measurements were

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carried out with a DDS-307 type conductivity bridge using 10^{-3} mol dm⁻³ solutions in acetone at 25 °C. IR spectra were recorded on Nicolet FT-170SX instrument using KBr discs in the 400–4000 cm⁻¹ region, ¹H NMR spectra were measured on a Varian Mercury plus 300 M spectrometer in CDCl₃ solution with TMS as internal standard. Fluorescence measurements were made on a Hitachi F-4500 spectrophotometer equipped with quartz curettes of 1 cm path length at room temperature. The excitation and emission slit widths were 10 nm.

2.3. Synthesis of the ligand

A solution of 3,3,7,7-tetrahydroxymethyl-5-oxanonane (2.5 g, 10 mmol) in THF was added dropwise into a THF solution that was suspended with NaH (1.6 g, 60%, 40 mmol), and the mixture was stirred under nitrogen at room temperature until no gas appeared. Then, a solution of *N*-benzyl-*N*-phenylchloroacetamide (44 mmol) in THF was added dropwise into the mixture. After the mixture was refluxed for 6 h, the

THF was evaporated and the residue was washed by column chromatography (silica gel, 2:1, CHCl₃/CH₃CO₂Et) and evaporated in vacuum resulted a yellow oil (4.3 g), yield: 50%. L, ¹H NMR spectrum (300 M, CDCl₃): δ = 6.92–7.26 (m, 40H), 4.84 (s, 8H; 4N–CH₂–R), 3.75 (s, 8H; 4O–CH₂–C(O)), 3.23 (s, 8H; 4C–CH₂–O), 3.11 (s, 4H; 2C–CH₂–O), 1.27 (q, 4H; 2R–CH₂–C), 0.76 (t, 6H; 2CH₃–R–C). IR: ν 1675s (C=O), 1108s (Ar–O–C). Formula weight of L^c: 1142.58. Analytical data, C 75.77 (calc. 75.63%); H 7.02 (6.88%); N 5.06 (4.90%).

2.4. Synthesis of complexes

An ethyl acetate solution of $Ln(NO_3)_3 \cdot 6H_2O$ [Ln = Eu(III) and Tb(III), 0.2 mmol] was added dropwise to a solution of the ligand L (0.1 mmol) in the ethyl acetate (30 ml). The mixture was stirred for 4 h and white precipitate formed. The precipitate was collected and washed three times with ethyl acetate. Further drying in vacuum afforded a pale white powder, yield: 75–80%.

3. Result and discussion

3.1. Properties of the complexes

Analytical data for the complexes listed in Table 1 conform to an 2:6:1 metal-to-nitrate-to-L stoichiometry [LnL]·[Ln(NO₃)₅]·(NO₃). All complexes are soluble in DMF, acetonitrile, THF, MeOH, acetone and dioxane, but sparingly soluble in water and ethyl acetate. The molar conductances of the complexes in acetone (see Table 1) indicate that all complexes act as 1:2 electrolytes [13].

3.2. IR spectra

The main infrared bands of the ligand and its complexes are presented in Table 2. The IR spectrum of free ligand shows bands at 1676 and 1108 cm⁻¹, which may be assigned to ν (C=O) and ν (C=O-C), respectively. In the IR spectra of all the lanthanide complexes, these bands shift by about 60 and 25 cm⁻¹ toward lower wave numbers, thus indicating that the carbonyl and ethe-

Table 1

Analytical and molar conductance data for the complexes (calculated values in parentheses)

Complexes	С	Н	Ν	Ln	Am (s cm ² mol ⁻¹)
$[EuL] \cdot [Eu(NO_3)_5] \cdot (NO_3)$	48.01 (47.53)	4.39 (4.32)	7.85 (7.70)	16.58 (16.71)	167
$[TbL] \cdot [Tb(NO_3)_5] \cdot (NO_3)$	47.06 (47.17)	4.20 (4.29)	7.52 (7.64)	17.69 (17.34)	171

Table 2

IR spectral data of the free ligands and their complexes (cm⁻¹)

Compound	v(C=0)	ν(C-O-C)	$v_1(NO_3^-)$	v ₃ (NO ₃ ⁻)	$v_4(NO_3^-)$	v(Free)
$\label{eq:linear} \begin{array}{c} \hline L \\ [EuL] \cdot [Ln(NO_3)_5] \cdot (NO_3) \\ [TbL] \cdot [Ln(NO_3)_5] \cdot (NO_3) \end{array}$	1676 1616 1621	1108 1093 1076	1492 1495	816 826	1310 1306	1384 1384

Table 3 Fluorescence data for the complexes

Complexes	Concentration (mol l^{-1})	Solvent	λ_{ex} (nm)	$\lambda_{em} (nm)$	RFI	Assignment
[TbL]·[Ln(NO ₃) ₅]·(NO ₃)	10^{-4}	Dioxane	326	492	360	${}^{5}D_{4}-{}^{7}F_{6}$
				547	401	${}^{5}D_{4}-{}^{7}F_{5}$
	10^{-4}	Acetone	344	493	240	${}^{5}D_{4}-{}^{7}F_{6}$
				547	352	${}^{5}D_{4}-{}^{7}F_{5}$
	10^{-4}	MeCN	329	492	438	${}^{5}D_{4}-{}^{7}F_{6}$
				547	782	${}^{5}D_{4}-{}^{7}F_{5}$
	10^{-4}	THF	329	491	319	${}^{5}D_{4}-{}^{7}F_{6}$
				547	277	${}^{5}D_{4}-{}^{7}F_{5}$
	10^{-4}	DMF	338	489	1108	${}^{5}D_{4}-{}^{7}F_{6}$
				547	547	${}^{5}D_{4}-{}^{7}F_{5}$
	10^{-4}	MeOH	331	492	459	${}^{5}D_{4}-{}^{7}F_{6}$
				547	773	${}^{5}D_{4}-{}^{7}F_{5}$
[EuL]·[Ln(NO ₃) ₅]·(NO ₃)	10^{-4}	Acetone	398	592	18	${}^{5}D_{0}-{}^{7}F_{1}$
				617	59	${}^{5}D_{0}-{}^{7}F_{2}$
	10^{-4}	MeCN	398	592	30	${}^{5}D_{0}-{}^{7}F_{1}$
				617	128	${}^{5}D_{0}-{}^{7}F_{2}$
	10^{-4}	DMF	398	591	36	${}^{5}D_{0}-{}^{7}F_{1}$
				617	56	${}^{5}D_{0}-{}^{7}F_{2}$
	10^{-4}	Dioxane	398	592	23	${}^{5}D_{0}-{}^{7}F_{1}$
				617	71	${}^{5}D_{0}-{}^{7}F_{2}$
	10^{-4}	THF	398	592	14	${}^{5}D_{0}-{}^{7}F_{1}$
				616	27	${}^{5}D_{0}-{}^{7}F_{2}$
	10^{-4}	MeOH	398	592	10	${}^{5}D_{0}-{}^{7}F_{1}$
				617	16	${}^{5}D_{0}-{}^{7}F_{2}$

RFI is relative fluorescence intensity.

real oxygen atoms take part in coordination to the metal ion (Table 2).

The absorption bands assigned to the coordinated nitrates were observed at about 1492 cm^{-1} (ν_1), 1310 cm^{-1} (ν_4) and 816 cm^{-1} (ν_3) for the complexes, respectively, implying that coordinated nitrate groups in the complexes are bidentate ligands [14]. The absorption band of about 1384 cm^{-1} suggests that there is free nitrate in the complexes, which is in agreement with the results of the conductivity experiments.

3.3. Fluorescence studies

Under identical experimental, the fluorescence characteristics of the complexes in dioxane, acetone, MeCN, THF, DMF and MeOH solutions are listed in Table 3. The ligand having multiple aromatic rings has a strong antenna effect. So its terbium and europium complexes have strong fluorescence. The fluorescence characteristic emission wavelengths of the terbium and europium ions were observed. In DMF solution, the terbium complex has the strongest fluorescence, and then in MeCN, MeOH, dioxane, acetone and THF solutions (Fig. 1). We can also see the fluorescence intensities for the europium complex become weaker from MeCN, dioxane, acetone, DMF, THF to MeOH solution (Fig. 2). This is due to the coordinating effects of solvents, which is solvate effect [15]. The amide-based portion of the ligand forms a caverned conformation suitable for the uptake of a lanthanide ion, but this ajar cavity could not prevent absolutely the solvent molecules from entering. Together with the raising coordination abilities of solutions for the lanthanide ions, the oscillatory motions of the entering molecules consume

more energy which the ligand triple level transfer to the emitting level of the lanthanide ion. Thus, the energy transfer could not be carried out perfectly.

In the emission spectra of the terbium complex, due to the present of a scattering signal near 491 nm, the peak height at 547 nm was used to measure the fluorescence intensities. Comparing Figs. 1 and 2, we can observe that the fluorescence intensities of terbium complex at 547 nm are stronger than those of europium complex at 617 nm in all sorts of solutions. Based on the theory of antenna effect [16,17], the luminescence of Ln^{3+}



Fig. 1. Emission spectra of the terbium complex in different solutions at room temperature concentration: $10^{-4} \text{ mol } l^{-1}$. In (1) DMF, (2) MeCN, (3) MeOH, (4) dioxane, (5) acetone and (6) THF solution.



Fig. 2. Emission spectra of the europium complex in different solutions at room temperature concentration: 10^{-4} mol⁻¹. In (1) MeCN, (2) dioxane, (3) acetone, (4) DMF, (5) THF and (6) MeOH solution.

chelates is related to the efficiency of the intramolecular energy transfer between the triple level of the ligand and the emitting level of the ions, which depends on the energy gap between the two levels. In organic solution, the energy gap between the ligand triple level and the emitting level of the terbium ion may be in favor of the energy transfer process.

4. Conclusion

According to the data and discussion above, the amide-based multipodal ligand could form complexes with lanthanide ions and exhibit a caverned conformation. The complexes exhibited characteristic fluorescence of europium and terbium ion, respectively. The different solvents may affect the fluorescence of europium and terbium ions. Based on those results, a series of new amide-based multipodal derivatives could be designed and synthesized to optimize the luminescent properties of these lanthanide ions.

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References

- N. Sabbatini, M. Guardigli, J.-M. Lehn, Coord. Chem. Rev. 123 (1993) 201.
- [2] S.T. Frey, M.L. Gong, W. de, W. Horrocks, Inorg. Chem. 33 (1994) 3229.
- [3] N. Sato, S. Shinkai, J. Chem. Soc., Perkin Trans. 2 (1993) 621.
- [4] C. Piguet, A.F. Williams, G. Bernardinelli, J.-C.G. Bünzli, Inorg. Chem. 32 (1993) 4139.
- [5] F.S. Richardson, Chem. Rev. 82 (1982) 541.
- [6] J.-C.G. Bünzli, in: J.-C.G. Bünzli, G.R. Choppin (Eds.), Lanthanide Probes in Life, Chemical and Earth Sciences, Elsevier, Amsterdam, 1989 (Chapter 7).
- [7] B.S. Panigrahi, Spectrochim. Acta 56 (2000) 1337.
- [8] C. Piguet, J.-C.G. Bünzli, G. Bernardinelli, G. Hopfgartner, S. Petoud, O. Schaad, J. Am. Chem. Soc. 118 (1996) 6681.
- [9] Y.-S. Yang, S.-H. Cai, Hua Xue Shi Ji 6 (1984) 133.
- [10] Y.Z. Ding, J.Z. Lu, Y.S. Yang, Hua Xue Shi Ji 8 (1986) 201.
- [11] G.Z. Tan, J.Z. Xu, T.Q. Jiao, You Ji Hua Xue 2 (1986) 143.
- [12] W. Yang, X.L. Teng, M. Chem, Talanta 46 (1998) 527.
- [13] W.J. Gear, Coord. Chem. Rev. 7 (1971) 81.
- [14] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, third ed., John Wiley, New York, 1978, p. 227.
- [15] H.Q. Liu, T.C. Cheung, C.M. Che, Chem. Commun. (1996) 1039.
- [16] J.-M. Lehn, Angew. Chem. Int. Ed. Engl. 29 (1990) 1304.
- [17] M. Larva, H. Takalo, K. Simberg, J. Kankare, J. Chem. Soc., Perkin Trans. 2 (1995) 995.