Synthesis, Characterization and Luminescence of Lanthanide Chloride Complexes with N,N,N′,N′-Tetra[(2-benzimidazolyl) methyl]-1,2-Ethanediamine

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Abstract: N,N,N′,N′-tetra[(2-benzimidazolyl)methyl]-1,2-ethanediamine (EDTB) lanthanide chloride complexes were prepared (Ln^{3+}=Eu^{3+}, Tb^{3+} or Gd^{3+}). The results of single crystal X-ray structural analysis show that $[(EDTB)GdCl_2]Cl(C_2H_5OH)(H_2O)_2$ crystal is in space group $P2_1/c$ with a=8.848(2) Å, b=26.313(5) Å, c=18.929(4) Å, β=97.82(3)°, V=4366(2) Å^3, Z=4. The luminescent properties of the terbium and europium complexes have been studied.

Keywords: N,N,N′,N′-Tetra[(2-benzimidazolyl)methyl]-1,2-ethanediamine, lanthanide complexes, crystal structure, luminescent properties.

Imidazole groups play an important role in the coordination chemistry of the metal ions in many biological systems[1]. Earlier work has established its suitability for formations of binuclear copper[1], iron[2] and manganese[3] complexes. Reaction of EDTB with $Cu(H_2O)_6(BF_4)_2$ in absolute ethanol has given a six-coordinate complex of $[Cu(EDTB)](BF_4)(BF_3 \cdot O(C_2H_5)_2)H_2O$[4]. Rare earth ions have similar physical and chemical properties with Ca^{2+} and Mg^{2+} which are important in biological systems. Wang *et al.*[5] presented crystal structures and luminescence spectra of ten-coordinate lanthanide complexes (Ln^{3+}=Ce^{3+}, Sm^{3+}, Eu^{3+} or Tb^{3+}) with 2, 6-bis (2-benzimidazolyl) pyridine. In this paper, we report the synthesis and characterization of lanthanide chloride complexes (Ln^{3+}=Eu^{3+}, Tb^{3+} or Gd^{3+}) with EDTB. The data show that the complexes of Tb and Eu have longer emission lifetime.

Experimental

The EDTB was synthesized according to the literature method[4]. The ligand EDTB (1.0 mmol) was added into a stirred solution of $LnCl_3$ (1.0mmol) in absolute anhydrous ethanol (40mL) and the mixture was refluxed for four hours under nitrogen atmosphere. Then the system was cooled and filtered. The precipitate was disolved in absolute anhydrous ethanol under heating. After cooling, the precipitate was collected and dried under vacuum. The single crystal of the gadolinium complex was prepared by slowly diffusing n-hexane into a solution of the product in ethanol for a week. The C, H, N elemental analysis agrees with the formula of $C_{36}H_{42}LnCl_3N_{10}O_3$ (Ln^{3+}=Eu^{3+}, Tb^{3+} or Gd^{3+}) with the calculated value in brackets. Ln=Eu: C 46.87 (46.94), H 4.40 (4.60), N 15.08 (15.21); Ln=Tb: C 46.73 (46.59), H 4.31 (4.56), N 14.73 (15.09); Ln=Gd: C 46.49 (46.47), H 4.38 (4.57), N 14.98 (15.12). Infrared spectra of the complexes showed ν_{N-H} (benzimidazolyl): 3369 cm^{-1}, ν_{C-H} (phenyl): 3042 cm^{-1}, $\nu_{C=N}$ (benzimidazolyl): 1624 cm^{-1} and ν_{C-C} (phenyl): 1471-1596 cm^{-1}.

The crystal of $[(EDTB)GdCl_2]Cl(C_2H_5OH)(H_2O)_2$ was sealed in a 0.5 mm Lindemann glass capillary. Diffraction measurement was made on a Rigaku AFC7R system using Mo $K\alpha$ radiation (λ=0.71073 Å) at room temperature (293 k). The crystallographic data are given in **Table 1**.

Table 1 Data collection and processing parameters of $[(EDTB)GdCl_2]Cl(C_2H_5OH)(H_2O)_2$

Molecular		$C_{36}H_{42}N_{10}GdCl_3O_3$	
M	926.4	μ /cm^{-1}	17.48
Crystal system	monoclinic	2θ range/°	5-55
Space group	$P2_1/c$	Collection range	$0 \leqslant h \leqslant 8$
Crystal size/mm	0.40×0.40×0.20		$0 \leqslant k \leqslant 28$
a/Å	8.848(2)		$-20 \leqslant l \leqslant 20$
b/Å	26.313(5)	No. of data independent	5038(R_{int} = 0.029)
c/Å	18.929(4)	No. of variables, p	484
β/°	97.82(3)	No. of data used, n	3655[$F_o > 6.0\sigma(F_o)$]
V/Å^3	4366(2)	R_F	0.041
Z	4	$_wR$	0.057
F(000)	1884	Goodness-of-Fit	1.48
D_c/ g·cm^{-3}	1.437	Largest and mean Δ/σ	0.041, 0.005

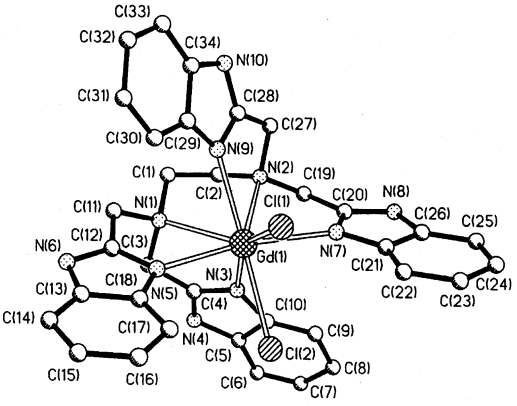
Results and Discussion

The selected bond lengths (Å) for $[(EDTB)GdCl_2]Cl(C_2H_5OH)(H_2O)_2$ are listed in **Table 2**. **Figure 1** shows the molecular structure. The Gd(Ⅲ) ion is eight-coordinated by six nitrogen atoms from one EDTB ligand and two chlorine atoms. The coordination polyhedron about Gd atom is in the form of a square antiprism with N(2), N(7), N(9) and Cl(1) in one plane, and N(1), N(3), N(5) and Cl(2) in the other one, in which N(3), N(5), N(7) and N(9) are from benzimidazolyl, while N(1) and N(2) from ethanediamine. The average deviations of these atoms from the planes are 0.127 Å and 0.107 Å respectively. The dihedral angle between the planes is 5°. The distances of Gd atom to both planes are 1.422 Å and 1.430 Å respectively. As show in **Table 2**, the Gd-N bond lengths in $[(EDTBGdCl_2)]Cl(C_2H_5OH)(H_2O)_2$ can be divided into two groups: (a) Gd-N(1) and Gd-N(2), average band length is 2.693 Å; (b) Gd- N (3), Gd-N(5), Gd-N(7) and Gd-N(9), average bond length is 2.504 Å, which appears that Gd-N bonds from benzimidazoles are stronger than Gd-N bonds from ethylenediamine.

Table 2 Selected Bond Lengths (Å) for $[(EDTB)GdCl_2]Cl(C_2H_5OH)(H_2O)_2$

Gd(1)-Cl(1)	2.662(2)	Gd(1)-Cl(2)	2.741(3)
Gd(1)-N(1)	2.697(5)	Gd(1)-N(2)	2.688(5)
Gd(1)-N(3)	2.510(4)	Gd(1)-N(5)	2.501(6)
Gd(1)-N(7)	2.510(6)	Gd(1)-N(9)	2.494(5)

Figure 1 Crystal structure of $[(EDTB)\ GdCl_2]Cl(C_2H_5OH)(H_2O)_2$



The free ligand EDTB and the gadolinium complex present no fluorescence in solid state. When the emission light was fixed at 545 nm, the excitation spectrum of the terbium complex in the solid state presents one main excitation band at 255 nm. When the emission light was fixed at 610 nm, the excitation spectrum of the europium complex in the solid state presents two main excitation bands at 246 and 342 nm.

Upon excitation around 250 nm, the terbium and europium complexes exhibit strong ionic characteristic red and green emission, respectively. For europium complex, the emission peaks at 591, 613, 649, 700 nm can be attributed to the $^5D_0 \rightarrow {}^7F_j$ (j=1-4) transition. The electric dipolar $^5D_0 \rightarrow {}^7F_2$ transition and the magnetic dipolar $^5D_0 \rightarrow {}^7F_1$ transition almost have the same intensity. The terbium complex also shows two strong fluorescent peaks at 492 nm and 546 nm, with the same intensities which can be attributed to the $^5D_4 \rightarrow {}^7F_j$ (j=5-6) electronic transitions. This really unusual phenomenon suggests the europium or terbium ion is located in a symmetry environment[6]. It is in agreement with the crystallographic results revealing that rare earth ion has a *center* of symmetry.

Comparing the two complexes, one can find that the fluorescent intensity of the terbium complex is greatly stronger than that of europium complex. It means the triplet energy level of the ligand matched as well with the 4f excited state energy level of terbium ion, but not matched well with that of the europium ion. Because the $^5D_4$ excited state energy level of terbium ion is higher than the $^5D_0$ excited state energy level of the europium ion. This effect results in the more energy transfer efficiency from the ligand to the terbium ion, and the stronger fluorescent intensity of the terbium complex.

The fluorescence lifetime could be evaluated by measuring the phase shift and the relative modulation of the samples at different modulated frequency[6]. Data shows that both samples exhibit only one fluorescent component and the emission lifetime of the europium and terbium complexes are 0.34ms and 1.9ms, respectively. Terbium complex in the solid state possesses longer fluorescence lifetime, which is about 4-5 times longer than that of terbium complexes with β–diketones[7], but shorter than that of its complexes with ligand containing phosphine oxide groups $Tb[Ph_2P(O)NP(O)Ph_2]_3$ (2.8ms)[8]. However, the lifetime of the Eu(Ⅲ) complex is agreed with the common europium complex with β–diketones[9].

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References

1. H. M. J. Hendriks, P. J. M. W. L. Birker, J. V. Rijn, *et al*., *J. Am. Chem. Soc*., **1982**, *104* (13), 3607.
2. A. K. Tripathi, P. Mathur, *J. Indian Chem. Soc*., **1993**, *70* (11-12), 991.
3. A. K. Tripathi, K. K. Sharma, P. Mathur, *Indian J. Chem., Sect. A*, **1991**, *30* (5), 400.
4. P. J. M. W. L. Birker, H. M. J. Hendriks, J. Reedijk *et al*., *Inorg. Chem*., **1981**, *20* (8): 2408.
5. S. X. Wang, Y. Zhu, Y. X. Cui, *et al*., *J. Chem. Soc. Dalton Trans*., **1994**, *17*, 2523.
6. J. R. Lakowicz, "*Topics in Fluorescence Spectroscopy*". Vol.1, Plenum, New York, **1991**, p.4-6.
7. Q. Li, D. J. Zhou, C. H. Huang, *et al*., *J. Chin. Rare Earth Soc*., **1997**, *15* (4), 295.
8. S. W. Magennis, S. Parsons, A. Corval, *et al*., *Chem. Commun*., **1999**, *1*, 61.
9. D. J. Zhou, C. H. Huang, G. Q. Yao *et al*., *J. Alloys and Compounds*, **1996**, *235*, 156.

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