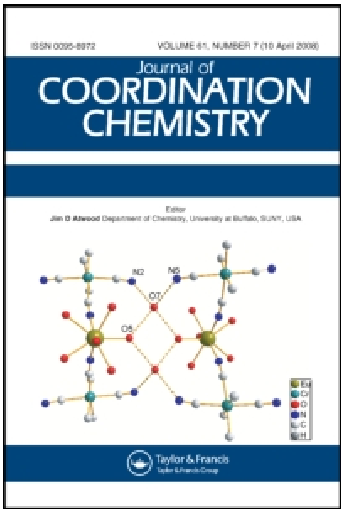

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Lanthanide trifluoromethanesulfonate complexes with ϵ-caprolactam: Synthesis, characterization and structure of the praseodymium compound

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LANTHANIDE TRIFLUOROMETHANESULFONATE COMPLEXES WITH ϵ-CAPROLACTAM: SYNTHESIS, CHARACTERIZATION AND STRUCTURE OF THE PRASEODYMIUM COMPOUND

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Complexes of formulas $[Ln(\epsilon\text{-cl})_8](F_3C\text{-}SO_3)_3$ (Ln = La-Eu) and $[Ln(\epsilon\text{-cl})_7](F_3C\text{-}SO_3)_3$ (Ln = Gd, Tb, Dy, Yb, Lu, ϵ-cl = ϵ-caprolactam) were synthesized and characterized by elemental analysis, infrared spectroscopy, visible absorption spectroscopy of the Nd compound and emission spectroscopy of the Eu compound and the Gd compound, doped with Eu. IR experimental data suggest that the ϵ-caprolactams are bonded to the central ions through the carbonyl oxygen and that the anions are not coordinated. The parameters calculated from the visible absorption spectrum of the Nd compound suggest electrostatic metal-ligand bonds. The emission spectrum of the europium compound suggests a D_{2d} distorted towards C_{2v} symmetry. X-ray single crystal analysis of the Pr compound shows that the anions are not coordinated and that the coordination polyhedron around the Pr^{3+} ion has a slightly distorted D_{2d} (dodecahedral) symmetry.

Keywords: lanthanide complexes; caprolactam; crystal structure

INTRODUCTION

Lanthanide complexes containing δ-valeroctam and the poorly-coordinating anions trifluoromethanesulfonate [1, 2] and perchlorate [3, 4] have been investigated in our laboratories. The following compositions were obtained: $[LnL_8]$ $(F_3CSO_3)_3$. (Ln = La-Lu, Y) [1], $[LnL_8]$ $(ClO_4)_3$ (Ln = La-Tb) and $[LnL_7](ClO_4)_3$ (Ln = Er-Lu, Y and L = δ-valeroctam).[3] The structure of the $[NdL_8](ClO_4)_3$ was determined showing that the neodymium ions are coordinated in a square-antiprismatic arrangement to eight oxygens of the δ-valeroctam ligands.[3]

In this work, in an attempt to verify the behavior of a bulky ligand in relation to lanthanide trifluoromethanesulfonates, complexes containing ϵ-caprolactam were prepared. The compounds had compositions: $[Ln(\epsilon\text{-cl})_8](F_3CSO_3)_3$ (Ln = La-Eu) and $[Ln(\epsilon\text{-cl})_7](F_3CSO_3)_3$ (Ln = Gd-Dy, Yb, Lu). The physiocochemical characterizations with the crystal structure of the Pr derivative are the subject of the present paper.

EXPERIMENTAL

The complexes were obtained by reaction of the hydrated lanthanide trifluoromethanesulfonates with a slight excess of ϵ-caprolactam in triethylorthoformate (teof). The solutions were concentrated in a rotary-evaporator and cooled to allow precipitation of the complexes. The solids were filtered, washed with teof and dried *in vacuo* over anhydrous calcium chloride. Single crystals of the Pr compound were obtained by slow evaporation of the solution.

Lanthanide analyses were carried out by titration with EDTA, using xylenol orange as indicator. CHN elemental analyses were performed on a Perkin-Elmer 240 elemental analyzer. IR spectra were recorded on a FTIR 1750 Perkin-Elmer spectrophotometer, using Nujol mulls between KBr plates. Visible absorption spectra were determined on a Zeiss DMR-10 spectrophotometer. Emission spectra were recorded on a Perkin-Elmer MPF-4 spectrofluorimeter. X-ray powder diffraction patterns were determined on a Rigaku RU-200B instrument using CuKα radiation. Single crystal X-ray diffraction analysis was carried out on an Enraf-Nonius CAD-4 Apparatus. Most calculations were carried out on a Vax computer, using the programs SHELX 76,[5] SHELXS 86 [6] and ORTEP.[7] Solution conductivities in acetonitrile and nitromethane were measured on a homemade bridge, consisting of a galvanometer, a resistance box

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*Corresponding author.

TABLE I Summary of analytical results.

Ln	*Analysis(%)*							
	Lanthanide		*Carbon*		*Hydrogen*		*Nitrogen*	
	Theor.	*Exp.*	*Theor.*	*Exp.*	*Theor.*	*Exp.*	*Theor.*	*Exp.*
La	9.3	9.4	41.1	41.1	6.0	5.4	7.5	7.5
Ce	9.4	9.5	41.1	41.3	6.0	5.7	7.5	7.7
Pr	9.4	9.7	41.0	40.9	6.0	5.8	7.5	7.5
Nd	9.6	9.7	40.9	40.9	5.9	5.7	7.5	7.2
Sm	10.0	10.3	40.9	40.8	5.9	5.8	7.4	7.2
Eu	10.1	10.2	40.7	40.6	5.9	5.6	7.4	7.4
Gd	11.3	10.8	38.7	37.8	5.6	5.5	7.0	7.0
Tb	11.4	11.1	38.7	38.9	5.6	5.6	7.0	6.9
Dy	11.6	11.5	38.6	38.4	5.5	5.5	7.0	7.2
Yb	12.3	12.7	38.3	37.9	5.5	5.8	6.9	6.6
Lu	12.4	12.2	38.2	37.8	5.5	5.4	6.9	7.0

and a cell ($K_c = 0.10708$ cm^{-1}) from Leeds and Northrup. Thermal analysis (TG/DTG) were performed on a Perkin-Elmer TGA 7 Delta series instrument, under dynamic air atmosphere and a heating rate of 10°C min^{-1}.

RESULTS AND DISCUSSION

Table I presents the analytical data for the compounds synthesized, indicating clearly the general formulas: $[\mathrm{Ln}(\epsilon\text{-cl})_8](\mathrm{F_3CSO_3})_3$ (Ln = La-Eu) and $[\mathrm{Ln}(\epsilon\text{-cl})_7](\mathrm{F_3CSO_3})_3$ (Ln = Gd, Tb, Dy, Yb, Lu).

Electrolytic molar conductance of the compounds vary between 250-290 S cm^2 mol^{-1} in acetonitrile and 90-130 S cm^2 mol^{-1} in nitromethane, suggesting 1:2 electrolytes.[8] The formation of ion pairs, however, is fairly common in this type of compound.[3, 9]

The IR absorption spectra of all compounds have the carbonyl stretch shifted to lower frequencies (~1620 cm^{-1}) as compared with free ε-caprolactam (1650 cm^{-1}),[10] indicating coordination through the carbonyl oxygen. With respect to the trifluoromethanesulfonate for $\nu_{as}SO_3$, $\nu_{s}SO_3$ and δSO_3, no shift is observed (except for a splitting of $\nu_{as}SO_3$, but not for the other frequencies) suggesting that the anions are not coordinated to the central ions.

X-ray powder diffraction patterns suggest the existence of six different structures: a) La, b) Ce-Sm, c) Eu, d) Gd, e) Tb, f) Dy, Yb, Lu. These results point to different arrangements of molecules inside the crystals throughout the series, despite the fact that only two stoichiometries exist.

Visible absorption spectra for the Nd compound, using a silicone mull for the solid and a 0.01 mol L^{-1} acetonitrile solution, were recorded. They are very

TABLE II Crystal data and structure refinement

Empirical formula	$C_{51} H_{88} F_9 N_8 O_{17} Pr S_3$
Formula weight	1493.38
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system	monoclinic
Space group	$P2_1/a$
Unit cell dimensions	$a = 20.124(2)$ Å $b = 15.529(3)$ Å $c = 22.889(4)$ Å $\beta = 102.957(10)°$
Volume	6970(2) $Å^3$
Z	4
Density (calculated)	1.423 Mg/m^3
Absorption coefficient	0.883 mm^{-1}
F(000)	3096
Crystal size	0.35 × 0.30 × 0.20 mm
Theta range for data collection	0.91 to 24.97°
Index ranges	$-23 < = h < = 0, 0 < = k < = 18, -26 < = l < = 27$
Reflections collected	12614
Independent reflections	12222 [R(int) = 0.0580]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	12211/0/802
Goodness-of-fit on F^2	1.067
Final R indices [I > 2sigma(I)]	$R1 = 0.0869$, wR2 = 0.1946
R indices (all data)	$R1 = 0.2344$, wR2 = 0.3265
Largest diff. peak and hole	1.341 and −0.637 e.A^{-3}

similar, indicating a small interaction with the solvent. The splitting of the $^4G_{5/2}$, $^2G_{7/2} \leftarrow {}^4I_{9/2}$ band suggests a non cubic coordination symmetry, having its baricenter at 17215 cm^{-1}. From these spectra the oscillator strength ($P = 18.6 \times 10^{-5}$) the nephelauxetic parameter [11] ($\beta = 0.993$), covalent factor [12] ($b^{1/2} = 0.060$) and Sinha's covalent parameter [13] ($\delta = 0.74$) were calculated. These values suggest an essentially electrostatic character for the metal-ligand bonds.

Figure 1 shows the emission spectrum of the Eu complex at 77K. The presence of a single weak $^5D_0 \rightarrow {}^7F_0$ peak, four peaks in the region of the $^5D_0 \rightarrow {}^7F_1$ transition (the first two due to E species, one due to distortion of the polyhedron and the fourth due to magnetic dipole allowed A_2 species) and three peaks and a shoulder for the $^5D_0 \rightarrow {}^7F_2$ transition (two due to E species, one to electric dipole allowed B_2 species and a shoulder due to distortion) were interpreted in terms of a D_{2d} symmetry distorted to C_{2v} for the coordination polyhedron around the Eu^{3+} ion.[14] The emission spectrum of the gadolinium compound doped with 2% (mol) of Eu is practically identical to that of the europium compound, the only difference being the appearance of the $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ bands.

TABLE III Atomic coordinates (for 1×10^4) and equivalent isotropic displacement parameters (Å^2 $\times 10^3$). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	*y*	*z*	*U(eq)*
Pr	2133(1)	727(1)	7334(1)	54(1)
S(1)	949(3)	4125(4)	8492(3)	90(2)
O(11)	500(11)	3912(13)	8850(10)	188(9)
O(12)	1404(7)	3473(9)	8398(7)	122(5)
O(13)	646(10)	4568(12)	7959(9)	177(9)
C(1)	1478(16)	4892(15)	8937(12)	112(8)
F(11)	1842(10)	4616(12)	9431(7)	172(7)
F(12)	1162(9)	5604(12)	9003(10)	217(10)
F(13)	1969(10)	5172(12)	8665(10)	192(8)
S(2)	3516(3)	2521(5)	5206(3)	107(2)
O(21)	3001(8)	2543(15)	4708(8)	182(9)
O(22)	3380(8)	1932(11)	5648(7)	136(6)
O(23)	3836(10)	3321(10)	5450(8)	147(6)
C(2)	4231(11)	2017(16)	4951(12)	131(10)
F(21)	4421(10)	2477(15)	4565(8)	215(10)
F(22)	4018(10)	1276(13)	4725(10)	230(13)
F(23)	4735(8)	1899(12)	5420(9)	185(7)
S(3)	1120(14)	810(16)	1552(10)	741(35)
O(31)	1178(19)	−36(16)	1684(17)	445(27)
O(32)	1737(12)	1128(15)	1462(12)	202(11)
O(33)	484(13)	1217(31)	1268(16)	442(44)
C(3)	1088(8)	1265(9)	2332(8)	68(4)
F(31)	1565(16)	915(19)	2679(13)	393(20)
F(32)	498(11)	952(15)	2351(15)	293(17)
F(33)	1122(13)	2070(14)	2253(11)	297(12)
O(1)	881(5)	599(7)	7078(5)	84(3)
N(1)	−214(6)	634(10)	7092(7)	89(5)
C(11)	329(8)	1007(11)	6968(8)	74(5)
C(12)	289(8)	1899(11)	6725(8)	79(5)
C(13)	156(11)	2551(12)	7164(10)	101(7)
C(14)	−592(9)	2617(12)	7217(10)	97(7)
C(15)	−886(10)	1814(13)	7430(9)	96(6)
C(16)	−901(8)	1053(12)	6990(10)	88(6)
O(2)	1687(6)	1175(8)	8201(5)	82(3)
N(2)	1063(9)	1656(10)	8814(7)	94(5)
C(21)	1301(9)	1016(11)	8529(8)	79(5)
C(22)	1118(14)	95(11)	8644(9)	133(10)
C(23)	1380(17)	−156(15)	9269(12)	178(15)
C(24)	897(19)	111(15)	9700(11)	179(16)
C(25)	896(18)	1115(17)	9781(11)	179(15)
C(26)	585(13)	1564(15)	9233(11)	137(10)
O(3)	3117(5)	1343(7)	8067(5)	72(3)
N(3)	2868(7)	2512(10)	8549(7)	91(5)
C(31)	3285(8)	1897(11)	8476(7)	66(5)
C(32)	3993(8)	1851(15)	8874(9)	105(8)
C(33)	3948(14)	1615(18)	9515(10)	155(13)

TABLE III *continued*

	x	*y*	*z*	*U(eq)*
C(34)	3808(16)	2388(18)	9885(9)	156(12)
C(35)	3081(13)	2764(19)	9643(11)	142(10)
C(36)	3029(13)	3175(13)	9020(12)	133(12)
O(4)	2510(6)	−416(8)	8080(5)	82(4)
N(4)	3657(8)	−467(12)	8307(8)	103(6)
C(41)	3047(10)	−783(12)	8334(8)	79(5)
C(42)	3018(11)	−1609(14)	8699(11)	110(8)
C(43)	3360(17)	−1450(18)	9364(11)	140(11)
C(44)	4153(12)	−1587(21)	9509(10)	131(10)
C(45)	4497(13)	−851(18)	9211(12)	131(10)
C(46)	4345(11)	−886(17)	8545(11)	122(8)
O(5)	3191(6)	325(8)	7079(6)	85(4)
N(5)	4213(13)	129(16)	6668(13)	241(11)
C(51)	3487(12)	−132(17)	6759(12)	117(8)
C(52)	3133(11)	−716(17)	6396(11)	145(8)
C(53)	3370(19)	−937(27)	5765(17)	252(16)
C(54)	3892(19)	−1513(21)	5969(15)	216(12)
C(55)	4518(12)	−932(15)	6040(10)	163(7)
C(56)	4644(20)	−631(27)	6743(19)	280(17)
O(6)	1858(6)	−705(8)	6842(6)	97(4)
N(6)	985(10)	−1353(13)	7078(13)	160(11)
C(61)	1566(11)	−1395(13)	6905(10)	100(7)
C(62)	1850(17)	−2226(14)	6766(14)	159(13)
C(63)	2000(17)	−2839(27)	7242(18)	236(29)
C(64)	1452(19)	−3242(19)	7498(15)	191(15)
C(65)	934(20)	−2670(27)	7685(18)	220(27)
C(66)	559(14)	−2103(22)	7159(22)	258(25)
O(7)	1946(7)	968(8)	6270(5)	95(4)
N(7)	2159(7)	822(10)	5375(6)	81(4)
C(71)	1754(8)	733(12)	5750(7)	72(4)
C(72)	1058(8)	326(12)	5527(7)	83(6)
C(73)	608(10)	910(15)	5082(10)	115(8)
C(74)	722(13)	794(17)	4426(9)	137(11)
C(75)	1442(16)	1082(19)	4367(10)	147(11)
C(76)	1995(11)	578(16)	4720(9)	119(8)
O(8)	2071(6)	2271(6)	7225(5)	77(3)
N(8)	1842(8)	3664(9)	7185(6)	82(4)
C(81)	2081(8)	2985(10)	6965(7)	66(4)
C(82)	2324(9)	3021(11)	6391(7)	79(5)
C(83)	1743(11)	3249(13)	5869(8)	103(7)
C(84)	1564(13)	4218(14)	5811(9)	123(8)
C(85)	1291(13)	4583(16)	6334(11)	134(9)
C(86)	1811(14)	4536(10)	6937(10)	128(10)

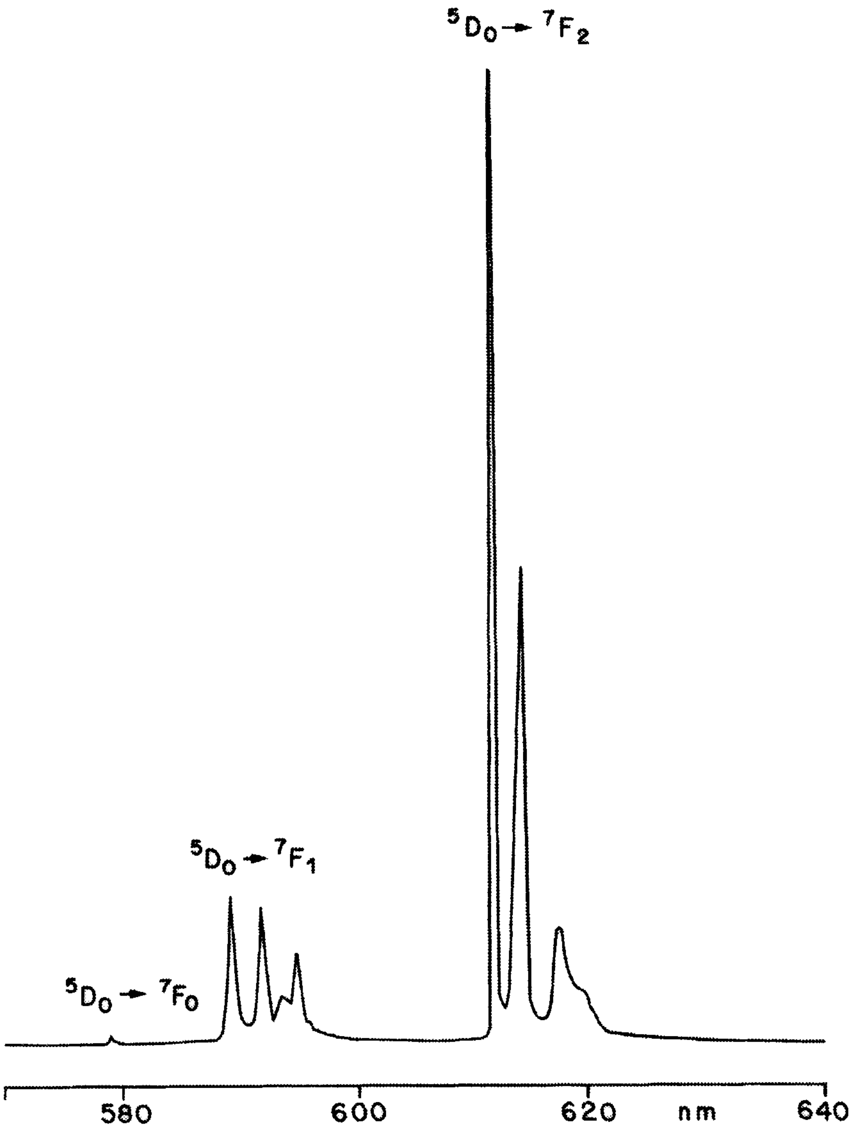

FIGURE 1 Emission spectrum of the europium complex at 77K.

Tables II, III and IV show the crystallographic parameters, fractional atomic coordinates and selected bond distances and angles, determined for the Pr compound by single crystal X-ray diffraction.

Figure 2 shows the ORTEP view of the complex species and Figure 3 details the coordination polyhedron. The unit cell contains four complex species. The anions are distant from the praseodymium ion, while the ϵ-caprolactams are arranged in a slightly distorted dodecahedron (D_{2d} distorted towards C_{2v}) around the central ion. Since this is a distorted dodecahedron, it is not clear, from the Pr-O distances, which of the oxygen atoms are in the two possible positions (in a perfect dodecahedron) with respect to the central ion. As can be seen in Table IV, three different Pr-O distances appear. It is important to emphasize the agreement of the luminescence spectrum indication of coordination symmetry with the

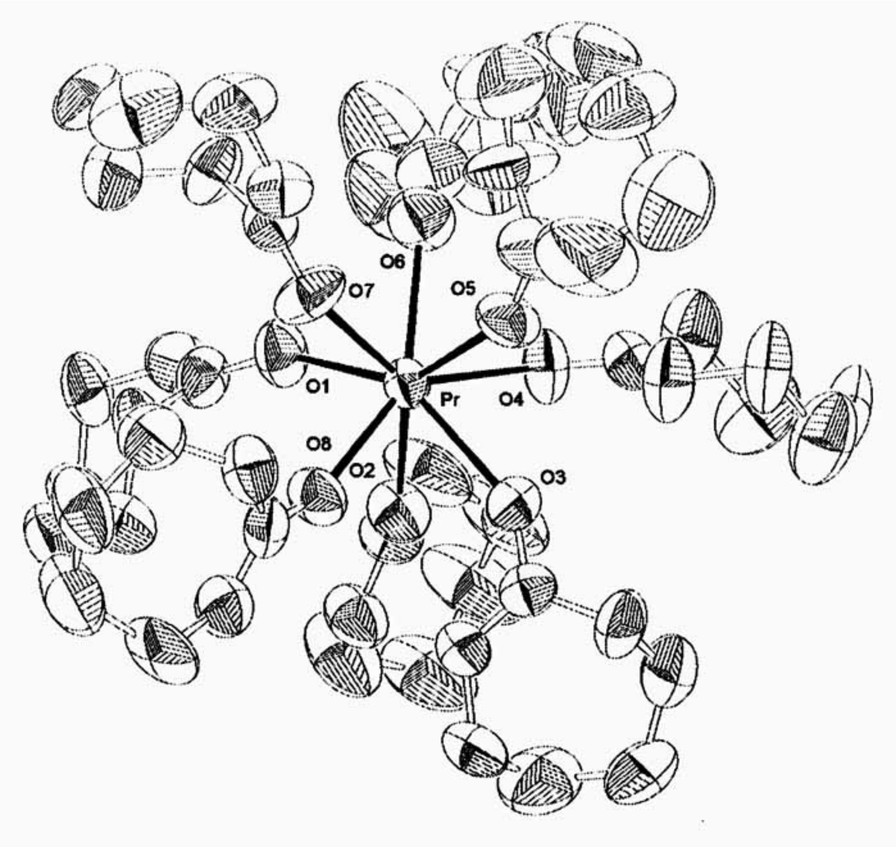

FIGURE 2 ORTEP view of the praseodymium complex.

actual structure, pointing out the reliability of emission spectroscopy for this purpose.

Thermal analyses were made for the compounds of Pr^{3+}-Tb^{3+}, Yb^{3+} and Lu^{3+}. In practically all cases the ligands (caprolactams) are lost up to 300°C (573 K). The final decomposition, according to Roberts and Bykowski [15] occurs with elimination of COF_2 and SO_2. Most of the residues at about 600°C (873 K) were identified as LnF_3, but at the end of the series at ~900°C (1173 K) LnOF was also obtained. Between ~120°C and ~400°C no patamars were observed, so it was impossible to identify intermediates. Figures 4 and 5 contain TG/DTG curves representative for the decomposition of the compounds.

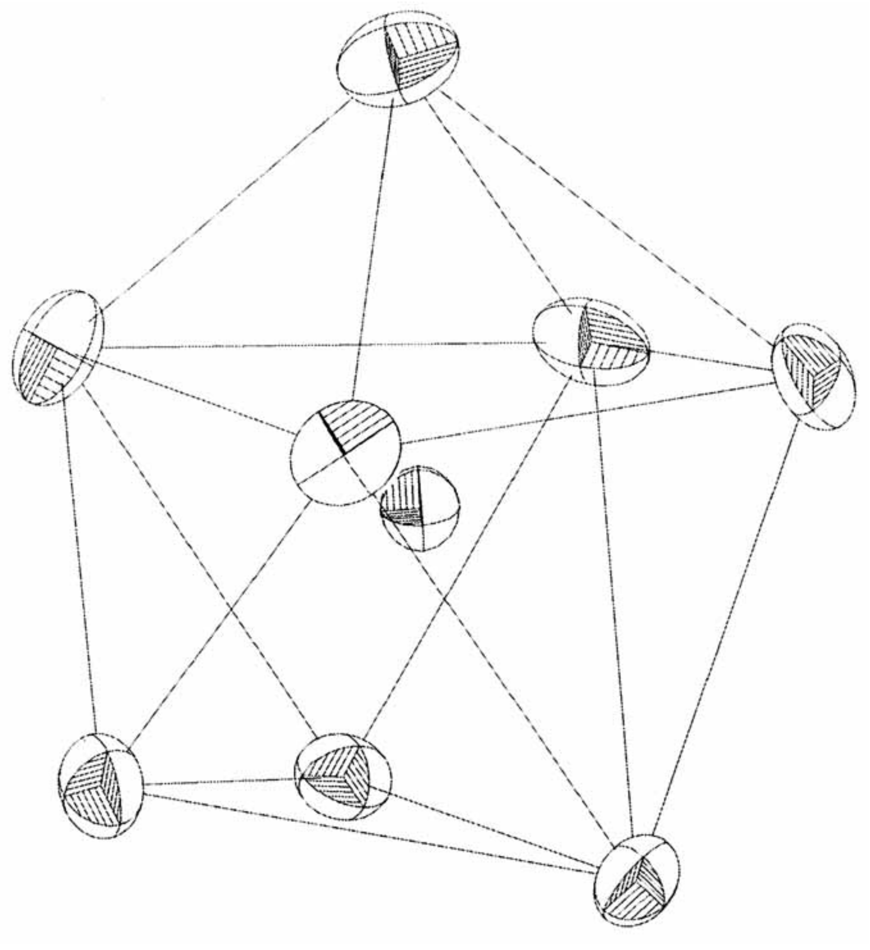

FIGURE 3 Details of the coordination polyhedron.

TABLE IV Bond lengths [Å] and angles [deg] around the Pr ion

Pr-O(5)	2.413(11)
Pr-O(7)	2.409(10)
Pr-O(8)	2.410(10)
Pr-O(4)	2.462(11)
Pr-O(2)	2.456(11)
Pr-O(1)	2.464(10)
Pr-O(3)	2.482(10)
Pr-O(6)	2.499(12)
O(5)-Pr-O(7)	75.0(5)
O(5)-Pr-O(8)	105.1(4)
O(7)-Pr-O(8)	75.4(4)
O(5)-Pr-O(4)	80.2(4)
O(7)-Pr-O(4)	140.1(4)
O(8)-Pr-O(4)	142.2(4)
O(5)-Pr-O(2)	140.5(4)
O(7)-Pr-O(2)	140.4(4)
O(8)-Pr-O(2)	77.4(4)
O(4)-Pr-O(2)	75.9(4)
O(5)-Pr-O(1)	146.3(4)
O(7)-Pr-O(1)	81.5(4)
O(8)-Pr-O(1)	91.6(4)
O(4)-Pr-O(1)	104.3(4)
O(2)-Pr-O(1)	71.0(4)
O(5)-Pr-O(3)	69.5(4)
O(7)-Pr-O(3)	122.9(4)
O(8)-Pr-O(3)	72.7(4)
O(4)-Pr-O(3)	74.6(4)
O(2)-Pr-O(3)	74.1(4)
O(1)-Pr-O(3)	144.1(4)
O(5)-Pr-O(6)	77.2(4)
O(7)-Pr-O(6)	73.4(4)
O(8)-Pr-O(6)	146.8(4)
O(4)-Pr-O(6)	70.9(4)
O(2)-Pr-O(6)	122.2(4)
O(1)-Pr-O(6)	73.1(4)
O(3)-Pr-O(6)	135.3(4)

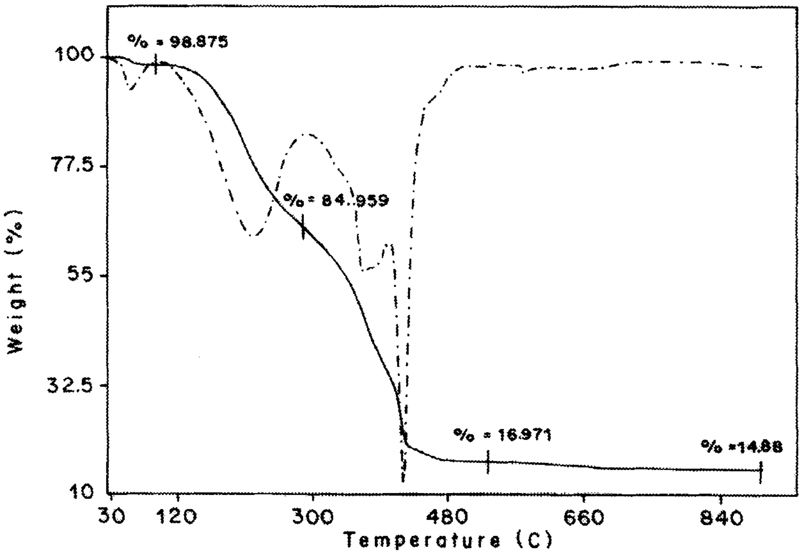

FIGURE 4 TG/DTG curves of the gadolinium complex.

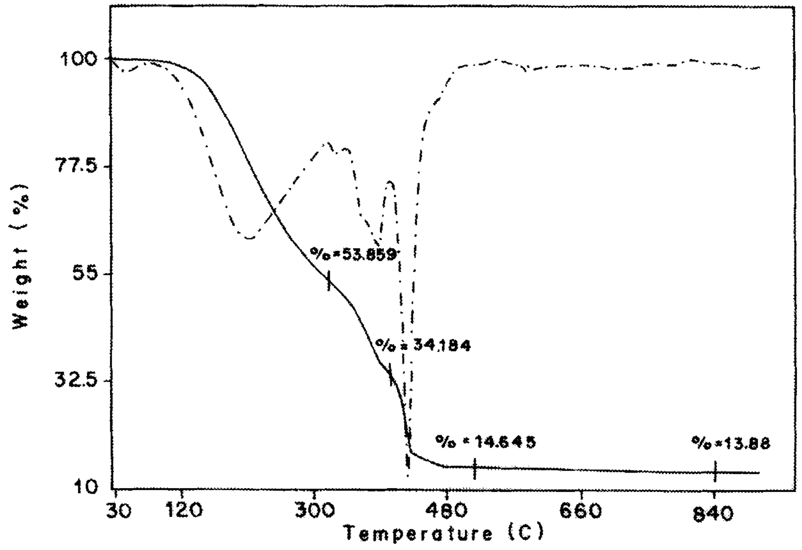

FIGURE 5 TG/DTG curves of the ytterbium complex.

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