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Crystal Structure and Emission Spectrum of the Undecacoordinate Complex Tris(nitrato)(1,4,7,10,13-pentaoxacyclopentadecane)europium(III)[1]

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The crystal and molecular structure of tris(nitrato)(1,4,7,10,13-pentaoxacyclopentadecane)europium(III), $Eu(NO_3)_3(C_{10}H_{20}O_5)$, has been determined from single-crystal X-ray diffraction. The complex crystallizes in the trigonal space group $P3_1$ with $Z = 3$. Lattice parameters are $a = 8.845$ (3) Å, $c = 20.330$ (4) Å, and $\gamma = 120°$. The structure was solved by Patterson and Fourier techniques and refined by least squares to a final conventional R value of 0.037. The europium(III) ion is 11-coordinate and bonded to three bidentate nitrate groups and to the five oxygen atoms of the crown ether. The Eu–O(nitrate) and Eu–O(ether) distances lie in the ranges 2.43–2.65 and 2.55–2.69 Å, respectively. The nitrate groups are planar with N–O bond lengths between 1.21 and 1.31 Å. The five CH_2CH_2 moieties of the macrocycle have a slight fluxional motion at room temperature. The coordination polyhedron of the Eu(III) ion is discussed. The ionic radius of the 11-coordinate Eu(III) ion is 1.25 Å. Crystal field splittings, obtained from the high-resolution fluorescence spectrum at 77 K, are reported for the $^5D_1$, $^5D_2$, $^7F_1$, $^7F_2$, and $^7F_4$ electronic levels. Interpretation of these splittings leads to the conclusion that the 11-coordinate polyhedron of the Eu(III) ion can be viewed as a distortion of either a pentagonal or a hexagonal symmetry.

Introduction

Complexes between lanthanoid salts and multidentate macrocyclic ligands, namely, crown ethers[3] and cryptands, attract considerable interest.[5] Among several important properties, crown ethers may, for instance, be used to force the rare earth ion to adopt any given coordination number (CN) between 7 and 12,[6] provided a suitable choice of the counterion, of the cavity diameter, and of the number of donor atoms is made. Of special interest are complexes in which the rare earth ion has a CN exceeding 9, since relatively few structural data are available. In particular, only six examples of 11-coordination are known:[7] $Y(BH_4)_3(THF)_3$,[9] $[Ce(NO_3)_4(H_2O)_2(NC_5H_4{-}C_5H_4N)]^-$,[10] $La(NO_3)_3(C_{23}H_{21}N_5O_2)$,[11] $[Sm(NO_3)_5(H_2O)]^{2-}$,[12] and $[Ln(NO_3)_3(H_2O)_5]{\cdot}H_2O$, Ln = La,[13] Ce.[14] In this paper, we report the crystal and molecular structure of an 11-coordinate complex of the Eu(III) ion with 15-crown-5 ether, $Eu(NO_3)_3(C_{10}H_{20}O_5)$, along with its high-resolution fluorescence spectrum.

Experimental Section

Europium nitrate complexes with 15-crown-5 ether in nonaqueous solvents such as acetonitrile,[6] depositing a well-crystallized, yellowish, and transparent material, which turns opaque in contact with air. Consequently, all manipulations and measurements were performed under strictly anhydrous conditions.

The crystals are uniaxial as observed under polarized light. Precession and Weissenberg photographs revealed trigonal symmetry and the systematic absences $l \neq 3n$ for $(00l)$. The two enantiomorphic space groups $P3_1$ and $P3_2$ (ITC No. 144 and 145) are compatible with these extinctions. Density measurements in $CHCl_3/CHBr_3$ yielded $Z = 3$. The crystal parameters and the details of intensity measurements are reported in Table I. The background noise and the variance of each reflection were calculated with use of the Lehmann–Larsen algorithm.[15] All intensities were corrected for absorption by the Gaussian integration method. The crystal stability was checked by periodically measuring three standard reflections: no significant variation of intensity was observed during the measurements. The structure was solved by Patterson and Fourier methods as described previously.[16] Atomic scattering factors of neutral atoms were taken from Cromer and Mann.[17] Dispersion corrections for europium were calculated by Cromer and Liberman.[18] A final refinement with anisotropic vibrational parameters converged to $R_F = 0.037$, without hydrogen atoms. No significant peak appeared on a final difference Fourier synthesis.

The absolute configuration of the crystals was determined with the help of the Bijvoet[19] pairs: $(F_{hk0} = F_{ih0} = F_{ki0}) \neq (F_{\overline{hk0}} = F_{\overline{ih0}} = F_{\overline{ki0}})$ with $i = -(h + k)$. A selection of the most important pairs, along with various agreement factors, is summarized in Table II and clearly points to space group $P3_1$. This is confirmed by Hamilton's test:[20] $R_w(P3_2)/R_w(P3_1) = 1.0637$; the minimum ratio for 99.5% confidence and for 1773 degrees of freedom (2026 reflections, 253 variables) is 1.0023.

The fluorescence measurements were performed at 77 K on finely powdered microcrystalline samples with use of the instrumentation previously described.[21,22]

Discussion of the Structure

The final atomic positional and thermal parameters are given in Table III.[23] Bond distances and angles are summarized in Table IV, and a perspective view of $Eu(NO_3)_3(C_{10}H_{20}O_5)$ is presented in Figure 1, which also indicates the numbering of the atoms. The arrangement of the molecules around the ternary helicoidal axis is pictured in Figure 2; the angle between this axis and the mean plane of the 15-crown-5 ether is 52°.

A noteworthy feature of the molecular structure is the 11-coordinate polyhedron around the metal ion: the Eu(III) ion is bonded, on one side, to the five oxygen atoms of the polyether and, on the opposite side, to three bidentate nitrate groups.

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(1) Part 11 of the series, "Complexes of Lanthanoid Salts with Macrocyclic Ligands". For part 10, see ref 6.

(2) (a) Institut de Chimie Minérale et Analytique. (b) Institut de Cristallographie.

(3) In this paper, we use the nomenclature proposed by Pedersen[4] for crown ethers; e.g., the title compound is a 1:1 complex between europium trinitrate and 15-crown-5 ether.

(4) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 7017.

(5) Kolthoff, I. M. *Anal. Chem.* **1979**, *51*, 1R.

(6) Bünzli, J.-C. G.; Wessner, D. *Helv. Chim. Acta* **1978**, *61*, 1454. Bünzli, J.-C. G.; Oanh, H. T. T.; Wessner, D. *Inorg. Chim. Acta* **1979**, *32*, L33. Bünzli, J.-C. G.; Wessner, D. *Helv. Chim. Acta* **1981**, *64*, 582.

(7) LaF_3 and CeF_3 are sometimes considered as containing 11-coordinate Ln(III) ions; however, two Ln–F distances are much longer than the other ones.[8]

(8) Cheetham, A. K.; Fender, B. E. F.; Fuess, H.; Wright, A. F. *Acta Crystallogr., Sect. B* **1976**, *B32*, 94.

(9) Segal, B. G.; Lippard, S. J. *Inorg. Chem.* **1978**, *17*, 844.

(10) Bukorwska-Strzyzewska, M.; Tosik, A. *Inorg. Chim. Acta* **1978**, *30*, 189.

(11) Thomas, J. E.; Palenik, R. C.; Palenik, G. J. *Inorg. Chim. Acta* **1979**, 37, L459.

(12) Burns, J. H. *Inorg. Chem.* **1979**, *18*, 3044.

(13) Eriksson, B.; Larsson, L. O.; Niinistö, L.; Valkonen, J. *Inorg. Chem.* **1980**, *19*, 1207.

(14) Milinski, M.; Ribar, B.; Satorić, M. *Cryst. Struct. Commun.* **1980**, *9*, 473.

(15) Blessing, P.; Coopens, P.; Becker, P. *J. Appl. Crystallogr.* **1972**, 488. Schwarzenbach, D. *Abstr. Eur. Cryst. Meet. 4th* **1977**, I-20.

(16) Bünzli, J.-C. G.; Klein, B.; Chapuis, G.; Schenk, K. J. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1307.

(17) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321.

(18) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(19) Bijvoet, J. M.; Peerdeman, A. F.; van Baumel, A. J. *Nature (London)* **1951**, *168*, 271.

(20) Hamilton, W. C. *Acta Crystallogr.* **1965**, *18*, 502.

(21) Bünzli, J.-C. G.; Klein, B. *Conf. Ser.—Inst. Phys.* **1978**, *37*, 115.

(22) Bünzli, J.-C. G.; Yersin, J.-R. *Inorg. Chem.* **1979**, *18*, 605.

(23) For a listing of the observed and calculated structure factors, see the description of supplementary material at the end of the paper.

Table I. Details of Data Collection

		(A) Crystal Parameters at 25 °C			
dimens, mm	0.21 × 0.21 × 0.33	*a*, Å	8.845 (3)	*Z*	3
morphology	trigonal prism {100}, {010}; trigonal bipyramid {101}, {011}	*c*, Å	20.330 (4)	formula	$C_{10}H_{20}N_3O_{14}Eu$
		V, Å^3	1377.3	mol wt	558.2
syst	trigonal	*F*(000)	828.0	abs coeff, cm^{-1}	35.3
space group	$P3_1$	*d*(obsd), g cm^{-3}	2.019	transmission	0.575–0.629
		d(calcd), g cm^{-3}	2.009		
		(B) Collection of Intensity Data			
diffractometer	Syntex $P2_1$	reflctns measd	$\pm h, +k, +l$	bkgd est	acc to ref 15
radiation	Mo Kα = 0.710 69 Å	method	θ–2θ scan	no. of collected data	2759
filter	Nb	(sin θ)/λ(max)	0.7045	no. of obsd data ($I > 3\sigma$)	2026

Table II. Typical Reflections and Agreement Factors of $Eu(NO_3)_3(C_{10}H_{20}O_5)$ for $P3_1$ and $P3_2$ Space Groups

reflctn	$\Delta_{obsd}{}^a$	$\Delta_{P3_1}{}^a$	$\Delta_{P3_2}{}^a$	definition	$P3_1$	$P3_2$
200	−0.15	−0.13	+0.13	$R_F = \Sigma \lvert F_o - F_c \rvert / \Sigma F_o$	0.0366	0.0388
220	−0.06	−0.05	+0.05	$R_w{}^b$	0.0408	0.0434
310	−0.04	−0.03	+0.03	$R_I = \Sigma \lvert I_o - I_c \rvert / \Sigma \lvert I_o \rvert$	0.0465	0.0518
350	−0.06	−0.07	+0.07	$R_F(hk0)$	0.0299	0.0405
410	+0.04	+0.05	−0.05	$R_w(hk0)$	0.0399	0.0478
510	−0.03	−0.03	+0.03	$R_I(hk0)$	0.0610	0.0841

[a] $\Delta = [F_{hk0}{}^2 - F_{\overline{hk0}}{}^2]/{}^1\!/_2(F_{hk0}{}^2 + F_{\overline{hk0}}{}^2)$. [b] $R_w = [\Sigma(1/\sigma^2)\cdot \lvert F_o - F_c \rvert^2 / \Sigma(1/\sigma^2) \lvert F_o \rvert^2]^{1/2}$.

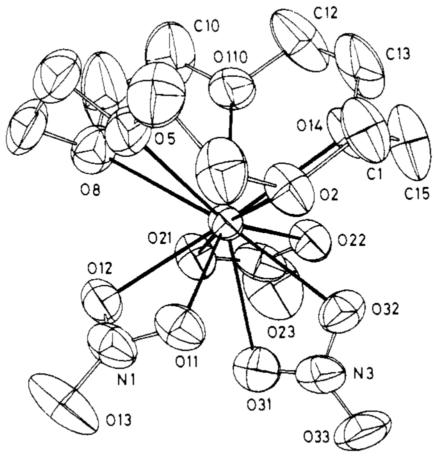

Figure 1. ORTEP drawing of $Eu(NO_3)_3(C_{10}H_{20}O_5)$.

No other europium complex has been reported with CN = 11, and this is the seventh case of 11-coordination found for rare earth ions (vide supra).

The Eu–O(nitrate) bond lengths range from 2.43 to 2.65 Å, one distance, namely, Eu–O(31) of 2.65 Å, being significantly longer than the mean Eu–O(nitrate) bond length, 2.53 (8) Å. In $(Phe_4As)_2[Eu(NO_3)_5]$ we have found a mean Eu–O(nitrate) bond length of 2.48 (4) Å (2.42–2.52 Å), which is exactly matched by the average of the five shorter Eu–O(nitrate) distances in the crown ether complex, 2.48 (3) Å (2.43–2.51 Å). A similar situation occurs for $[Sm(NO_3)_5(H_2O)]^{2-}$, one Sm–O(nitrate) distance being 0.12 Å longer than the average distance, 2.55 Å,[12] and for two 11-coordinate complexes of La(III)[13] and Ce(III)[10] in which two Ln–O(nitrate) bond lengths are significantly longer. The Eu–O(ether) bond lengths range from 2.55 to 2.69 Å, with a mean value of 2.63 (6) Å.

Undecacoordination is not common in inorganic chemistry, and to our knowledge, no quantitative data are available that describe the more favorable polyhedra.[24] When Gillespie's method[25] based on the repulsion of electron pairs is used, one polyhedron of lowest energy turns out to be the 1:5:5 monocapped pentagonal antiprism (MPA) of C_{5v} symmetry, which in fact is a truncated icosahedron (cf. Figure 3). The complex with 15-crown-5 ether does not have unidentate ligands, and therefore the coordination polyhedron of the Eu(III) ion is expected to be severely distorted, especially in view of the steric constraint imposed by the macrocycle. The pentagonal base of the MPA is indeed distorted into a triangle P1, O(5)–O(8)–O(110), and a quadrilateral P2, O(2)–O(5)–O(110)–O-

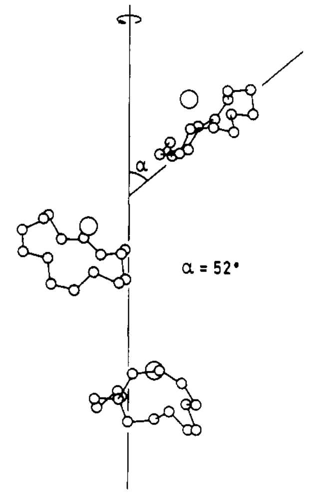

Figure 2. Arrangement of the complex molecules around the helicoidal axis.

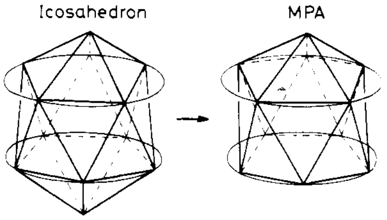

Figure 3. Ideal coordination polyhedra.

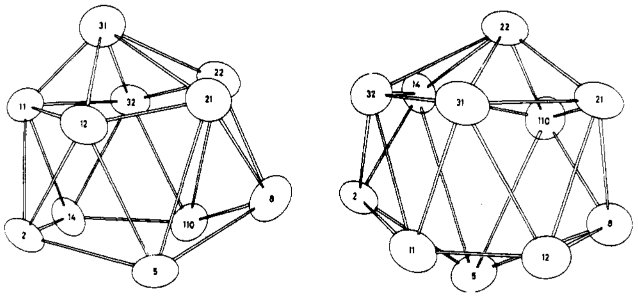

Figure 4. Coordination polyhedron of $Eu(NO_3)_3(C_{10}H_{20}O_5)$.

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(24) Drew, M. G. B. *Coord. Chem. Rev.* **1977**, *24*, 179.

(25) Gillespie, R. J. "Molecular Geometry"; Van Nostrand-Reinhold: London, 1972.

Table III. Final Positional and Thermal[a] Parameters ($\times 10^2$) with Estimated Standard Deviations in Parentheses

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Eu(1)	0.93143 (9)	0.75782 (9)	0.0000 (3)	4.12 (2)	4.27 (4)	3.26 (2)	2.63 (4)	−0.06 (3)	−0.14 (3)
N(1)	0.045 (2)	0.282 (2)	0.2237 (7)	4.3 (7)	6.2 (9)	4.9 (8)	1.0 (7)	0.3 (6)	0.9 (7)
O(11)	0.004 (1)	0.349 (2)	0.2730 (6)	5.5 (6)	5.7 (7)	4.6 (6)	1.7 (5)	−0.2 (5)	0.0 (5)
O(12)	0.991 (2)	0.120 (2)	0.2297 (6)	5.4 (7)	6.5 (7)	4.6 (6)	2.8 (6)	0.8 (5)	0.2 (5)
O(13)	0.129 (2)	0.370 (2)	0.1758 (7)	11 (1)	9 (1)	4.3 (7)	1 (1)	2.0 (8)	0.7 (7)
N(2)	0.509 (2)	0.776 (2)	0.2823 (8)	7 (1)	5.7 (9)	4.8 (8)	1.1 (8)	−1.3 (7)	0.0 (7)
O(21)	0.662 (1)	0.815 (2)	0.2630 (6)	4.1 (6)	6.3 (7)	5.4 (7)	1.1 (5)	−0.4 (5)	−1.4 (6)
O(22)	0.142 (2)	0.646 (2)	−0.0015 (6)	6.5 (8)	7.6 (9)	5.0 (7)	4.9 (7)	0.3 (6)	0.1 (6)
O(23)	0.374 (2)	0.666 (3)	0.254 (1)	7 (1)	11 (1)	12 (2)	−1 (1)	−2 (1)	−5 (1)
N(3)	0.616 (2)	0.211 (2)	0.2706 (8)	3.5 (7)	4.9 (8)	7 (1)	0.5 (6)	0.5 (7)	3.0 (7)
O(31)	0.659 (2)	0.119 (2)	0.2456 (7)	5.3 (7)	6.3 (8)	6.8 (8)	2.0 (6)	−0.3 (6)	0.3 (7)
O(32)	0.664 (2)	0.229 (2)	0.3310 (7)	5.9 (8)	6.8 (8)	6.3 (8)	3.9 (7)	−1.4 (6)	−0.5 (6)
O(33)	0.525 (2)	0.267 (2)	0.2495 (9)	7 (1)	12 (1)	12 (1)	6 (1)	0.3 (9)	5 (1)
C(1)	0.665 (2)	0.558 (3)	0.1433 (8)	6 (1)	9 (1)	5.1 (9)	4 (1)	2.7 (8)	3.2 (9)
O(2)	0.652 (1)	0.614 (2)	0.0774 (5)	5.2 (6)	8.0 (8)	4.4 (6)	4.4 (6)	1.2 (5)	0.8 (5)
C(3)	0.547 (3)	0.699 (3)	0.075 (1)	7 (1)	8 (1)	8 (1)	6 (1)	1 (1)	1 (1)
C(4)	0.662 (3)	0.888 (3)	0.090 (1)	9 (1)	8 (1)	7 (1)	6 (1)	3 (1)	1 (1)
O(5)	0.807 (2)	0.952 (2)	0.0416 (6)	10 (1)	6.2 (7)	5.4 (7)	5.4 (8)	0.9 (7)	−0.2 (6)
C(6)	0.908 (4)	0.137 (3)	0.043 (1)	12 (2)	6 (1)	7 (1)	6 (1)	2 (1)	0 (1)
C(7)	0.166 (3)	−0.025 (3)	0.316 (1)	5 (1)	13 (2)	9 (1)	6 (1)	−1 (1)	−2 (1)
O(8)	−0.020 (2)	0.875 (2)	0.3137 (7)	6.6 (8)	5.6 (8)	8 (1)	3.8 (7)	0.7 (7)	1.0 (7)
C(9)	0.296 (4)	0.198 (4)	0.010 (2)	11 (2)	6 (2)	21 (4)	−1 (1)	−7 (2)	5 (2)
C(10)	0.328 (3)	0.136 (3)	0.064 (2)	8 (1)	6 (1)	15 (3)	1 (1)	−4 (2)	1 (2)
O(110)	0.204 (2)	0.958 (2)	0.0766 (6)	6.4 (8)	5.5 (7)	6.1 (7)	1.7 (6)	−1.6 (6)	−0.9 (6)
C(12)	0.226 (3)	0.897 (4)	0.140 (1)	7 (1)	14 (2)	6 (1)	4 (2)	−1 (1)	2 (1)
C(13)	0.096 (4)	0.734 (4)	0.155 (1)	15 (3)	9 (2)	10 (2)	0 (2)	−10 (2)	2 (2)
O(14)	−0.045 (2)	0.649 (2)	0.1135 (5)	5.0 (6)	8.3 (9)	3.9 (6)	2.7 (6)	−0.1 (5)	1.7 (6)
C(15)	0.800 (3)	0.508 (3)	0.142 (1)	8 (1)	11 (2)	8 (1)	6 (1)	3 (1)	5 (1)

[a] Anisotropic thermal factors: $\exp[-2\pi^2\Sigma(i,j)[h_ih_jU_{ij}]A^*_iA^*_j]$.

Table IV. Bond Lengths (Å) and Angles (Deg) with Estimated Standard Deviations in Parentheses

(A) Europium Coordination Polyhedron			
Eu-O(11)	2.50 (1)	Eu-O(2)	2.66 (1)
Eu-O(12)	2.47 (1)	Eu-O(5)	2.60 (2)
Eu-O(21)	2.43 (1)	Eu-O(8)	2.69 (1)
Eu-O(22)	2.51 (2)	Eu-O(110)	2.67 (1)
Eu-O(31)	2.65 (2)	Eu-O(14)	2.55 (1)
Eu-O(32)	2.47 (1)		
O-O (same nitrate)	2.15(1) (2.14-2.16)		
O-O (vicinal nitrates)	2.85(6) (2.76-2.93)		
O(nitrate)-O(ether)	2.9(1) (2.72-3.12)		
O-O (ether, consec O)	2.66(5) (2.62-2.73)		
O-Eu-O (same nitrate)	50.9(9) (49.8-51.5)		
O-Eu-O (vicinal nitrates)	69(3) (65.6-72.2)		
O(nitrate)-Eu-O(ether)	54(1) (51.6-55.8)		
O-Eu-O (ether, consec O)	61(1) (58.8-62.2)		
(B) Nitrates			
N(1)-O(11)	1.31 (2)	N(2)-O(23)	1.24 (2)
N(1)-O(12)	1.27 (2)	N(3)-O(31)	1.27 (3)
N(1)-O(13)	1.24 (2)	N(3)-O(32)	1.28 (2)
N(2)-O(21)	1.28 (2)	N(3)-O(33)	1.21 (3)
N(2)-O(22)	1.25 (2)		
O(11)-N(1)-O(12)	114 (1)	O(22)-N(2)-O(23)	122 (2)
O(11)-N(1)-O(13)	122 (2)	O(31)-N(3)-O(32)	116 (2)
O(12)-N(1)-O(13)	124 (2)	O(31)-N(3)-O(33)	122 (2)
O(21)-N(2)-O(22)	115 (1)	O(32)-N(3)-O(33)	122 (2)
O(21)-N(2)-O(23)	123 (2)		
(C) Macrocycle			
C(1)-O(2)	1.45 (2)	O(2)-C(3)	1.46 (3)
C(3)-C(4)	1.49 (3)	C(4)-O(5)	1.48 (3)
O(5)-C(6)	1.42 (3)	C(6)-C(7)	1.52 (4)
C(7)-O(8)	1.42 (2)	O(8)-C(9)	1.45 (4)
C(9)-C(10)	1.32 (5)	C(10)-O(110)	1.42 (2)
O(110)-C(12)	1.44 (3)	C(12)-C(13)	1.36 (4)
C(13)-O(14)	1.37 (3)	O(14)-C(15)	1.44 (2)
C(15)-C(1)	1.47 (4)		

(14). The standard deviation of the mean plane through the latter set of atoms is $\sigma = 0.16$ Å, and the dihedral angle between the two planes is 142° (cf. Figure 4). The dihedral angles between P1, P2, and the plane P3, defined by O(2), O(8), and O(14), are 22 and 17°, respectively. The top part of the polyhedron corresponds to the oxygen atoms of the nitrate groups. Atom O(31), which forms the longest Eu–O bond, is the upper vertex of the pentagonal pyramid; the best plane through atoms O(11), O(12), O(21), O(22), and O(32) has $\sigma = 0.21$ Å and is almost parallel to P3 (dihedral angle 7°). The coordination polytope is therefore a 2:3:5:1 polyhedron, and it may be described as a distorted MPA. Indeed, when the polyhedron is drawn with another atom as the upper vertex, O(22) for instance (cf. Figure 4), the similarity with the MPA is also striking: the best plane through O(21), O(31), O(32), O(110), and O(14), which includes oxygen atoms from both the nitrates and the polyether, has $\sigma = 0.21$ Å. Mean values of some edges and O–Eu–O angles are listed in Table IV.

It is relevant to note that other 11-coordinate polyhedra have been described: a C_s octadecahedron for Ce(III),[10] a D_{2d} dodecahedron for La(III), with the assumption the nitrate groups occupy only one coordination site,[13] and a decahexahedron for the other 11-coordinate complex of La(III).[11]

The effective ionic radii[26] of 11-coordinate Ln(III) ions can be evaluated from the available structural data. They are in good agreement with the values obtained from extrapolation of ionic radii vs. CN plots:[27] $r_i = 1.33$ (extrapolated value 1.32), 1.32 (1.29), 1.23 (1.21), and 1.25 (1.20) Å for Ln = La, Ce, Sm, and Eu, respectively.

The three nitrate groups are perfectly planar, and their local symmetry is very close to C_{2v}, the observed deviations being within experimental errors. With respect to the mean N–O distance of 1.245 Å observed for symmetrical nitrate groups,[28] the terminal N–O bonds are shortened (average 1.23 (2) Å)

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(26) With use of Shannon's definition,[27] without correction for covalency effects and for the distortion of the coordination polyhedron. The radii of the oxygen atoms have been estimated from structural data of related complexes containing metal ions, the ionic radii of which are precisely known; we have found 1.352, 1.314, and 1.310 Å for H_2O, NO_3^-, and O(polyether), respectively.

(27) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751.

(28) Addison, C. C.; Logan, N.; Wallwork, S. C.; Garner, C. D. *Q. Rev., Chem. Soc.* **1971**, *25*, 289.

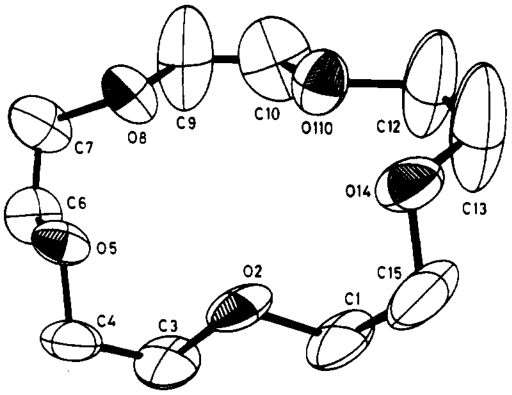

Figure 5. Conformation of the 15-crown-5 ether.

Table V. Torsion Angles (Deg) in the Complexed 15-Crown-5 Ether (Absolute Values)

C(1)-O(2)-C(3)-C(4)	95	C(9)-C(10)-O(110)-C(12)	173
O(2)-C(3)-C(4)-O(5)	64	C(10)-O(110)-C(12)-C(13)	58
C(3)-C(4)-O(5)-C(6)	44	O(110)-C(12)-C(13)-O(14)	53
C(4)-O(5)-C(6)-C(7)	11	C(12)-C(13)-O(14)-C(15)	80
O(5)-C(6)-C(7)-O(8)	4	C(13)-O(14)-C(15)-C(1)	119
C(6)-C(7)-O(8)-C(9)	40	O(14)-C(15)-C(1)-O(2)	69
C(7)-O(8)-C(9)-C(10)	57	C(15)-C(1)-O(2)-C(3)	168
O(8)-C(9)-C(10)-O(110)	38		

and the N-O bonds involving the coordinated oxygen atoms are lengthened (average 1.28 (2) Å). The O-N-O angle involving bonded oxygen atoms is smaller than 120° (average 115 (1)°) and the two other angles are accordingly larger (average 122.5 (8)°). There is no structural difference between $N(3)O_3^-$, which has one significantly longer Eu-O bond length, and the two other nitrate groups. The Eu-N(3) distance (3.00 (2) Å) is, however, slightly longer than the two other ones, 2.94 (2) and 2.90 (2) Å.

The macrocycle adopts a conformation (cf. Figure 5) that tends to equalize all the Eu-O(ether) bond lengths similarly to what was observed for the 1:1 complex between neodymium nitrate and 18-crown-6 ether.[29] Some torsion angles therefore do not correspond to an energetically favorable situation. For instance, four O-C-C-O torsion angles are nearly synclinal, in good agreement with previous observations in structures of related polyethers,[30,31] but the conformation around the fifth C-C bond is *syn*-periplanar. There are also evident deviations from the energetically favorable *trans* arrangement around the C-O bonds (cf. Table V). The mean C-C and C-O distances and the mean C-C-O and C-O-C angles are 1.43 (9) Å, 1.44 (4) Å, 112 (5)°, and 113 (2)°, respectively. The large dispersion of the individual values (cf. Table IV) can be explained by a partial fluxional disorder of the bis(methylene) moieties, principally $-C(9)H_2-C(10)H_2-$ and $-C(12)H_2-C(13)H_2-$, around the oxygen atoms of the polyether, which are held in more fixed positions by the ion/dipole interaction with the europium(III) ion. This can be seen from the larger mean value of the U_{ii} thermal parameters (cf. Table III) for the carbon atoms, 9.1%, as compared to 6.3% for the oxygen atoms of the macrocycle. Consequently, the rather short C-C distances probably arise from an additional motion not taken into account in our refinement.[31]

Fluorescence Spectrum

Parts of the excitation and emission spectra at 77 K of $Eu(NO_3)_3(C_{10}H_{20}O_5)$ are displayed in Figure 6.[32] The fluorescence arises from both the $^5D_0$ and the $^5D_1$ excited states. There is only one sharp $^5D_0 \rightarrow {}^7F_0$ transition, with a width at half-height of 2.7 cm^{-1}, indicating the presence of only one site for the Eu(III) ion, which is consistent with the crystal structure discussed above. The integrated and corrected relative intensities of the $^5D_0 \rightarrow {}^7F_J$ transitions are 2.5%, 31%, 100%, and 53% for J = 0, 1, 2, and 4, respectively, reflecting the low site symmetry (C_1) of the Eu(III) ion. Consequently, most electronic sublevels could be located (Table VI, Figure 7). However, a closer look at this figure suggests that the

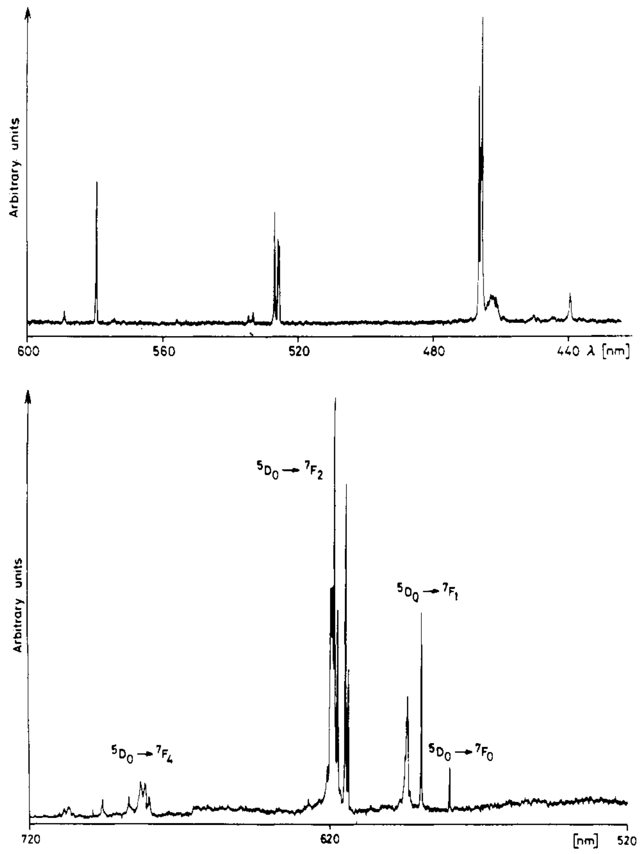

Figure 6. Top part: excitation spectrum at 77 K of $Eu(NO_3)_3(C_{10}H_{20}O_5)$ (λ_{anal} = 618.0 nm). Lower part: fluorescence spectrum at 77 K (λ_{exc} = 397.7 nm, band-pass 0.16 nm).

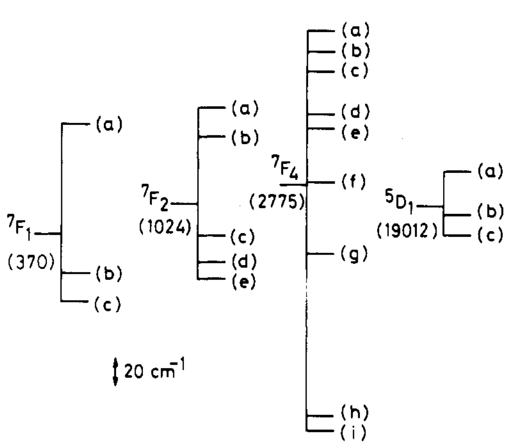

Figure 7. Crystal field splitting of the ^5D_J and ^7F_J levels of $Eu(NO_3)_3(C_{10}H_{20}O_5)$. The barycenter of the transitions is given in parentheses (cm^{-1}). For $^7F_4$ the vertical scale was reduced by a factor of 2.

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(29) Bünzli, J.-C. G.; Klein, B.; Wessner, D. *Inorg. Chim. Acta* **1980**, *44*, L147.

(30) Hanson, I. R. *Acta Crystallogr., Sect. B* **1978**, *B34*, 1026.

(31) Dunitz, J. D.; Dobler, M.; Seiler, P.; Phizackerley, R. P. *Acta Crystallogr., Sect. B* **1974**, *B30*, 2733.

(32) Tables of 21 excitation bands (410-589 nm) with their assignments and of 52 emission bands (533-766 nm) with their relative intensities and their assignments are available as supplementary material.

Table VI. Energy Levels (cm^{-1}) of the Eu(III) Ion in $Eu(NO_3)_3(C_{10}H_{20}O_5)$ (Excitation and Emission Spectra at 77 K)

$^7F_0$	0	$^7F_5$ (a)	3849
$^7F_1$ (a)	278	(b)	3883
(b)	410	(c)	3924
(c)	421	(d)	3949
$^7F_2$ (a)	954	(e)	3975
(b)	975	(f)	4017
(c)	1046	(g)	4068
(d)	1067	(h)	4196
(e)	1078	$^5D_0$	17259
$^7F_3$ (a)	1815	$^5D_1$ (a)	18984
(b)	1844	(b)	19022
(c)	1954	(c)	19031
(d)	2020	$^5D_2$ (a)	21455
(e)	2158	(b)	21478
$^7F_4$ (a)	2547	(c)	21492
(b)	2577	$^5D_3$ (a)	24272
(c)	2607	(b)	24301
(d)	2671	(c)	24325
(e)	2690	(d)	24343
(f)	2768	(e)	24366
(g)	2875		
(h)	3109		
(i)	3135		

crystal field splitting of the J levels arises from a distortion of a higher symmetry, some of the sublevels appearing as closely spaced doublets or triplets. This pseudosymmetry may be determined considering the splitting generated in a crystal field of a given symmetry[33] and the group-theory labeling of the sublevels.[34] The $J = 1$ levels clearly consist of an E(doublet) + A(singlet) pattern, suggesting that the pseudosymmetry is either pentagonal[35] or hexagonal. The $J = 2$ levels seem to be comprised of a doublet and a triplet (E + T), pointing to an octahedral symmetry, in contradiction with the previous statement. For such a pseudosymmetry, the $J = 1$ levels should appear as doublets, which is obviously not the case, and we therefore rather interpret the splitting pattern of the $J = 2$ level as a 2 E + A one, consistent with the symmetries proposed above. In crystal fields of pentagonal and hexagonal symmetries, the $J = 4$ level is split into 4 E + A and a 3 E + 3 A pattern, respectively. Both are consistent with the observed $^7F_4$ sublevels. The 11-coordinate polyhedron of the Eu(III) ion can now be viewed as arising either from the distortion of the MPA (C_{5v}), as discussed above, or from the expansion of the 10-coordinate polyhedron of pseudo-D_{3h} symmetry occurring for $Eu(NO_3)_5^{2-}$ species.[36]

One last feature of the fluorescence spectrum has to be discussed. As shown in Figure 8, the $^5D_0 \rightarrow {}^7F_2$ transition displays six bands, upon excitation to the $^5L_6$ or to the $^5D_0$ levels. The somewhat broader components at 618.6 and 619.1 nm could therefore arise from a spurious effect. However, this feature is reproducible for batches of complex synthesized independently and it does not arise from the luminescence of another rare earth ion present as an impurity. Because of the rather large intensity of these two bands we do not think they arise from a vibronic satellite.[37] Two possible explanations remain. (i) The partial fluxional disorder of the macrocycle creates, at 77 K, two very slightly different environments for the Eu(III) ions. (ii) Energy migrates within the microcrystals to reach luminescent traps arising from crystal defects or from impurities, which produce the extraneous band(s).[38] To test these hypotheses, we have doped $La(NO_3)_3(C_{10}H_{20}O_5)$ with 1.4% europium[39] and recorded its emission spectrum, which is partially displayed on Figure 8. This spectrum is similar to the one of the isostructural Eu complex,[6] except for slight energy shifts due to the different cell parameters. The $^5D_0 \rightarrow {}^7F_2$ transition is comprised of four sharp bands, at 612.9, 613.9, 616.9, and 618.0 nm, which correspond to the transitions to the $^7F_2$(a, b, c, e) sublevels observed for the europium complex. The two "additional" bands have disappeared, and the transition to the fifth sublevel (d) occurs as a weak component at 617.4 nm. Therefore, we think the two luminescence bands at 618.6 and 619.1 nm do arise from luminescent traps.

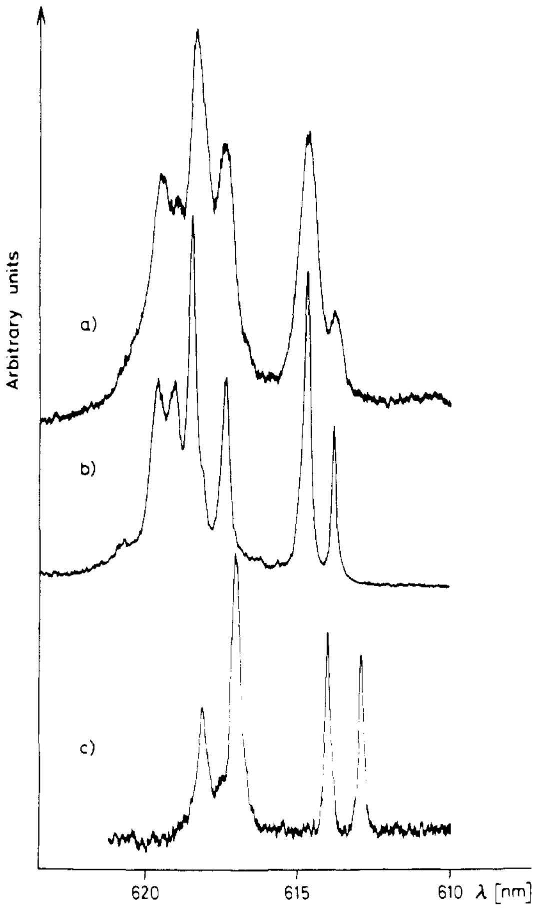

Figure 8. $^5D_0 \rightarrow {}^7F_2$ transition: (a and b) $Eu(NO_3)_3(C_{10}H_{20}O_5)$; (c) $La(NO_3)_3(C_{10}H_{20}O_5)$ doped with 1.4% Eu. λ_{exc} = 580 nm (analyzing band-pass 0.24 nm) for (a) and 579.7 nm (0.08 nm) for (b) and (c).

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Registry No. $Eu(NO_3)_3(C_{10}H_{20}O_5)$, 67216-29-9.

Supplementary Material Available: Listings of structure factor amplitudes, 21 excitation bands (77 K, 410–589 nm, Table S1), and 52 emission bands (77 K, 533–766 nm, Tables S2) (17 pages). Ordering information is given on any current masthead page.

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(33) Runciman, W. A. *Philos. Mag.* **1956**, *1*, 1075.

(34) A complete table of all the selection rules for $^5D_0 \rightarrow {}^7F_J$ transitions (J = 0, 1, 2, 3, 4) in fields of icosahedral, pentagonal, octahedral, hexagonal, tetragonal, and lower symmetries is available upon request.

(35) Pentagonal symmetry includes the following groups: D_{5d}, D_5, C_{5v}, C_{5h}, C_5.

(36) Bünzli, J.-C. G.; Klein, B.; Pradervand, G.-O.; Porcher, P., to be submitted for publication.

(37) The broadening of the fluorescence bands at higher temperatures prevents the observation of their eventual increase in intensity.

(38) Blasse, G., personal communication, 1980.

(39) The doped complex was crystallized out of solutions containing 15% Eu. The Eu content of the solid was determined by a fluorometric method.