167. Synthesis, Crystal and Molecular Structure of the 3:2 Complex between Europium Nitrate and the A-Isomer of Dicyclohexyl-18-crown-6: Conformational Study of the Ligand[1])

by Francesco Nicolò, Dominique Plancherel, and Jean-Claude G. Bünzli*

Institut de Chimie minérale et analytique, Université de Lausanne, Place du Château 3, CH–1005 Lausanne

and Gervais Chapuis

Institut de Cristallographie, Université de Lausanne, BSP, CH–1015 Lausanne

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The crystal and molecular structure of bis[dinitrato-(2,5,8,15,18,21-hexaoxatricyclo[20.4.0.0^{9,14}]hexacosane)europium(III)]pentakis(nitrato) europiate(III) ([Eu(NO$_3$)$_2$·L$_A$]$_2$[Eu(NO$_3$)$_5$]) has been determined from single-crystal X-ray diffraction. The complex crystallizes in the monoclinic space group $P2_1/c$ (ITC No. 14): $a = 13.614(3)$Å, $b = 21.697(4)$Å, $c = 22.591(5)$Å, $\beta = 107.15(2)°$, $Z = 4$. The structure was refined to a final R value of 0.055 ($R_w = 0.055$). The asymmetric unit contains three independent ions with approximate C_2 symmetry: [Eu(NO$_3$)$_5$]$^{2-}$ and two distinct [Eu(NO$_3$)$_2$·L$_A$]$^+$ cations with the macrocyclic ligand in the *cis-syn-cis*-conformation (A-isomer). The Eu(III) ions are 10-coordinated with the following mean bond lengths: Eu–O(nitrate) = 2.46(3)Å in the anion and the two cations, Eu–O(ether) = 2.55(9)Å in both cations. For the uncomplexed A- and B-isomers, as well as for their complexes with various metal ions, a conformational analysis has been made on the six O-atoms of the ligand which can be considered as a fluxional ring. In the presently reported europium complex cations, the oxygen-ring conformation is almost a perfect boat with the metal ions lying in the least-squares plane of the O-atoms (deviation: 0.02–0.05Å). The same conformation prevails in all the complexes containing the A-isomer (exception: dimethylthallium complex) and in most of the complexes with the B-isomer. For this isomer, a chair conformation is found in the uncomplexed ligand, in the sodium complex, and in the complex with dimethylthallium. The occurrence of these conformations is discussed with respect to the crystallographic symmetry of the complexes and the relative mean M–O and O–O distances.

1. Introduction. – Synthetic ionophores react with lanthanide ions to give complexes having potential applications in industrial, analytical, and medicinal chemistry [2][3]. These complexes are of the host-guest type, and the extent of the Ln(III)/ligand interaction depends upon the mutual topological fit between the two reacting species. The conformation the ionophore achieved upon complexation is, therefore, an important
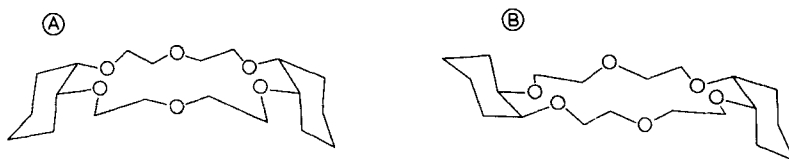

Fig. 1. *Conformations of the* cis-syn-cis (A) *and* cis-anti-cis (B) *isomers of dicyclohexyl-18-crown-6* L$_A$ *and* L$_B$, *respectively*

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[1]) Part 28 of the series 'Complexes of Lanthanoid Salts with Macrocyclic Ligands'; Part 27: [1].

factor. In this respect, one ligand of interest is dicyclohexyl-18-crown-6 (= *2,5,8,15,18,21-Hexaoxatricyclo[20.4.0.0⁹,¹⁴]hexacosane; L*); five isomers are known [4] and two of them are fairly easy to separate with a good purity, the *cis-syn-cis*-A-isomer (L_A) and the *cis-anti-cis*-B-isomer (L_B) *(Fig. 1)*. The reaction between these isomers and lanthanide nitrates results in the formation of 1:1 and 3:2 complexes [3]. Crystal structure determinations have been reported for $La(NO_3)_3 \cdot L_A$ [6] and $[Ln(NO_3)_2 \cdot L_B][Ln(NO_3)_5ONO_2Ln(NO_3) \cdot L_B](Ln = La, Pr)$ [7].

In this communication, we report the crystal and molecular structure of the 3:2 complex between europium nitrate and L_A along with a conformational study of the six ether O-atoms in uncomplexed L_A and L_B and in their complexes with various cations.

2. Experimental. – *Synthesis of the Complex.* Europium nitrate was prepared from the oxide (99.99%, *Glucydur*). The ligand L_A was separated from a mixture of A and B isomers *(Fluka, purum)* by a procedure given in [5], and its purity was checked by elemental analysis, by its m.p. (61–62°) and by ¹³C-NMR spectroscopy [8]. 1 mmol of $Eu(NO_3)_3 \cdot n \ H_2O$ (*n* between 1 and 4) was dissolved in 15 ml of abs. EtOH. A soln. of 1 mmol of L_A in 15 ml of EtOH was added under inert atmosphere, and the mixture was refluxed during 1 h. The solvent was partially distilled and the soln. cooled to r.t. and left for 24 h at 4°. The filtered material was recrystallized twice in abs. EtOH. Anal. calc. for C 27.31, H 4.13, Eu 25.92, N 7.17; found: C 27.39, H 4.20, Eu 25.95, N 7.08.

Crystal Data. $[(C_{20}H_{36}O_6)_2Eu_3(NO_3)_9]$, $M = 1758.93$, monoclinic, space group $P2_1/c$ (ITC No. 14), $a = 13.614(3)$, $b = 21.697(4)$, $c = 22.591(5)$Å, $\beta = 107.15(2)°$, $V = 6376$ Å³, $Z = 4$, F(000) = 3504, $D_c = 1.83$, $D_m = 1.84$ (by flotation in a mixture of CCl_4/CH_2Br_2), Nb-filtered MoK_α radiation ($\lambda = 0.71069$ Å), $\mu(MoK_\alpha) = 30.20$ cm⁻¹.

Data Collection and Refinement. A colourless crystal with dimensions $0.35 \times 0.22 \times 0.18$ mm was mounted on a *Syntex P2₁* four-circle diffractometer. The cell dimensions were obtained from 20 accurately centered reflections with $25° < 2\theta < 30°$. A total of 13 617 intensities were recorded at r.t. by the θ–2θ scan method up to $2\theta = 50°$ and evaluated by the *Lehmann-Larsen* algorithm. The intensities of 3 reference reflections were monitored periodically. A slight decrease of the standards was observed during the data collection. The space group was uniquely determined by systematic absences: $0k0: k = 2n$ and $h0l: l = 2n$. Another choice of the axis gave an angle β of 89.62(2)°; the corresponding intensities, however, confirmed clearly the absence of orthorhombic symmetry.

The data-reduction was performed by the XRAY system of programs [9]. The reflections were corrected for absorption by the *Gaussian* integration method, for *Lorentz*-polarization and secondary extinction effects. The solution and refinement of the structure were performed with the SHELX76 program system [10]. From the 10 965 unique reflections, 4807 were considered as observed ($F_{obs} > 7\sigma(F_{obs})$). Atomic scattering factors and dispersion corrections were taken from [11]. Two of the three independent Eu-atoms were located from a three-dimensional *Patterson* map, whereas all the other non H-atoms were located from successive *Fourier* syntheses. The hetero-atoms were refined anisotropically using a block matrix least-squares technique.

The H-atoms were included in the model with positions calculated from geometrical considerations; their parameters were, however, not refined (C–H = 0.98 Å and $U = 0.060$ Å²). The C–C distances in the ethylene bridges were constrained to 1.52(1)Å. Both the C–O and the C–C (cyclohexyl) bond lengths were constrained to be equal; their mean values converged to 1.44 and 1.52 Å, respectively. The refinement converged to $R = 0.0550$ and $R_w = 0.0546$. A final difference *Fourier* synthesis showed residual peaks up to 1.4 e/Å³ near the disordered cyclohexyl of the Eu(2) cation. An attempt to interpret these maxima as an additional conformation of the cyclohexyl ring was unsuccessfull. The weighting scheme used in the refinement was $1.1562/[\sigma^2(F)+0.00040 \ F^2]$, where $\sigma(F)$ is derived from counting statistics. This choice gave the smallest variation of $w \cdot \Delta F^2$ as a function of F^2_{obs} and $\sin\theta/\lambda$. The geometrical and conformational calculations were performed with the PARST program [12], and the figures were obtained from ORTEP [13]. Selected bond lengths and angles are given in *Table 1* and mean planes in *Table 2*. Supplementary material available: list of atomic coordinates and equivalent temperature factors, list of all bond angles, list of H-atom coordinates, and list of observed and calculated structural factors.

Table 1. *Selected Bond Lengths* [Å] *and Angles* [°]. Standard deviations in parentheses.

Eu(1)—O(1)	2.48(1)	Eu(2)—O(101)	2.48(2)	Eu(3)—O(52)	2.43(2)
Eu(1)—O(2)	2.67(1)	Eu(2)—O(102)	2.68(1)	Eu(3)—O(53)	2.37(3)
Eu(1)—O(3)	2.52(1)	Eu(2)—O(103)	2.52(1)	Eu(3)—O(62)	2.48(1)
Eu(1)—O(4)	2.48(1)	Eu(2)—O(104)	2.53(1)	Eu(3)—O(63)	2.51(2)
Eu(1)—O(5)	2.67(1)	Eu(2)—O(105)	2.66(1)	Eu(3)—O(72)	2.45(1)
Eu(1)—O(6)	2.50(1)	Eu(2)—O(106)	2.46(1)	Eu(3)—O(73)	2.47(1)
Eu(1)—O(12)	2.46(1)	Eu(2)—O(42)	2.46(1)	Eu(3)—O(82)	2.43(1)
Eu(1)—O(13)	2.42(1)	Eu(2)—O(43)	2.44(1)	Eu(3)—O(83)	2.50(1)
Eu(1)—O(22)	2.48(1)	Eu(2)—O(32)	2.47(1)	Eu(3)—O(92)	2.43(1)
Eu(1)—O(23)	2.46(1)	Eu(2)—O(33)	2.45(1)	Eu(3)—O(93)	2.50(1)

O(5)—Eu(1)—O(6)	63.2(3)	O(102)—Eu(2)—O(103)	63.2(3)
O(4)—Eu(1)—O(5)	60.7(3)	O(101)—Eu(2)—O(106)	63.5(3)
O(3)—Eu(1)—O(4)	63.8(3)	O(101)—Eu(2)—O(102)	59.3(3)
O(2)—Eu(1)—O(3)	61.9(3)	O(42)—Eu(2)—O(43)	51.8(4)
O(1)—Eu(1)—O(6)	63.3(3)	O(32)—Eu(2)—O(33)	52.0(3)
O(1)—Eu(1)—O(2)	60.7(3)	O(92)—Eu(3)—O(93)	50.6(4)
O(12)—Eu(1)—O(13)	52.3(4)	O(82)—Eu(3)—O(83)	49.6(5)
O(22)—Eu(1)—O(23)	50.9(3)	O(72)—Eu(3)—O(73)	50.3(5)
O(105)—Eu(2)—O(106)	64.2(3)	O(62)—Eu(3)—O(63)	50.4(6)
O(104)—Eu(2)—O(105)	59.0(4)	O(52)—Eu(3)—O(53)	48.1(8)
O(103)—Eu(2)—O(104)	65.3(3)		

N(1)—O(11)	1.22(2)	N(4)—O(41)	1.21(2)	N(5)—O(51)	1.22(3)
N(1)—O(12)	1.27(2)	N(4)—O(42)	1.27(3)	N(5)—O(52)	1.26(4)
N(1)—O(13)	1.26(2)	N(4)—O(43)	1.25(2)	N(5)—O(53)	1.15(4)
N(2)—O(21)	1.19(2)	N(3)—O(31)	1.22(2)	N(6)—O(61)	1.22(3)
N(2)—O(22)	1.28(2)	N(3)—O(32)	1.27(2)	N(6)—O(62)	1.23(3)
N(2)—O(23)	1.25(2)	N(3)—O(33)	1.26(2)	N(6)—O(63)	1.27(3)
N(7)—O(71)	1.18(3)	N(8)—O(81)	1.23(2)	N(9)—O(91)	1.22(2)
N(7)—O(72)	1.24(3)	N(8)—O(82)	1.23(2)	N(9)—O(92)	1.26(2)
N(7)—O(73)	1.25(2)	N(8)—O(83)	1.23(2)	N(9)—O(93)	1.24(2)

O(12)—N(1)—O(13)	117(2)	O(51)—N(5)—O(52)	121(3)
O(11)—N(1)—O(13)	122(2)	O(62)—N(6)—O(63)	116(2)
O(11)—N(1)—O(12)	121(2)	O(61)—N(6)—O(63)	120(2)
O(22)—N(2)—O(23)	114(1)	O(61)—N(6)—O(62)	124(2)
O(21)—N(2)—O(23)	125(1)	O(72)—N(7)—O(73)	114(2)
O(21)—N(2)—O(22)	121(1)	O(71)—N(7)—O(73)	122(2)
O(32)—N(3)—O(33)	117(1)	O(71)—N(7)—O(72)	123(2)
O(31)—N(3)—O(33)	121(1)	O(82)—N(8)—O(83)	115(2)
O(31)—N(3)—O(32)	122(1)	O(81)—N(8)—O(83)	121(2)
O(42)—N(4)—O(43)	117(2)	O(81)—N(8)—O(82)	124(2)
O(41)—N(4)—O(43)	123(2)	O(92)—N(9)—O(93)	115(2)
O(41)—N(4)—O(42)	121(2)	O(91)—N(9)—O(93)	122(2)
O(52)—N(5)—O(53)	108(3)	O(91)—N(9)—O(92)	122(2)
O(51)—N(5)—O(53)	131(3)		

C—C (crown)	1.52(2)	C—O (crown)	1.44(2)	C—C (hexyl)	1.52(3)

Table 2. *Selected Least-Square Planes*[a]) *with Deviations* [Å] *and Dihedral Angles*[°]

Plane 1	O(1)*	−0.47	O(2)*	−0.23	O(3)*	0.70	O(4)*	−0.33	O(5)*	−0.34
	O(6)*	0.57	Eu(1)	−0.05	N(1)	2.80	N(2)	−2.97		
Plane 2	N(2)*	0.01	O(21)*	0.00	O(22)*	0.00	O(23)*	0.00	Eu(1)	0.14
Plane 3	N(1)*	−0.01	O(11)*	0.00	O(12)*	0.00	O(13)*	0.00	Eu(1)	0.27

Table 2 (cont.)

Plane 4	O(101)* − 0.41	O(102)* − 0.22	O(103)* 0.64	O(104)* − 0.57	O(105)* − 0.05
	O(106)* 0.66	Eu(2) − 0.01	N(4) 2.84	N(3) − 2.88	
Plane 5	N(3)* − 0.01	O(31)* 0.00	O(32)* 0.00	O(33)* 0.00	Eu(2) − 0.03
Plane 6	N(4)* 0.02	O(41)* − 0.01	O(42)* − 0.01	O(43)* 0.00	Eu(2) − 0.21
Plane 7	Eu(3)* 0.00	N(7)* − 0.10	N(8)* − 0.07	N(9)* −0.08	O(72) − 0.49
	O(73) 0.19	O(82) 0.12	O(83) − 0.07	O(92) −0.35	O(93) 0.36
	N(5) 2.88	N(6) − 2.89			
Plane 8	N(5)* − 0.02	O(51)* 0.00	O(52)* 0.00	O(53)* 0.01	Eu(3) − 0.06
Plane 9	N(6)* − 0.01	O(61)* 0.00	O(62)* 0.00	O(63)* 0.00	Eu(3) − 0.03

Dihedral angles

1–2 = 85.5(5)	1–3 = 82.6(5)	2–3 = 85.1(6)
1–4 = 7.8(2)	4–5 = 88.2(6)	4–6 = 80.8(5)
5–6 = 81.4(7)	7–8 = 86.9(6)	7–9 = 87.8(7)
8–9 = 87.0(1)		

[a])   Atoms defining the plane are characterized by *.

3. Description of the Structure. – The asymmetric unit contains three distinct ions placed on general positions. They have approximate C_2 symmetry and no substantial interaction between them: $[Eu(NO_3)_5]^{2-}$ and two crystallographically independent but structurally very similar $[Eu(NO_3)_2 L_A]^+$ cations with the polyether in the *cis-syn-cis*-conformation. The mean planes of the crown ethers are almost parallel, their dihedral angle being close to 8° *(Fig. 2, Table 2)*. The structure is similar to that reported for the 3:2 complexes with the *cis-anti-cis*-isomer L_B (Ln = La, Pr) [7]. In these compounds, however, a strong interaction takes place between the pentakis(nitrato) anion and one complex cation. They are linked by a bridging nitrate-ion bidentate to the cation and monodentate to the anion. One Ln(III) ion is, therefore, 11-coordinate: $[Ln(NO_3)_2 \cdot L_B]$ $[Ln(NO_3)_5$ $ONO_2Ln(NO_3) \cdot L_B]$.

The $[Eu(NO_3)_5]^{2-}$ anion displays a regular geometry with three nitrates (N(7), N(8), N(9)) almost in the same plane and two axial nitrates lying in perpendicular planes
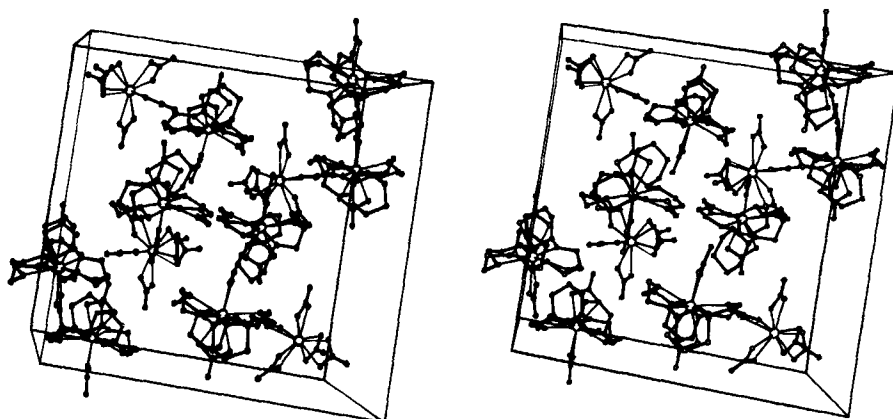

Fig. 2. *Stereoscopic view of the crystal packing in $[Eu(NO_3)_2 \cdot L_A]_2[Eu(NO_3)_5]$.* The H-atoms have been omitted for clarity.
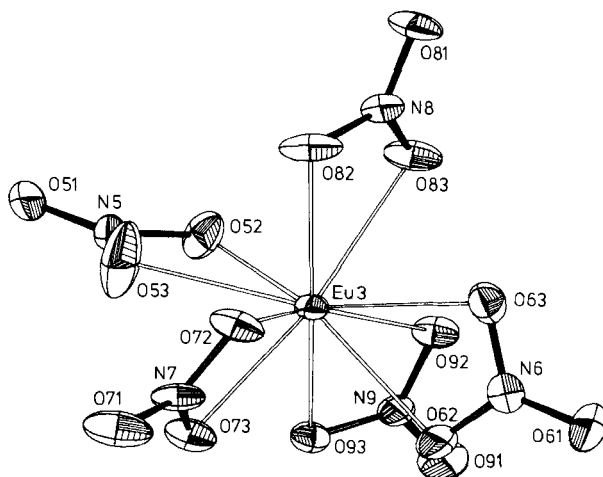
Fig. 3. *Molecular structure of the [Eu(NO₃)₅]²⁻anion showing the atom-numbering scheme.* Thermal ellipsoïds are drawn at 20% probability.

(Fig. 3). They show large thermal ellipsoïds and the corresponding mean Eu–O distances deviate from the mean bond length of 2.46(4) Å *(Table 1)*. Relatively long contact distances (2.3–2.8 Å) have been detected between the calculated positions of the H-atoms of the polyether and the nitrate groups, which may partially explain the thermal disorder. The calculated ionic radius of the 10-coordinate Eu(III) ion is 1.14 Å using *Shannon*'s definition [14], as compared to 1.17 Å in [Phe₄As]₂[Eu(NO₃)₅] [15]. The anion has an approximate C_2 axis through Eu(3) and N(7). The idealized polytope that fits best the experimental coordination polyhedron *(Fig. 4a)* is the 4A,6B-expanded dodecahedron with C_{2v} symmetry [16]: the normalized standard deviation is 0.168 (*cf.* [17]). The five N-atoms, however, are arranged in a nearly perfect trigonal bipyramidal geometry with D_{3h} symmetry, as already noted for other pentakis(nitrato) anions [17]. The angles between the Eu–N lines are 120(3)° in the plane, 90(5)° between planar and axial nitrates
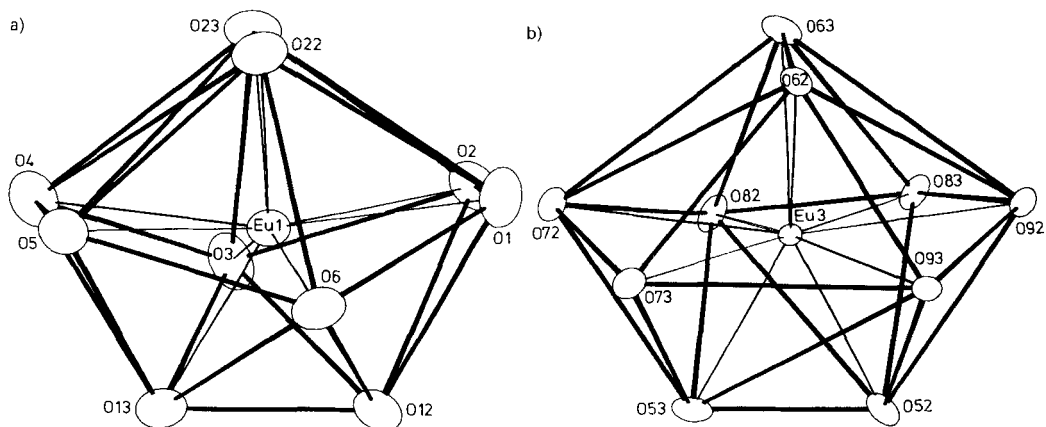

Fig. 4. *Coordination polyhedra of* a) *[Eu(3)(NO₃)₅]²⁻ and* b) *[Eu(1)(NO₃)₂ · L_A]⁺*
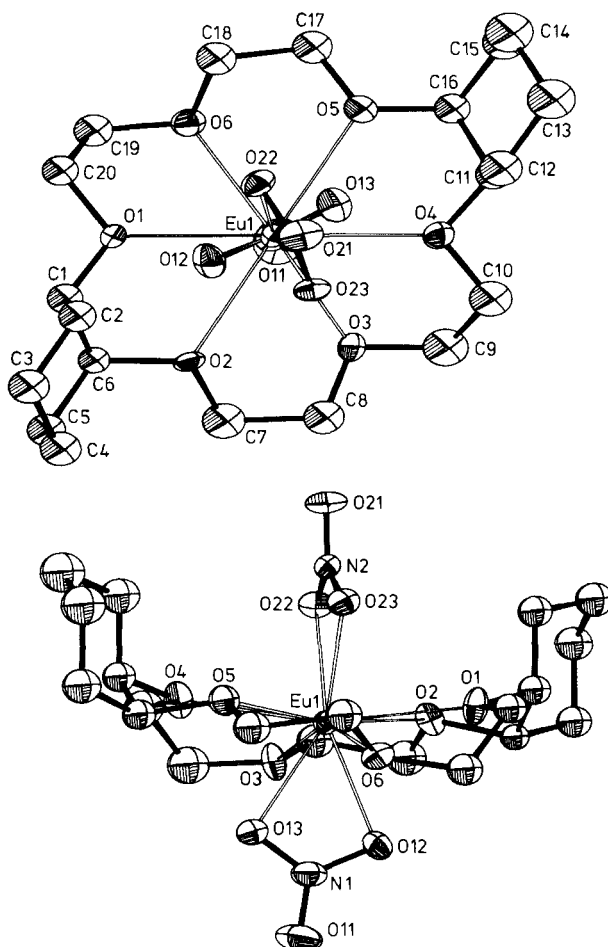
Fig. 5. *Molecular structure of the* $[Eu(1)(NO_3)_2 \cdot L_A]^+$ *complex cation showing the atom-numbering scheme. Thermal ellipsoïds are drawn at 20% probability.*

and 178° between axial nitrates which are nearly perpendicular (87°) to each other. This allows a more homogeneous coordination shell around the metal ion.

The two $[Eu(NO_3)_2 \cdot L_A]^+$ cations have almost the same structure, with two bidentate nitrato groups directed along the normal to the mean plane of the polyether *(Fig. 5)*. The nitrates lie in nearly perpendicular planes (85 and 81° for Eu(1) and Eu(2), respectively), and their axes define approximate twofold axis for the cations, as in other complexes with L_A [18]. The plane of the nitrate, which is on the side of the cyclohexyl rings, bisects their dihedral angles (34° and 34.1°). In the $[Ln(NO_3)_2 \cdot L_B]^+$ complexes, one nitrate is almost parallel to the cyclohexyl plane while the other is nearly perpendicular to the cyclic alkane substituent lying on the same side [7]. This analogy confirms that the crossed disposition of the two opposite nitrates is determined by the coordination requirement of the metal ion, independently of steric effects from the lateral cyclohexyl substituents. The least-squares planes defined by the O-atoms of the polyethers contain the Eu(III) ions. The

mean Eu–O(ether) bond lengths are 2.55(9) Å, but the six bonds are not equivalent: the Eu–O distances range from 2.48 to 2.67 for Eu(1) and from 2.46 to 2.68 Å for Eu(2). In each complex cation, there are two long bonds between Eu(III) and two opposite O-atoms (*ca.* 2.67 Å), resulting in an elliptical shape of the polyether cavity. The mean O-atom contact distance is 3.14 Å in both noncomplexed L_A and L_B [19]. In the reported cations, it amounts to 2.64 Å, a value shorter than the sum of the *van der Waals* radii (2.80 Å). An analogous observation has been reported for the UO_2^{2+} complex with L_B [20]. As in the $[Eu(NO_3)_5]^{2-}$ anion, the coordination polyhedra of the Eu(III) ions is best described by a 4A,6B-expanded dodecahedron with C_{2v} symmetry.

4. Conformational Study of the Ligand. – With respect to the coordinative properties of cyclic polyethers, the geometrical arrangement of the O-atoms near the metal center is a more important factor than the conformation of the ethylene bridges. We have, therefore, considered the six O-atoms of ligands L_A and L_B as defining fluxional rings on which a ring-puckering analysis has been performed [12][21]. To investigate, whether a general trend governs the conformation of these rings, we have carried out this study for uncomplexed L_A and L_B as well as for their metal complexes for which atomic coordinates were available. Relevant data are summarized in *Table 3*. The parameter Q is

Table 3. *Conformation of the O-Atoms in Dicyclohexyl-18-crown-6 (L) Complexes, along with M–O Distances and O···O Contact Distances. See text for explanations.*

Complex species	Isomer	Q [22]	Θ [°]	$\delta(M)^a)$ [Å]	M–O [Å]	O···O [Å]	Ref.
Uncomplexed L	A	1.41	81	$-^b)$	2.69 (2.16–2.99)$^b)$	2.83	[20]
$[(H_3O)\cdot L]^+$	A	1.47	75	$-0.82^c)$	2.75 (2.56–2.92)$^c)$	2.79	[23]
$[(H_3O)\cdot L]^+$	A	1.40	82	$-0.74^c)$	2.73 (2.54–2.94)$^c)$	2.75	[23]
$[Tl(CH_3)_2\cdot L]^+$	A	0.32	22	-0.01	2.80 (2.68–2.98)	2.81	[18]
$[Ba(H_2O)(NCS)_2\cdot L]$	A	0.36	90	0.61	2.83 (2.78–2.92)	2.78	[24]
$[Sr(NO_3)_2\cdot L]$	A	0.87	90	0.06	2.73 (2.65–2.85)	2.77	[25]
$[Eu(1)(NO_3)_2\cdot L]^+$	A	1.14	88	-0.05	2.56 (2.48–2.67)	2.64	This work
$[Eu(2)(NO_3)_2\cdot L]^+$	A	1.18	84	-0.02	2.55 (2.46–2.68)	2.65	This work
Uncomplexed L	B	0.32	0	$-^b)$	2.73 (2.31–3.07)$^b)$	2.80	[20]
$[Na(H_2O)_2\cdot L]^+$	B	0.31	0	0.00	2.79 (2.68–3.00)	2.80	[4]
$[Tl(CH_3)_2\cdot L]^+$	B	0.31	0	0.00	2.79 (2.74–2.87)	2.80	[18]
$[La(NO_3)_2\cdot L]^+$	B	0.86	88	-0.03	2.61 (2.57–2.70)	2.66	[7]
$[Pr(NO_3)_2\cdot L]^+$	B	1.02	90	0.03	2.58 (2.52–2.66)	2.65	[7]
$[UO_2\cdot L]^{2+}$	B	0.70	78	-0.02	2.51 (2.43–2.68)	2.55	[20]
$[Na(H_2O)(18C6)]^{+d)}$	–	1.79	72	-0.61	2.55 (2.45–2.62)	2.76	[26]

$^a)$ Metal deviation from the least-squares plane of the six O-atoms (positive, if on the side of the apexes of the boat conformation).
$^b)$ M is considered as being the center of the O-atoms.
$^c)$ M is considered as being O (water).
$^d)$ 18C6 = 18-crown-6(= 1,4,7,10,13,16-hexaoxacyclooctadecane).

proportional to the deviation from planarity of the ring, and the angle θ is characteristic of the ring conformation: a value of 0° or 180° defines a chair conformation while 90° points to a boat conformation [22].

According to this latter criterion, the uncomplexed L_A ligand presents a boat conformation, and so do the two Eu(III) complex cations. Indeed, it is easily seen from *Fig. 4b*

that two opposite O-atoms are significantly out of the mean plane (cf. Table 2). A similar situation is met with the other complexes with L_A, except with Tl(I). In this case the O-ring arrangement is closer to a chair conformation. The uncomplexed L_B ligand as well as its Tl(I) and Na(I) complexes adopt a perfect chair conformation, while the f-element complexes have a boat conformation.

Complexes with L have usually an approximate local symmetry element: $C_2(\perp)$, i.e. perpendicular to the mean O-atom plane, or σ_v for L_A and $C_2(\parallel)$, i.e. in the mean O-atom plane, or C_i for L_B. If this symmetry operation is also crystallographic, a boat conformation is expected for $C_2(\perp)$ and a chair conformation for $C_2(\parallel)$ or C_i. This rule is followed by all the compounds analyzed in Table 3 with the exception of the Tl(I) complex with L_A which displays a distorted chair conformation. A possible explanation for the occurrence of a boat or of a chair conformation may be found by considering the contraction of the O-atom ring upon coordination to the metal ion. In a planar hexagon, this contraction results in a shortening of the O–O contact distances only. In a folded hexagon, the contraction induces also a change in the angles, so that the shortening of the O–O contact distances is less important. The observed conformations may, therefore, be rationalized by comparing the mean distances M–O and O···O. The chair conformations found in the studied complexes are less puckered, i.e. flatter, than the boat conformations. As a result, the M–O and O···O distances are comparable, while they differ more substantially in the boat conformations. The predictions of this crude model are not in line with the observed geometry, if the contraction forces on the ether O-atoms are not uniformly distributed around the ring (i.e. in uncomplexed ligands or complexes with H_3O^+ having directional H-bonds with only three O-atoms of the ligand). On the other hand, the model correctly predicts a shorter Na–O distance in the complex with the unsubstituted 18-crown-6 than in the complex with L_B.

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