127. Crystal and Molecular Structure of the 4:3 Complex between Lanthanum Nitrate and Pentaethyleneglycol Dimethyl Ether[1])

by **Jean-Claude G. Bünzli***, **Jean-Marc Pfefferlé** and **Bruno Ammann**

Institut de chimie minérale et analytique, Université de Lausanne, 3, place du Château, CH–1005 Lausanne,

and **Gervais Chapuis** and **F.-Javier Zuniga**

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

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Summary

The crystal and molecular structure of $[La(NO_3)_3]_4(C_{12}H_{26}O_6)_3$ has been determined from low-temperature single-crystal X-ray diffraction data. The complex crystallizes in the monoclinic space group $I2$ with $Z = 2$. Lattice parameters at 150 K are $a = 12.234$ (6) Å, $b = 11.105$ (5), $c = 26.613$ (9), $\beta = 90.65$ (4)°. The structure was solved by *Patterson* and *Fourier* techniques and refined to a conventional R_F-value of 0.068. The compound contains three dinitrato complex cations $[La(NO_3)_2C_{12}H_{26}O_6]^+$ with 10-coordinate lanthanum ions and one hexanitrato anion, $[La(NO_3)_6]^{3-}$, with a 12-coordinate La(III)-ion. One complex cation has a C_2-symmetry while the two others,which are crystallographically equivalent, have no symmetry and contain a disordered ligand molecule. The polyether adopts a ring-like conformation in all the complex moieties. The La–O(nitrate) distances lie in the ranges 2.52–2.53 and 2.49–2.62 Å, with average values of 2.53 (7) and 2.56 (6) Å, respectively, for the species with C_2- and C_1-symmetry; the La–O(ether) bond lengths lie in the range 2.54–2.79 Å (average: 2.6 (1)) for the C_2-moiety and their mean value amounts to 2.6 (2) for the disordered species. The hexanitrate has a C_2-symmetry and the La–O distances range between 2.56 and 2.67 Å with an average value of 2.64 (4) Å. The effective ionic radii of the 10- and 12-coordinate La(III) ions are estimated as 1.28 and 1.33 Å, respectively.

Introduction. – Rare earth salts react with crown ethers in organic solvents to yield stable complexes with different metal/ligand ratios [1–5]. In particular, 18-crown-6 ether[2]) forms both 1:1 and 4:3 complexes with lanthanoid nitrates [4]; according to X-ray structural data [6], these latter have to be formulated as $[Ln(NO_3)_2(18\text{-crown-}6)]_3[Ln(NO_3)_6]$. The large stability of the hexanitrato anion probably explains why such complexes can be isolated. Polyethyleneglycols and their methyl ethers also react with lanthanide salts to form complexes with similar stoichiometries [1] [7]. It was therefore

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[1]) Part 16 of the Series 'Complexes of Lanthanoid Salts with Macrocyclic Ligands'; Part 15 see [1].

[2]) Systematic name: *1,4,7,10,13,16-hexaoxacyclooctadecane*.

interesting to investigate whether the 4:3 complexes between lanthanide nitrate and 18-podand-6, the open-chain analogue of 18-crown-6 ether, also contain this hexanitrato ion. We present here the crystal and molecular structure of $[La(NO_3)_3]_4$(18-podand-6)$_3$, as determined from single-crystal X-ray diffraction data at 150 K.

Experimental. – *Synthesis of the Complex.* The complex was isolated from a CH_3CN solution following the procedure used for synthesizing 18-crown-6 complexes [4]. Crystallization at low temperature (–5°) yielded a 1:1 complex, $La(NO_3)_3 \cdot C_{12}H_{26}O_6$, as confirmed by elemental analysis and lanthanum titration. However, crystals grown under such conditions readily decompose liberating a viscous liquid, as can be observed under the microscope. This certainly corresponds to a 1:1→4:3 transformation identical to that observed for the 18-crown-6 complexes [4]. Indeed, slow evaporation of the solution at room temperature and under Ar-atmosphere produces nice colourless and monoclinic crystals the elemental analysis of which corresponds to the formula $C_{36}H_{78}N_{12}O_{54}La_4$ (M.W. = 2099.43) [8]. Hydrated lanthanum nitrate was prepared as described in [9] and 18-podand-6, from *Riedel-de Haen AG*, was used without further purification.

Crystal Data Collection. Precession and *Weissenberg* photographs revealed monoclinic symmetry and the systematic absences $h + k + l = 2n$ which are compatible with the space groups: *I2*, *Im*, *I2/m*. Density measurements in $CHCl_3/CHBr_3$ at 295 K yielded $Z = 2$: $d_{obs} = 1.865$, $d_{calc} = 1.847$.

A crystal of approximate dimensions 0.30 × 0.15 × 0.10 mm was selected for intensity data collection. A *Syntex P2₁* diffractometer was used for measurements at room temperature whereas low-temperature data were collected at 150 K on an *Enraf-Nonius* diffractometer (MoK_α-radiation, with Nb filter). A total of 3757 (298 K) and 5514 (150 K) reflections were collected by the θ-2θ scan method up to $2\theta = 50°$, of which 1662 and 2770, respectively, were larger than 3σ.

The dimensions of the unit cell are $a = 12.376$ (4), $b = 11.187$ (4), $c = 27.304$ (8) Å, $\beta = 91.75$ (3), at room temperature; a slight contraction occurs at 150 K: $a = 12.234$ (6), $b = 11.105$ (5), $c = 26.613$ (9) Å, $\beta = 90.65$ (4).

Structure Determination. – Atomic scattering factors of neutral atoms were taken from [10] and the intensities were corrected for absorption by the *Gaussian* integration method. Dispersion corrections for lanthanum were taken from [11].

For the 298-K data, a *Wilson* graph and a statistical analysis of the normalized intensities were inconclusive to decide whether the structure is centrosymmetric or not; it is possible that the lanthanum ions form a centrosymmetric substructure. In the course of the structure determination it occurred that the *Im* space group was not compatible with the positions found for the ligand atoms around La(1) and it was therefore abandoned. Moreover, attempts made to solve the structure in the *I2* and *I2/m* space groups using *Fourier* and *Patterson* techniques were unsuccessful. A total of 46 atoms were found, the 3 independent La, 6 nitrates, one incomplete polyether and some atoms of the second ligand; the R_F-value was 0.094. The problems occurred from disorders in both the polyethers and some nitrato groups, so that the structure had to be solved from low-temperature data.

The structure refined with the 150-K data converged best in the *I2* space group and gave rise to further difficulties. Semi-direct methods yielded a final R_F-value of 0.061, but the temperature factors of the ligand atoms around La(3) were too large and several C–C and C–O distances were out of their expected ranges. A tentative fit of the data using the conformation of the polyether bonded to La(1) as a model for the La(3) cluster failed. Finally, the structure was refined by assigning two different positions to the podand around La(3) with weights equal to ½. A succession of *Fourier* syntheses and *Fourier* difference maps unraveled 34 of the 36 atoms, 11 O-atoms and 23 C-atoms. The overall refinement converged to $R_F = 0.068$, with anisotropic thermal parameters for La, N, and O, and isotropic parameters for the C-atoms. A better refinement was not possible since the peaks generated by the atoms are smaller than those arising from *Fourier*-series termination effects. Six O-atoms belonging to one position of the ligand could be identified but the polyether molecules could not be found completely. A more complicated model should probably be used to solve the disorder with, for instance two positions for each O-atom and four positions for each C-atom. Final positional and thermal parameters are available upon request from *J.-C. B.*

Results and Discussion. – Complexes with 4:3 stoichiometry, $[Ln(NO_3)_3]_4$(18-podand-6)$_3$, are obtained for Ln = Ce to Eu; the 1:1 complex that crystallizes at low temperature with Ln = La reveals to be quite unstable and undergoes a transformation into the 4:3 complex at room temperature [8]. Crystals of the latter can be obtained and their monoclinic centered unit cell is very similar to that of $[Nd(NO_3)_2(18\text{-}crown\text{-}6)]_3[Nd(NO_3)_6]$ [6]; after transformation of the *I* axes into *C* axes one obtains, at room temperature: $a = 29.63$ Å, $b = 11.187$ Å, $c = 12.376$ Å, $\beta = 112.92°$ as compared to $a = 29.461$ Å, $b = 11.246$ Å, $c = 12.057$ Å, and $\beta = 115.34°$ for the crown ether complex [6].

The resolution of the structure from the 150-K data revealed that the crystal contains isolated complex ions with no prominent intermolecular interactions between them. Three different moieties are found in the ratio 1:1:2: a complex cation $[La(1)(NO_3)_2C_{12}H_{26}O_6]^+$ with C_2-symmetry, a hexanitrato anion $[La(2)(NO_3)_6]^{3-}$ with C_2-symmetry, and complex cations $[La(3)(NO_3)_2C_{12}H_{26}O_6]^+$ without symmetry and with a disordered ligand. The packing of these ions in the crystal lattice is partially displayed in *Fig. 1.* All the atoms around the two independent lanthanum ions La(1) and La(2) have been found and are given in *Fig. 1;* the La(3)-cluster is shown with its two nitrato groups and the 11 resolved O-atoms belonging to the two different positions of the polyether. Bond lengths and angles are reported in the *Table.*

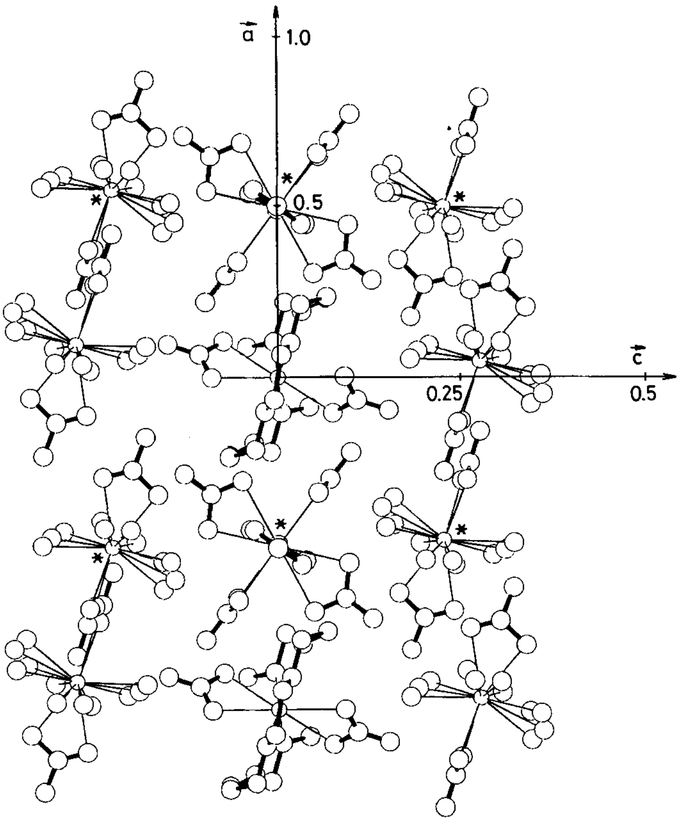


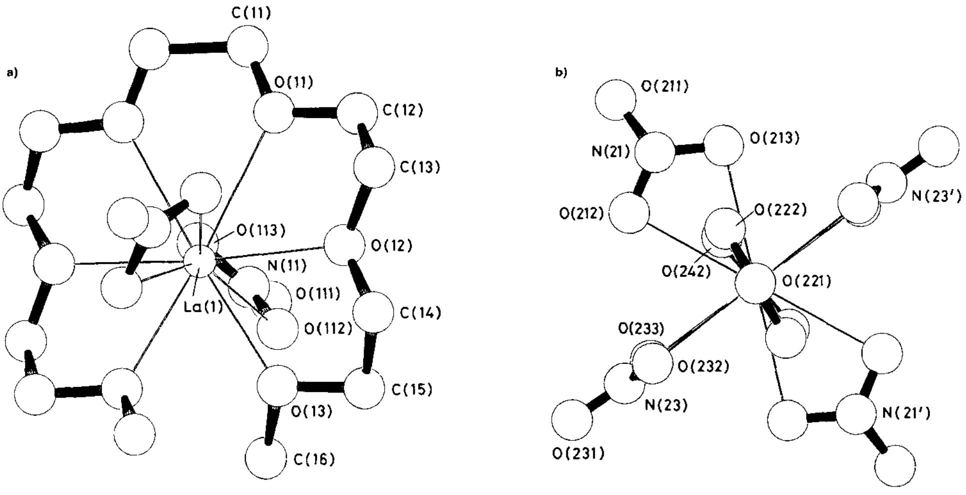
Fig. 1. *Packing of the different clusters in crystals of* $[La(NO_3)_2(18\text{-}podand\text{-}6)]_3[La(NO_3)_6]$. The projection is along the *b*-axis. All the atoms surrounding La(1) and La(2) are drawn; the La(3) cluster is partially shown only and contains the two NO_3^- groups and the 11 O-atoms that could be resolved and which belong to two different positions of the ligand. The stars denote atoms with (*x*, ½, *z*) coordinates.

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

$[La(NO_3)_2C_{12}H_{26}O_6]^+$, C_2-symmetry			
La(1)–O(11)	2.79 (3)	O(11)–La(1)–O(12)	64 (1)
La(1)–O(12)	2.59 (2)	O(12)–La(1)–O(13)	62 (1)
La(1)–O(13)	2.54 (3)	O(112)–La(1)–O(113)	49 (1)
La(1)–O(112)	2.53 (3)	O(11)–La(1)–O(113)	73 (1)
La(1)–O(113)	2.52 (3)		
N(11)–O(111)	1.22 (3)	O(111)–N(11)–O(112)	118 (4)
N(11)–O(112)	1.32 (5)	O(111)–N(11)–O(113)	129 (4)
N(11)–O(113)	1.18 (4)	O(112)–N(11)–O(113)	113 (3)
La–O(NO_3) mean	2.53 (7)	C–O mean 1.48 (9)	
La–O(ether) mean	2.6 (1)	C–C mean 1.57 (9)	
$[La(NO_3)_6]^{3-}$, C_2-symmetry			
La(2)–O(212)	2.68 (2)	O(212)–La(2)–O(213)	47.7 (5)
La(2)–O(213)	2.62 (2)	O(213)–La(2)–O(222)	66 (1)
La(2)–O(222)	2.56 (4)	O(232)–La(2)–O(233)	47 (1)
La(2)–O(232)	2.63 (4)	O(233)–La(2)–O(242)	68 (1)
La(2)–O(233)	2.66 (3)		
La(2)–O(242)	2.67 (3)	La(2)–O mean	2.64 (4)
N(21)–O(211)	1.33 (5)	O(211)–N(21)–O(212)	112 (4)
N(21)–O(212)	1.24 (4)	O(211)–N(21)–O(213)	115 (4)
N(21)–O(213)	1.28 (3)	O(212)–N(21)–O(213)	116 (3)
N(22)–O(221)	1.34 (5)	O(221)–N(22)–O(222)	116 (2)
N(22)–O(222)	1.28 (5)	O(222)–N(22)–O(223)	128 (4)
N(23)–O(231)	1.22 (3)	O(231)–N(23)–O(232)	117 (5)
N(23)–O(232)	1.33 (6)	O(231)–N(23)–O(233)	126 (5)
N(23)–O(233)	1.16 (6)	O(232)–N(23)–O(233)	117 (3)
N(24)–O(241)	1.1 (1)	O(241)–N(24)–O(242)	124 (2)
N(24)–O(242)	1.28 (4)	O(242)–N(24)–O(243)	112 (3)
$[La(NO_3)_2C_{12}H_{26}O_6]^+$, C_1-symmetry, disordered ligand			
La(3)–O(ether) mean	2.6 (2)[a]		
La(3)–O(312)	2.54 (2)	La(3)–O(322)	2.49 (4)
La(3)–O(313)	2.59 (2)	La(3)–O(323)	2.62 (5)
N(31)–O(311)	1.25 (3)	O(311)–N(31)–O(312)	120 (2)
N(31)–O(312)	1.24 (3)	O(311)–N(31)–O(313)	122 (2)
N(31)–O(313)	1.21 (3)	O(312)–N(31)–O(313)	118 (2)
N(32)–O(321)	1.24 (3)	O(321)–N(32)–O(322)	128 (5)
N(32)–O(322)	1.31 (6)	O(321)–N(32)–O(323)	115 (5)
N(32)–O(323)	1.15 (7)	O(322)–N(32)–O(323)	117 (3)

[a]) Calculated with 11 La–O distances *(cf. text)*.

The La(1)-ion is 10-coordinate being bonded to two bidentate nitrate ions and to the six O-atoms of the polyether; this $[La(NO_3)_2(18\text{-podand-}6)]^+$ cation has a C_2-symmetry and the ligand adopts a ring-like conformation *(Fig. 2a)*. The structure is similar to that found for $[Nd(NO_3)_2(18\text{-crown-}6)]^+$, with the following differences: *i*) the symmetry is lower, C_2 *vs.* D_{2h}; *ii*) the six O-atoms of the ligand are not perfectly coplanar *(Fig. 3a)* but their mean plane contains the La-atom, and *iii*) the bond length and angle values are more scattered. Moreover, the nitrate ions are planar, but their local symmetry is C_s rather than C_{2v} as usually observed in similar complexes [12] [13]. In



$[La(NO_3)_2 \cdot C_{12}H_{26}O_6]^+$, C_2 symmetry

$[La(NO_3)_6]^{3-}$, C_2 symmetry

Fig. 2. *View of* a) *the* $[La(1)(NO_3)_2(18\text{-podand-}6)]^+$ *cation with* C_2*-symmetry, and* b) *the* $[La(2)(NO_3)_6]^{3-}$ *anion with* C_2*-symmetry*

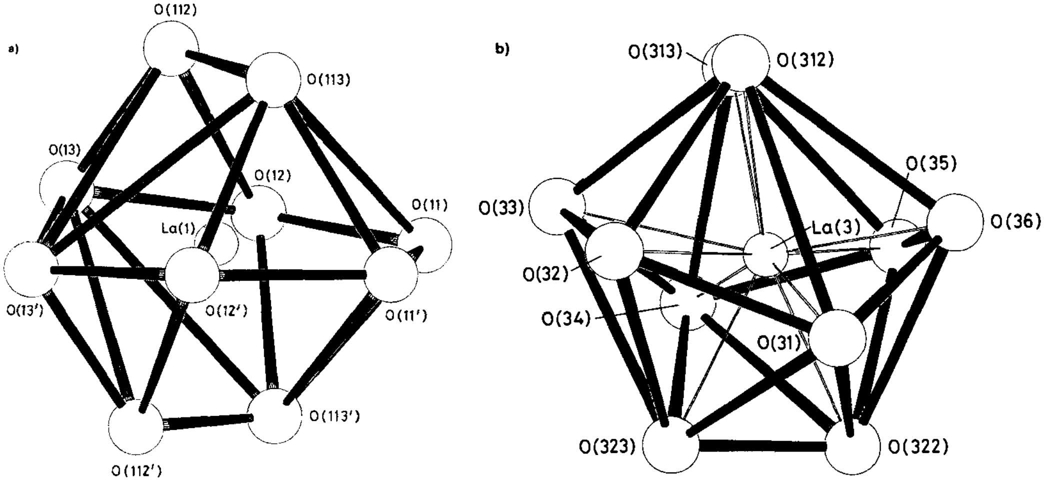


Fig. 3. *Coordination polyhedra of* a) *La(1) in* $[La(NO_3)_2(18\text{-podand-}6)]^+$ (C_2-symmetry), *and* b) *La(3) surrounded by two* NO_3^- *groups and the 6 O-atoms belonging to one polyether conformation*

particular, the N(11)–O(112) distance is substantially longer than N(11)–O(113), despite the fact that both La(1)–O(112) and La(1)–O(113) bond lengths are equal. The average La–O(ether) and La–O(nitrate) distances are 2.6 (1) and 2.53 (7) Å, as compared to 2.58 (3) and 2.42 (2) Å, respectively, for the Nd–O distances in the corresponding 18-crown-6 complex. It is noteworthy that the Ln–O distances we find are about 4% shorter than in the 11-coordinate 1:1 complex between $La(NO_3)_3$ and tetraethyleneglycol [12], which reflects a smaller ionic radius for La(III).

The La(2)-ion is 12-coordinate and surrounded by six bidentate nitrate ions *(Fig. 2b)*. The hexanitrato moiety is less symmetrical than $[Nd(NO_3)_6]^{3-}$ in the 4:3 complex with the crown ether but the bond lengths present a similar scatter. The nitrato groups with N(21) and N(23) as central atoms are not quite planar and their local symmetry departs from C_{2v}; $N(23)O_3^-$ presents a distortion similar to that observed for $N(11)O_3^-$, with two quite different N–O(La) distances. The non-bonded O-atom of $N(24)O_3^-$ has a large thermal ellipsoid resulting in a large imprecision in the N–O bond length. The average La–O(nitrate) distance is 2.64 (4) Å.

The podand around the La(3) atom is disordered and the structure could be partially solved using two different sets of coordinates for this molecule. Six O-atoms belonging to one configuration could be found, but not all the corresponding C-atoms. Five O-atoms were resolved for the other configuration. From the available data, one sees, however, that the overall structure of the cluster around La(3) closely resembles that found around La(1). The La(3) ion is coordinated to two bidentate nitrate ions and to the six O-atoms from the polyether *(Fig. 3b)*. The site symmetry is C_1 and the average La–O(ether) and La–O(nitrate) bond lengths are 2.6 (1) and 2.56 (6), respectively, that is identical to those found for La(1)–O bonds.

From these data, one can estimate the effective ionic radius [14] of the lanthanide ion, using 1.314 Å and 1.310 Å for the radii of the O-atoms in NO_3^- and the polyether, respectively [15]. One finds 1.28 (11) and 1.27 (10) Å for the 10-coordinate La(1) and La(3) ions, respectively, and 1.33 (4) Å for the 12-coordinate La(2) ion. Extrapolation of ionic radii *vs.* coordination number plots [14] gives $r_i = 1.30$ for CN = 10 and $r_i = 1.35$ for CN = 12. The slight differences with our data can be accounted for by the fairly irregular, and broad distribution of the La–O bond lengths in the three independent moieties found in this structure.

In conclusion, the structure of the 4:3 podate is essentially similar, although more distorted, to that of the corresponding 4:3 complexes with the 18-crown-6 ether. The lanthanum complex must therefore be formulated as $[La(NO_3)_2(\text{18-podand-6})]_3$-$[La(NO_3)_6]$.

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