

## Molecular Structures of Complexes of Rare-Earth Metals with Benzo-12-crown-4

S. V. LINDEMAN and YU. T. STRUCHKOV

*Nesmeyanov Institute of Organoelement Compounds, Academy of Sciences of the USSR, Moscow, U.S.S.R.*

Z. M. ALIBAEVA, N. I. SNEZHKO, L. I. MARTYNYENKO and N. I. PECHUROVA  
*Department of Chemistry, Moscow State University, Moscow, U.S.S.R.*

(Received : 18 January 1989; in final form: 18 July 1990)

**Abstract.** An X-ray diffraction study of the complexes  $[\text{Nd}(\text{NO}_3)_3(\text{B12C4})]$  (**I**),  $[\text{La}(\text{NO}_3)_3(\text{B12C4})(\text{H}_2\text{O})] \cdot \text{MeCN}$  (**II**), and  $[\text{Er}(\text{NO}_3)_3(\text{H}_2\text{O})_3] \cdot 2(\text{B12C4}) \cdot \text{MeCN}$  (**III**), (B12C4 = benzo-12-crown-4) has been carried out. Crystals of **I** are monoclinic,  $a = 8.050(2)$ ,  $b = 29.92(1)$ ,  $c = 7.741(2)$  Å,  $\beta = 102.71(2)^\circ$ , space group  $P2_1/c$ ,  $Z = 4$ ,  $R = 0.047$  for 4718 reflections. Crystals of **II** are triclinic,  $a = 8.211(2)$ ,  $b = 10.613(3)$ ,  $c = 12.837(4)$  Å,  $\alpha = 94.46(3)$ ,  $\beta = 108.19(2)$ ,  $\gamma = 89.98(3)^\circ$ , space group  $P\bar{1}$ ,  $Z = 2$ ,  $R = 0.037$  for 5611 reflections. Crystals of **III** are monoclinic,  $a = 9.847(3)$ ,  $b = 17.201(4)$ ,  $c = 21.664(5)$  Å,  $\beta = 100.85(2)^\circ$ , space group  $P2_1/n$ ,  $Z = 4$ ,  $R = 0.040$  for 8328 reflections. The chemical structures of the complexes have been elucidated. The correlation between the radius of a particular lanthanide-ion and its coordination number (10 in **I**, 11 in **II** and 9 in **III**) and consequently its influence on the composition of the complex is discussed. The possibilities of conformational changes in the B12C4 molecule depending on the type and size of the coordinated moiety (ions Nd(III) and La(III) in **I** and **II** and the H<sub>2</sub>O molecule in **III**) are considered.

**Key words.** Crown ethers, rare-earth metals, crystal structure

### 1. Introduction

Rare-earth metals exhibit high coordination numbers and varying stoichiometry in their complexes with the macrocyclic polyethers [1]. In many cases determination of the composition and the type of the coordination polyhedra presents certain difficulties, which can be overcome only by means of an X-ray diffraction study. Relationships between the coordination ability, the number of coordination sites, the conformational flexibility of the crown-ligand, the size of the coordinated ion or molecule as well as the type of the counter-ion or other molecules, which may compete with the macrocyclic ligand in the complexation process, are also of interest. In this respect complexes of rare-earth metals with benzo-12-crown-4 (B12C4), which is one of the simplest polyether ligands from the structural point of view, represent the most convenient subject for such studies.

### 2. Experimental

The synthesis of the lanthanide complexes with B12C4 has been carried out according to the conventional technique [2]. Single crystals were prepared by slow

evaporation of the saturated solutions in acetonitrile. Unit cell parameters and intensities of diffracted reflections for the complexes [Nd(NO<sub>3</sub>)<sub>3</sub>(B12C4)] (I), [La(NO<sub>3</sub>)<sub>3</sub>(B12C4)(H<sub>2</sub>O)]·MeCN (II) and [Er(NO<sub>3</sub>)<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>]·2(B12C4)·MeCN (III) were measured with an automatic four-circle 'Syntex P2<sub>1</sub>' diffractometer at -120°C ( $\lambda$ MoK $\alpha$ , graphite monochromator,  $\theta/2\theta$ -scan,  $2\theta_{\max}$  = 66, 60 and 60° respectively).

Crystals of I are monoclinic,  $a = 8.050(2)$ ,  $b = 29.92(1)$ ,  $c = 7.741(2)$  Å,  $\beta = 102.71(2)^\circ$ , space group  $P2_1/c$ ,  $Z = 4$  [Nd(NO<sub>3</sub>)<sub>3</sub>(B12C4)],  $d_c = 2.025$  g/cm<sup>3</sup>,  $\mu(\text{MoK}\alpha) = 29.4$  cm<sup>-1</sup>; crystals of II are triclinic,  $a = 8.211(2)$ ,  $b = 10.613(3)$ ,  $c = 12.837(4)$  Å,  $\alpha = 94.46(3)$ ,  $\beta = 108.19(2)$ ,  $\gamma = 89.98(3)^\circ$ , space group  $P\bar{1}$ ,  $Z = 2$  [La(NO<sub>3</sub>)<sub>3</sub>(B12C4)(H<sub>2</sub>O)]·MeCN,  $d_c = 1.907$  g/cm<sup>3</sup>,  $\mu(\text{MoK}\alpha) = 21.0$  cm<sup>-1</sup>; crystals of III are monoclinic,  $a = 9.847(3)$ ,  $b = 17.201(4)$ ,  $c = 21.664(5)$  Å,  $\beta = 100.85(2)^\circ$ , space group  $P2_1/n$ ,  $Z = 4$  [Er(NO<sub>3</sub>)<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>]·2(B12C4)·MeCN,  $d_c = 1.653$  g/cm<sup>3</sup>,  $\mu(\text{MoK}\alpha) = 24.4$  cm<sup>-1</sup>. The structures were solved by the heavy atom method and refined by the block-diagonal least-squares technique in the anisotropic approximation for non-hydrogen atoms. Hydrogen atoms were located

Table I. The coordinates ( $\times 10^4$ ) and the temperature factors  $B_{\text{eq}}$  (Å<sup>2</sup>) ( $B_{\text{eq}} = 1/3 \sum_i \sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$ ) of the non-hydrogen atoms of structure I

Atom	x	y	z	$B_{\text{eq}}$
Nd	6275.5(3)	3916.5(1)	3370.0(3)	0.99(1)
O(1)	3369(4)	3934(1)	1149(4)	1.2(1)
C(2)	2323(6)	3556(2)	908(5)	1.3(1)
C(3)	2654(6)	3229(2)	2191(6)	1.5(1)
O(4)	3966(4)	3314(1)	3634(4)	1.6(1)
C(5)	3884(7)	3115(2)	5322(6)	2.0(1)
C(6)	5345(7)	3316(2)	6651(6)	2.0(1)
O(7)	5501(4)	3785(1)	6384(4)	1.4(1)
C(8)	4164(7)	4050(2)	6842(6)	1.7(1)
C(9)	4241(6)	4505(2)	6034(6)	1.6(1)
O(10)	4115(4)	4456(1)	4143(4)	1.3(1)
C(11)	2384(6)	4445(2)	3107(6)	1.5(1)
C(12)	2487(6)	4360(2)	1245(6)	1.4(1)
C(13)	1068(6)	3502(2)	-626(6)	1.8(1)
C(14)	109(6)	3103(2)	-818(7)	2.3(1)
C(15)	419(7)	2780(2)	475(7)	2.4(1)
C(16)	1692(7)	2837(2)	2005(7)	2.1(1)
N(1)	9132(5)	4331(2)	5829(5)	1.5(1)
O(1.1)	9085(5)	3914(1)	5557(5)	1.9(1)
O(1.2)	7842(4)	4552(1)	5054(4)	1.8(1)
O(1.3)	10374(5)	4521(2)	6749(5)	2.4(1)
N(2)	6887(6)	3026(2)	2085(6)	2.0(1)
O(2.1)	7649(5)	3165(1)	3609(5)	2.1(1)
O(2.2)	6065(5)	3323(1)	1065(5)	2.0(1)
O(2.3)	6935(6)	2640(2)	1621(7)	3.3(1)
N(3)	7701(6)	4394(2)	718(5)	1.8(1)
O(3.1)	8557(4)	4107(2)	1745(4)	1.9(1)
O(3.2)	6203(4)	4472(1)	966(5)	2.0(1)
O(3.3)	8210(6)	4571(2)	-465(6)	3.2(1)

Table II. The coordinates ( $\times 10^4$ ) and the temperature factors  $B_{\text{eq}}$  ( $\text{\AA}^2$ ) of the non-hydrogen atoms of structure II (the water and methyl H-atoms coordinates are also given  $\times 10^3$ )

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}$
La	3709.1(2)	7850.1(2)	6868.6(2)	1.33(1)
O(1)	6190(4)	8874(3)	8622(3)	2.6(1)
C(2)	7189(5)	8066(4)	9362(3)	2.0(1)
C(3)	7250(4)	6805(4)	8989(3)	1.7(1)
O(4)	6422(3)	6469(3)	7883(2)	1.6(1)
C(5)	7602(5)	5995(4)	7311(3)	2.1(1)
C(6)	6563(5)	5734(4)	6112(3)	2.2(1)
O(7)	5697(4)	6853(3)	5688(2)	2.0(1)
C(8)	6847(9)	7646(6)	5357(5)	5.0(2)
C(9)	6542(10)	8893(6)	5510(6)	5.6(3)
O(10)	6265(5)	9223(3)	6587(3)	3.5(1)
C(11)	7693(6)	9685(5)	7469(6)	4.3(2)
C(12)	7069(7)	9982(4)	8425(5)	3.7(1)
C(13)	8031(6)	8477(5)	10462(4)	2.9(1)
C(14)	8907(6)	7599(6)	11168(4)	3.1(1)
C(15)	8896(6)	6343(5)	10806(4)	2.9(1)
C(16)	8068(5)	5927(4)	9703(3)	2.2(1)
N(1)	1739(4)	10343(3)	6488(3)	2.0(1)
O(1.1)	909(4)	9318(3)	6178(3)	2.5(1)
O(1.2)	3345(4)	10300(3)	6932(3)	2.9(1)
O(1.3)	1046(4)	11378(3)	6365(3)	2.7(1)
N(2)	2575(4)	7589(4)	8881(3)	2.1(1)
O(2.1)	3521(4)	6776(3)	8585(2)	2.1(1)
O(2.2)	2243(4)	8564(3)	8347(3)	2.5(1)
O(2.3)	2010(5)	7431(4)	9634(3)	3.9(1)
N(3)	1428(4)	5507(3)	6330(3)	1.9(1)
O(3.1)	2966(3)	5471(3)	6304(2)	1.9(1)
O(3.2)	868(3)	6603(3)	6482(3)	2.3(1)
O(3.3)	563(4)	4552(3)	6236(3)	3.3(1)
O(W)	2338(4)	7911(3)	4814(2)	2.3(1)
N	3362(6)	7110(5)	2905(4)	3.7(1)
C(1N)	4262(6)	6868(4)	2414(4)	2.7(1)
C(2N)	5420(7)	6549(5)	1792(5)	3.3(2)
H(1W)	137(7)	809(5)	459(5)	
H(2W)	263(7)	761(5)	435(5)	
H(CN1)	522(7)	564(5)	164(5)	
H(CN2)	662(7)	676(5)	219(5)	
H(CN3)	556(7)	711(5)	153(5)	

in the difference Fourier synthesis (excluding hydrogen atoms of acetonitrile in structure III which could not be located) and included into the refinement with the fixed value of  $B_{\text{iso}} = 4.0 \text{ \AA}^2$ . The final  $R$ -factors are as follows:  $R = 0.047$ ,  $R_w = 0.073$  for 4718 reflections with  $I > 3\sigma(I)$  for structure I;  $R = 0.037$ ,  $R_w = 0.044$  for 5611 reflections with  $I > 2\sigma(I)$  for structure II;  $R = 0.040$ ,  $R_w = 0.053$  for 8328 reflections with  $I > 4\sigma(I)$  for structure III. Atomic coordinates for the structures I–III are given in Tables I–III. All calculations were carried out with an ‘Eclipse S/200’ computer using the INEXTL program package [3].

Table III. The coordinates ( $\times 10^4$ ) and the temperature factors  $B_{\text{eq}}$  ( $\text{\AA}^2$ ) of the non-hydrogen atoms of structure III (the water H-atoms coordinates are also given  $\times 10^3$ )

Atom	$x$	$y$	$z$	$B_{\text{eq}}$
Er	7190.6(2)	2263.0(1)	6184.3(1)	1.35(1)
O(1W)	5259(3)	1880(2)	5464(1)	2.3(1)
O(2W)	6176(3)	1365(2)	6782(1)	1.8(1)
O(3W)	5510(3)	3050(2)	6478(1)	2.0(1)
N(1)	8605(3)	1197(2)	5525(2)	2.1(1)
O(1.1)	8780(4)	1932(2)	5500(2)	2.0(1)
O(1.2)	7780(3)	978(2)	5883(2)	2.6(1)
O(1.3)	9167(3)	739(2)	5235(2)	2.2(1)
N(2)	9089(4)	2334(2)	7347(2)	2.1(1)
O(2.1)	9311(3)	1926(2)	6886(1)	2.8(1)
O(2.2)	7957(3)	2703(2)	7251(1)	1.8(1)
O(2.3)	9891(4)	2367(2)	7843(2)	3.8(1)
N(3)	7916(3)	3625(2)	5586(2)	2.0(1)
O(3.1)	8475(3)	3423(2)	6143(1)	2.1(1)
O(3.2)	6913(3)	3199(2)	5324(1)	2.2(1)
O(3.3)	8322(4)	4179(2)	5329(2)	3.0(1)
O(1)	4712(3)	35(2)	7363(1)	2.1(1)
C(2)	4373(4)	438(2)	7856(2)	1.8(1)
C(3)	3541(4)	1093(2)	7690(2)	2.0(1)
O(4)	3281(3)	1332(2)	7070(1)	2.1(1)
C(5)	2257(4)	887(3)	6657(2)	2.6(1)
C(6)	2425(4)	1023(3)	5990(2)	2.9(1)
O(7)	3742(3)	757(2)	5876(1)	2.3(1)
C(8)	3823(5)	-64(3)	5791(2)	2.5(1)
C(9)	5311(5)	-286(3)	5814(2)	2.4(1)
O(10)	6134(3)	-195(2)	6427(1)	1.9(1)
C(11)	5997(5)	-807(2)	6855(2)	2.4(1)
C(12)	5885(4)	-468(3)	7474(2)	2.3(1)
C(13)	4781(4)	231(2)	8487(2)	2.2(1)
C(14)	4288(5)	666(3)	8942(2)	2.6(1)
C(15)	3415(5)	1298(3)	8775(2)	2.9(1)
C(16)	3044(4)	1502(3)	8154(2)	2.5(1)
O(1A)	3099(3)	3911(2)	6863(1)	2.4(1)
C(2A)	3568(4)	3904(2)	7488(2)	2.0(1)
C(3A)	4876(4)	4278(2)	7693(2)	2.1(1)
O(4A)	5610(3)	4533(2)	7241(1)	2.2(1)
C(5A)	5081(5)	5236(3)	6923(2)	2.9(1)
C(6A)	5627(6)	5278(3)	6319(2)	3.1(1)
O(7A)	5214(3)	4642(2)	5915(1)	2.8(1)
C(8A)	3857(5)	4740(3)	5553(2)	3.4(1)
C(9A)	3381(6)	3974(3)	5234(2)	3.5(1)
O(10A)	3142(3)	3376(2)	5664(2)	3.0(1)
C(11A)	1869(5)	3448(3)	5892(3)	3.2(1)
C(12A)	2127(4)	3330(3)	6595(2)	2.9(1)
C(13A)	2913(4)	3583(3)	7935(2)	2.6(1)
C(14A)	3492(5)	3646(3)	8575(2)	3.0(1)
C(15A)	4733(5)	4037(3)	8763(2)	3.2(1)
C(16A)	5429(5)	4357(3)	8323(2)	2.5(1)
N	3541(6)	2355(3)	4333(2)	4.7(1)
C(1N)	2638(6)	2528(3)	3949(2)	3.0(1)
C(2N)	1527(6)	2776(3)	3442(2)	3.4(1)

Table III. (continued)

Atom	x	y	z	$B_{eq}$
H(1W1)	502(6)	214(3)	515(3)	
H(1W2)	498(6)	150(3)	549(3)	
H(2W1)	544(6)	139(3)	678(3)	
H(2W2)	592(6)	99(3)	673(3)	
H(3W1)	568(6)	356(3)	675(3)	
H(3W2)	473(6)	301(4)	621(2)	

### 3. Results and Discussion

The Nd(III) ion in complex I is coordinated by the three *cis*-located bidentate NO<sub>3</sub> ligands and by the tetradentate B12C4 molecule (Figure 1) (the overall coordination number is equal to 10). The Nd—O(NO<sub>3</sub>) distances span the range 2.487–2.509(4) Å (av. 2.497(4) Å) and are somewhat shorter than in the similar nitrate/crown complexes of 12-coordinated Nd(III) (2.57–2.66 Å [4–6]). Even shorter Nd—O(NO<sub>3</sub>) distances (down to 2.42 Å) have been found for the 10-coordinated Nd(III) in the complex cation with *trans*-located bidentate NO<sub>3</sub> ligands [4].

The Nd—O(B12C4) distances in complex I are much longer than the Nd—O(NO<sub>3</sub>) distances and vary over a wide range of 2.538 to 2.630(4) Å (av. 2.581(4) Å). A similar effect is also observed in other complexes with crown-ethers. For example in the nitrate complexes of Nd(III) with 18C6 ligand the Nd—O distances are 2.54–2.79 Å [4–6].

The coordination polyhedron of Nd(III) is a distorted two-capped tetragonal antiprism with the 'caps' O(1) and O(1.1) situated over the 'square' faces [O(4), O(10), O(2.2), O(3.2)] and [O(7), O(1.2), O(2.1), O(3.1)], respectively. The first 'square' face is planar within 0.07 Å, whereas the second is considerably distorted – displacement of the O-atoms from the mean plane of the face exceeds 0.3 Å. The dihedral angle between the mean planes of the 'square' faces is 6.3(3)°. The relative twist angle of these faces is ca. 35° (45° for the ideal antiprism).

The observed significant distortions from the geometry of the corresponding ideal polyhedron are evidently due to the formation of the small chelate rings, primarily four-membered with the participation of bidentate NO<sub>3</sub> ligands. One of these rings [Nd, O(2.1), N(2), O(2.2)] is folded by 12.0(3)°, whereas two other rings are approximately planar.

The five-membered chelate rings formed by the crown ligand exhibit yet more significant deviations from planarity. For instance the [Nd, O(1), C(2), C(3), O(4)] ring has a distinct envelope conformation (the Nd-ion displacement from the plane of the other atoms is 0.724(1) Å, the folding angle along the O(1)—O(4) line is 18.8(3)°). The [Nd, O(4), C(5), C(6), O(7)] ring has also an envelope conformation with the displacement of the O(7) atom (the folding angle along the Nd—C(6) line amounts to 56.5(3)°). The conformations of the remaining two five-membered chelate rings are in fact identical: the C(9)- and C(12)-envelopes which are somewhat distorted towards the 8,9- and 11,12-half-chairs, respectively (the folding angles are 48.6 and 50.1(3)°, the deviation of atoms from planes are 0.131 and 0.567(5) Å for C(8) and C(9) and 0.179 and 0.548(5) Å for C(11) and C(12)).

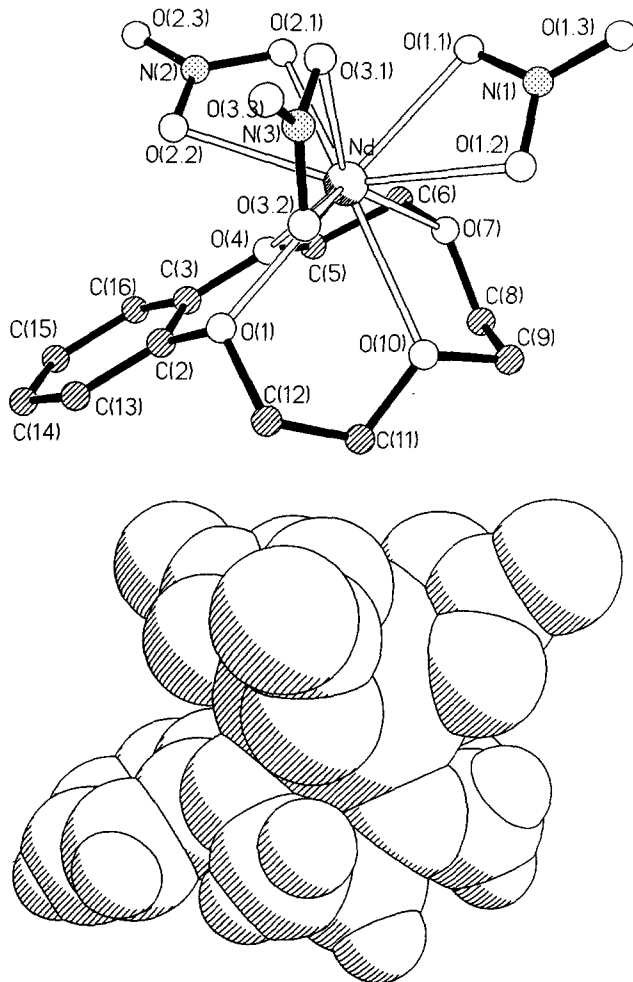


Fig. 1. The structure of complex I (bottom: the space-filling plot).

The observed conformation of the five-membered chelate rings is favourable for coordination of the Nd-ion by lone electron pairs of the ether O atoms: the C—O⋯Nd angles vary in the range of 109.1–121.6(1)°.

In the similar complex II the larger lanthanide ion (ionic radius 1.04 Å for La(III) instead of 0.99 Å for Nd(III) [7]) along with the three bidentate nitrate and one tetradentate B12C4 ligands is coordinated by a water molecule, thus acquiring the coordination number 11 (Figure 2). Analogous to the complex I, the La—O(NO<sub>3</sub>) distances (2.572–2.727(3) Å, av. 2.620(3) Å) are smaller than the La—O(B12C4) distances, which vary in the range of 2.675–2.715(3) Å (av. 2.694(3) Å).

The additional aqua ligand in complex II causes a drastic rearrangement of the coordination polyhedron of the lanthanide cation. Eleven-vertex polyhedra are rare and their topological and comparative analysis in the literature [8, 9] is by no means

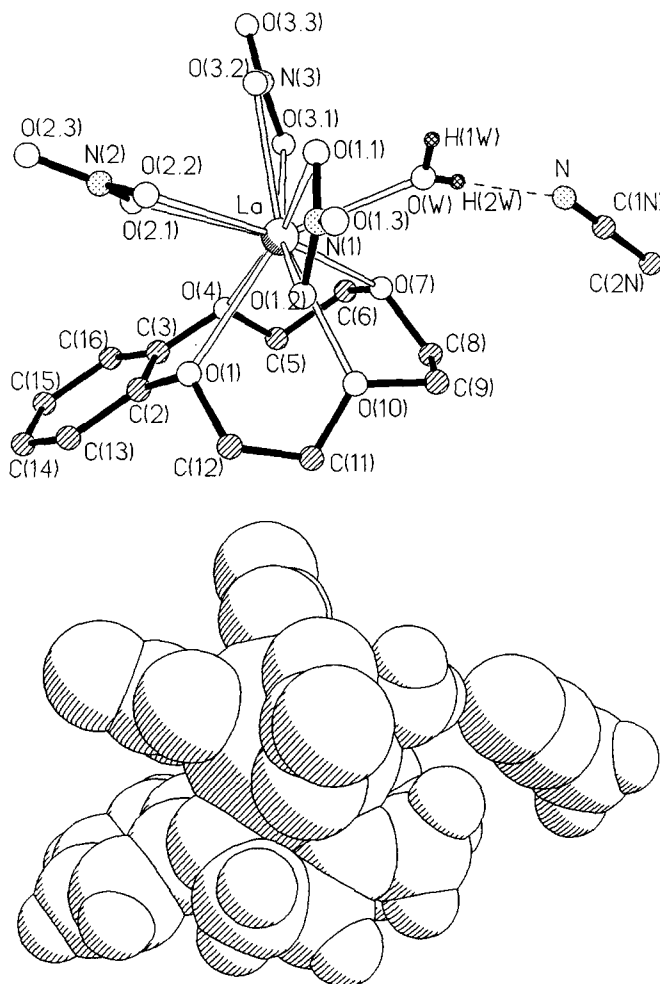
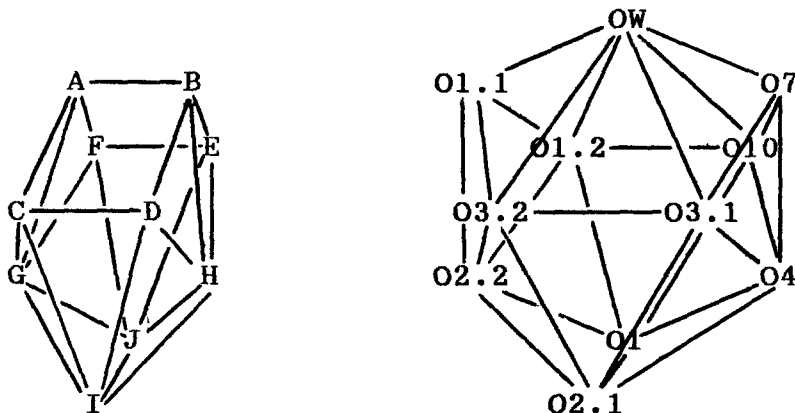


Fig. 2. The structure of complex II.

comprehensive. Therefore it is difficult to give a simple description of the Ln polyhedron in II. However, one may note that this polyhedron originates from the ten-vertex sphenocrown [8] rather than from the two-capped square antiprism of complex I: the additional O(W) vertex is 'inserted' into the AB edge (using the labelling conventions adopted in [8]) of the initial ten-vertex sphenocrown (see Scheme 1).

The distortions of the chelate four-membered rings formed by the bidentate nitrate ligands are comparatively small: the folding angles along the O...O lines are 0.6, 6.0, and 7.7(3)° for the N(1), N(2), and N(3) nitrate ligands respectively. However, in comparison with the Nd(III) complex the La(III) ion in II is moved away from the mean plane of the B12C4 ligand (due to the increase of the ionic radius), which leads to a considerable change in the conformation of the five-membered rings, in particular to the increase of their non-planarity.



Scheme 1.

Thus, the [La, O(1), C(2), C(3), O(4)] ring in complex **II** is folded along the O...O line by  $25.2(2)^\circ$  (the displacement of La(III) from the plane of the other atoms is  $0.992(1)$  Å) which is  $6.4^\circ$  larger than the folding of the analogous ring in complex **I**. The [La, O(4), C(5), C(6), O(7)] ring adopts the shape of a C6 envelope (an O7-envelope in **I**), the folding angle being  $49.6^\circ$ . The [La, O(7), C(8), C(9), O(10)] ring has a conformation of a severely distorted C9,O10-half-chair with a significant contribution of the O10-envelope form, in contrast to the C9-envelope in **I**. However, the [La, O(10), C(11), C(12), O(1)] ring retains the conformation of an O12-envelope, found also in complex **I**, with the same folding angle ( $47.3^\circ$ ).

Comparison of the complexes **I** and **II** (Table IV, Figure 3) demonstrates a considerable conformational flexibility of the B12C4 molecule, which is clearly displayed by its adjustment to the larger coordinated ion. Whereas the conformation of the [C(9), C(10)...C(3), O(4)] moiety of the macrocycles remains invariant in going from **I** to **II**, significant conformational changes occur in the other parts of the B12C4 molecules, involving mainly those torsion angles – C(2)C(3)O(4)C(5) ( $\Delta = 33.0^\circ$ ) and C(9)C(8)O(7)C(6) ( $\Delta = 17.6^\circ$ ), which determine the orientation of the lone electron pairs of the O(4) and O(7) atoms relative to the mean plane of the

Table IV. The endocyclic torsion angles (degrees) in B12C4 molecules in structures I–III

Angle	I	II	IIIa	IIIb
O(1)C(2)C(3)O(4)	2.1(4)	5.1(3)	-7.9(3)	-7.0(3)
C(2)C(3)O(4)C(5)	151.0(7)	118.0(5)	77.8(5)	76.1(5)
C(3)O(4)C(5)C(6)	-172.8(7)	-176.9(5)	-160.9(6)	-160.5(6)
O(4)C(5)C(6)O(7)	42.8(4)	56.0(3)	63.0(4)	60.3(4)
C(5)C(6)O(7)C(8)	70.8(6)	83.8(6)	78.5(5)	82.1(6)
C(6)O(7)C(8)C(9)	-164.9(7)	-147.3(8)	-168.1(6)	-168.6(7)
O(7)C(8)C(9)O(10)	55.7(4)	43.7(4)	68.9(4)	68.3(5)
C(8)C(9)O(10)C(11)	87.1(6)	95.1(8)	78.9(5)	77.1(6)
C(9)O(10)C(11)C(12)	-175.9(6)	178.1(8)	-136.2(6)	-133.7(6)
O(10)C(11)C(12)O(1)	59.0(4)	54.2(4)	58.3(4)	59.3(4)
C(11)C(12)O(1)C(2)	87.8(6)	91.9(6)	-179.1(6)	-176.1(6)
C(12)O(1)C(2)C(3)	-120.1(6)	-122.5(5)	159.4(6)	156.7(6)



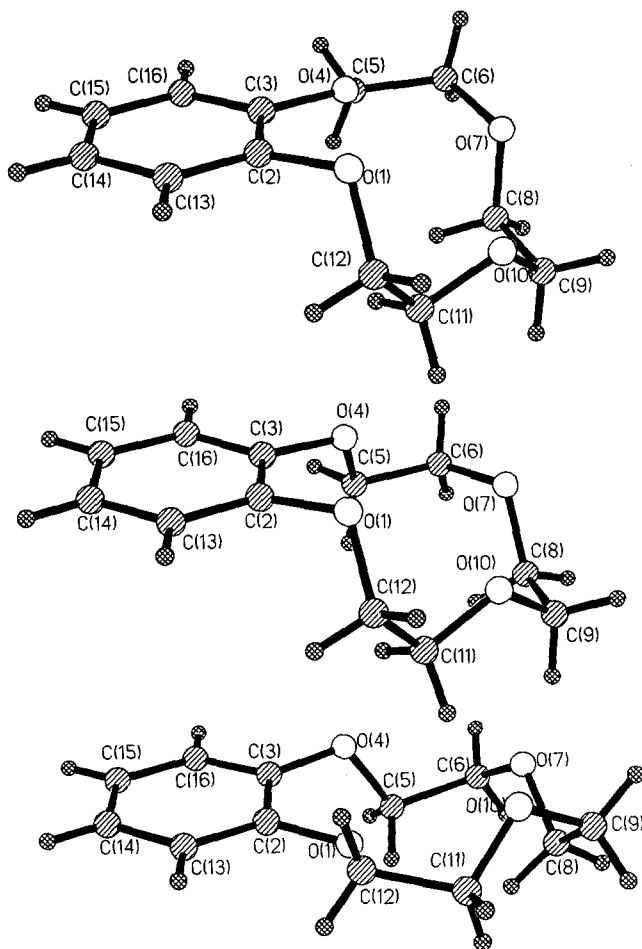


Fig. 3. Conformations of B12C4 molecules in the complexes **I** (top), **II** (middle) and **III** (bottom). All projections are given in the same orientation relative to the benzene moiety of the molecules. For structure **III** only the conformation of the *A* molecule is shown (molecule *B* has a similar conformation).

macrocycle. Changing these angles results just in the increase of the displacement of the lone electron pairs of the oxygen atoms from the mean plane of the macrocycle in complex **II**. This displacement provides the most favourable conditions for coordination of the rare earth ion with greater radius (all  $\text{La}\cdots\text{O}-\text{R}$  bond angles in complex **II** vary in the range  $112.8-122.8(1)^\circ$ ).

As in other lanthanide nitrate crown complexes with aqua-ligands [10-12] the  $\text{La}-\text{O}(\text{W})$  distance of  $2.530(3)$  Å in complex **II** is ca.  $0.1$  Å shorter than the  $\text{La}-\text{O}(\text{NO}_3)$  distances. The water molecule forms H-bonds with the nitrate group of the neighboring complex (with formation of centrosymmetric dimers) and with the non-coordinated solvate acetonitrile molecule ( $\text{O}(\text{W})\cdots\text{O}(1.3)$   $2.851(5)$  Å;  $\text{O}(\text{W})\cdots\text{N}$   $2.898(6)$  Å). The intracomplex H-bond  $\text{O}(\text{W})\cdots\text{O}(1.1)$  ( $\text{O}\cdots\text{O}$   $2.747(4)$  Å) is also likely to be formed (i.e. the  $\text{H}(\text{OW}.1)$  atom takes part in a non-symmetric bifurcated H-bond).

All other conditions being equal, transition from the Nd complex (**I**) to the

Er complex (**III**) with the smaller cationic radius (by ca.  $0.15 \text{ \AA}$  [7, 11]), should lead to a decrease of the lanthanide coordination number, i.e. to full or partial displacement of the nitrate or crown ligand from the coordination sphere. It is known that in some nitrate 9-coordinated complexes of rare-earth metals with a smaller radius than that of the Nd(III) ion, the crown ligands are displaced from the coordination sphere by water molecules partially (in  $\text{Sm}(\text{NO}_3)_3(\text{H}_2\text{O})\text{L}$ : L = (2-methoxy-1,3-xylyl)-18-crown-5 coordinates Sm(III) by the three out of six O atoms [10]) or completely (in the  $[\text{Dy}(\text{NO}_3)_3(\text{H}_2\text{O})_3]\text{L}$  [11]). Moreover in some cases water molecules also displace nitrate ligands (e.g. in the complex  $[\text{Y}(\text{NO}_3)_2(\text{H}_2\text{O})](\text{NO}_3)(15\text{C}5)_2$  [12]).

Indeed, the Er(III) ion in complex **III** (Figure 4) has a low coordination number

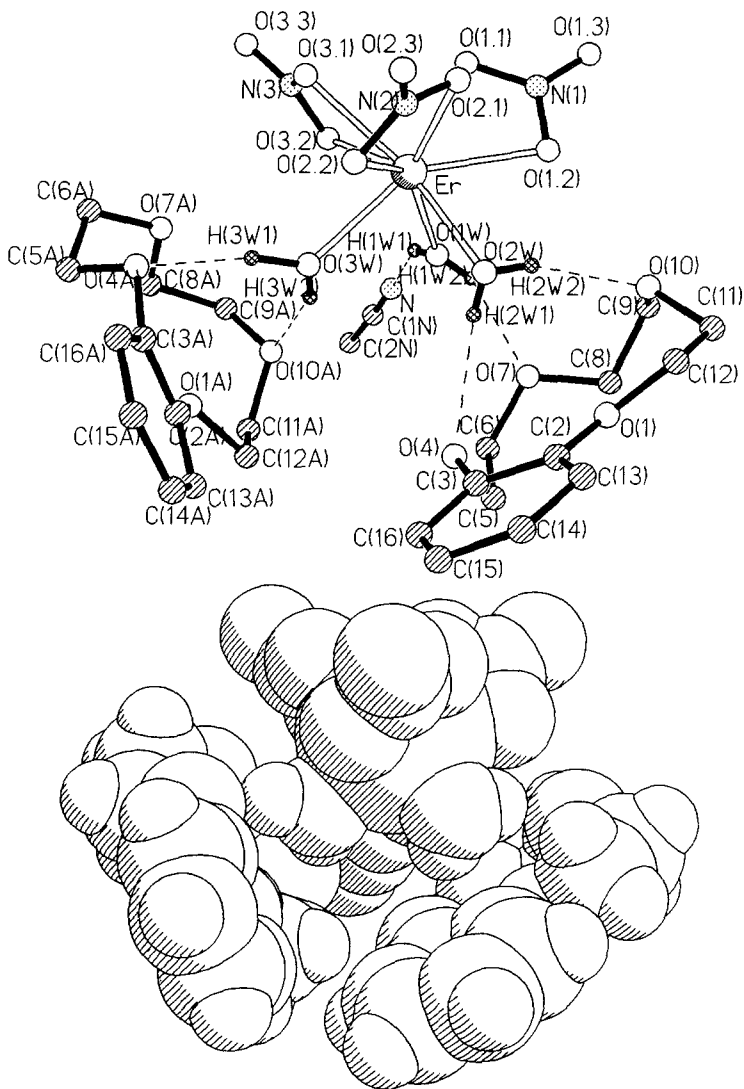


Fig. 4. The structure of complex **III**.

of 9. It is coordinated by three bidentate nitrate ligands (Er—O(NO<sub>3</sub>) 2.373–2.440(3) Å, ave. 2.410(3) Å) and by three aqua ligands (Er—O(H<sub>2</sub>O) 2.317–2.356(3) Å, ave. 2.330(3) Å). Two B12C4 and one acetonitrile molecules are located in the outer coordination sphere. The coordination polyhedron of the Er(III) ion is a distorted three-capped trigonal prism with the relative twist angle of the triangular bases [O(1.1)O(2.1)O(3.1)] and [O(1W)O(2W)O(3W)] equal to ca. 20° and with a dihedral angle of 5.8(3)° between them. The capping atoms O(1.2), O(2.2) and O(3.2) located over the side faces of the prism are shifted from the equatorial plane passing through the Er(III) ion in the direction of the basal atoms O(1.1), O(2.1) and O(3.1) by 0.37 Å. The distortion of the coordination polyhedron consists also in the rotation of the equatorial triangle [O(1.2)O(2.2)O(3.2)] with respect to the basal triangle [O(1.1)O(2.1)O(3.1)] by ca. 45° instead of the ideal value 60°. The small chelate rings, which cause such distortions of the coordination polyhedron, are only slightly distorted themselves: the folding angles along the O··O lines being equal to 2.2, 0.4 and 5.7° for nitrate ligands N(1), N(2) and N(3), respectively.

The outer B12C4 ligands and acetonitrile molecule do not coordinate the metal ion but are involved in complex **III** via H-bonding with the coordinated water molecules (Figure 4). The molecule *A* of the crown ligand forms one H-bond with O(1W) and two with O(2W) (O··O 2.694–3.031(3) Å, H··O 2.05–2.33(2) Å, the O—H··O angles 150–162(3)°). The molecule *B* forms two H-bonds with O(3W) (O··O 3.032 and 2.705(3) Å, H··O 1.99 and 1.89(2) Å, O—H··O 169 and 156(3)°). The acetonitrile molecule is H-bonded to O(1W) (O··N 2.823(4) Å, H··N 2.10(2) Å, O—H··N 149(3)°).

The different type of coordination of the B12C4 molecule in complex **III** as compared with complexes **I** and **II** leads to a drastic change in its conformation (Figure 3, Table IV). The main difference consists in the change of orientations of the lone electron pairs of the O(1) atom: in complexes **I** and **II** their directions coincide with that of the lone electron pairs of other oxygen atoms thus leading to coordination of the lanthanide cation. On the contrary, in complex **III** the electron pairs of the O(1) atom are directed inside the macrocycle and even somewhat turned towards the direction opposite to the coordinated water molecule which makes these lone pairs inaccessible for coordination. There is also a certain difference in orientation of the lone electron pairs of the O(4) atom though the axial orientation relative to the macrocycle exhibited in complexes **I** and **II** is preserved, these pairs deviate towards the interior and not the exterior of the ring.

It may probably be explained by the fact that the van-der-Waals radius of a coordinated water molecule (even taking into account its effective decrease due to the formation of H-bonds) is somewhat greater than, e.g. the La(III) ionic radius. As a result further 'opening' of the macrocycle cavity occurs: the torsion angle C(2)C(3)O(4)C(5) value changes from 151.0(7)° in **I** to 118.0(5)° in **II** and to 77.8 and 76.1(5)° in **III**. The lone electron pairs of the O(7) and O(10) atoms preserve the axial orientation relative to the macrocycle as well as the coordination ability (in the present case by water molecules).

It is noteworthy that despite the different types of coordination of the *A* and *B* crown ether molecules in structure **III** (molecule *A* is coordinated by the three H atoms of the two water molecules and molecule *B* is coordinated by two H atoms of the one water molecule) their conformations are in fact identical (Table IV).

The geometrical parameters of the B12C4 molecules in all structures are unexceptional: the mean CH<sub>2</sub>—CH<sub>2</sub> and O—CH<sub>2</sub> bond lengths are 1.490 and 1.440 Å. A significant spread in the values of the bond angles at the ether O atoms (109.7–119.0°) as well as the CCO bond angles at the methylene carbon atoms (105.6–113.7°) suggest a certain steric strain of the macrocycle in the studied structures.

Complete crystallographic data on the structures have been deposited with the Cambridge Structural Data Centre.

## References

1. J. -C. G. Bunzli, B. Klein, D. Wessner, and N. W. Alcock: *Inorg. Chim. Acta* **59**, 269 (1982).
2. Z. M. Alibaeva, N. I. Pechurova, I. V. Podgornaya, V. A. Popova, N. I. Snezhko, and L. I. Martynenko: *Zh. Neorg. Khim* **32**, 906 (1987). (*Chem. Abstr.* **107**, 50808t (1987)).
3. R. G. Gerr, A. I. Yanovsky, and Yu. T. Struchkov: *Kristallografia* **28**, 1029 (1983) (*Phys. Abstr.* **A87**, 60786 (1984)).
4. J. -C. Bunzli, B. Klein, D. Wessner, K. J. Schenk, G. Chapuis, G. Bombieri, and G. de Paoli: *Inorg. Chim. Acta* **54**, L43 (1981).
5. G. Bombieri, G. de Paoli, F. Benetollo, and A. Cassol: *J. Inorg. Nucl. Chem.* **42**, 1417 (1980).
6. J. -C. Bunzli, B. Klein, and D. Wessner: *Inorg. Chim. Acta* **44**, L147 (1980).
7. G. B. Bokii: *Crystal Chemistry (Kristalokhimiya)*, Nauka (Moscow, USSR) (1971) (*Chem. Abstr.* **77**, 119446e (1972)).
8. D. L. Kepert: *Inorganic Stereochemistry*, Springer Verlag (1982).
9. M. G. B. Drew: *Coord. Chem. Rev.* **24**, 179 (1977).
10. G. Tomat, G. Valle, A. Cassol, and P. di Bernardo: *Inorg. Chim. Acta* **76**, L13 (1983).
11. G. Tomat, G. Valle, P. di Bernardo, and P. L. Zanonato: *Inorg. Chim. Acta* **110**, 113 (1985).
12. R. D. Rogers, and L. K. Kurihara: *J. Less -Common Metals* **127**, 199 (1987).