Synthesis and crystal structures of Pr^{III} and Nd^{III} complexes with the macrocyclic cavitand cucurbit[6]uril

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The $[\{Pr(NO_3)_2(H_2O)_3\}\{Pr(NO_3)(H_2O)_4\}(C_{36}H_{36}N_{24}O_{12})](NO_3)_3\cdot 4H_2O$ and $[\{Nd(NO_3)(H_2O)_4\}_2(NO_3@C_{36}H_{36}N_{24}O_{12})][Nd(NO_3)_6]$ complexes were prepared by heating a mixture of lanthanide nitrates, cucurbit[6]uril, and water in a sealed tube. X-ray diffraction study demonstrated that the metal atoms in the former complex are linked to the macrocycle through tridentate coordination of the portal oxygen atoms of cucurbit[6]uril to the praseodymium(III) cation. The neodymium(III) complex is the first example of lanthanide compounds with cucurbit[6]uril belonging to coordination polymers.

Key words: praseodymium, neodymium, aqua complex, cucurbit[6]uril, crystal structure, X-ray diffraction analysis.

Cucurbit[6]uril ($C_{36}H_{36}N_{24}O_{12}$, CB[6]) is an organic macrocyclic cavitand consisting of six glycoluril fragments linked to each other by 12 methylene bridges. The CB[6] molecule has a barrel-like shape. Due to the presence of 12 polarized carbonyl groups, the macrocycle can act as a polydentate ligand and form complexes with oxophilic metals.[1—7] Lanthanide complexes are of particular interest, because they find wide use, for example, as luminescent labels in biology and medicine.[8,9] In solution, lanthanide cations form complexes with large coordination numbers and various, often unique, coordination environments. High rates of ligand exchange make it difficult to isolate complexes into the solid phase, particularly, from aqueous solutions. Kinetic instability can be successfully overcome by increasing thermodynamic stability of complexes due to the use of the chelate or macrocyclic effects.[10] However, most of these reactions were studied in organic solvents.[11—13] The use of cucurbit[6]uril as a polydentate ligand proved to be efficient for isolation of kinetically labile trivalent lanthanide complexes from aqueous solutions. Earlier,[14—17] we have synthesized and structurally characterized complexes with La^{3+}, Ce^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Ho^{3+}, and Yb^{3+} cations, in which the metal/cucurbit[6]uril ratio is 1 : 1, 2 : 1, 2 : 2, or 2 : 3, and the CB[6] molecule is coordinated to the lanthanide cations through the portal oxygen atoms as a ligand having different dentation. All these compounds have molecular island structures.

In the present study, we synthesized a new Pr^{3+} complex with CB[6], $[\{Pr(NO_3)_2(H_2O)_3\}\{Pr(NO_3)(H_2O)_4\}(C_{36}H_{36}N_{24}O_{12})](NO_3)_3\cdot 4H_2O$ (**1**), and established its crystal structure. The structure of this compound differs from those of the known lanthanide complexes with CB[6]. We also synthesized the first lanthanide complex with CB[6], which has a polymeric chain structure, *viz.*, the new coordination neodymium(III) polymer $[\{Nd(NO_3)(H_2O)_4\}_2(NO_3@C_{36}H_{36}N_{24}O_{12})][Nd(NO_3)_6]$ (**2**).

Results and Discussion

Compound **1** was synthesized by heating a 0.6 *M* aqueous solution of praseodymium(III) nitrate and cucurbit[6]uril in a sealed tube at 120 °C for 5 h followed by slow cooling and crystallization.

X-ray diffraction study demonstrated that compound **1** crystallizes in the triclinic system and has an island structure including the following structural elements: the complex cation $[\{Pr(NO_3)_2(H_2O)_3\}\{Pr(NO_3)(H_2O)_4\}(C_{36}H_{36}N_{24}O_{12})]^{3+}$, water molecules of crystallization, and additional nitrate anions.

The structure of the complex praseodymium(III) cation $[\{Pr(NO_3)_2(H_2O)_3\}\{Pr(NO_3)(H_2O)_4\}(C_{36}H_{36}N_{24}O_{12})]^{3+}$ is shown in Fig. 1. The praseodymium atom is coordinated by three oxygen atoms of the carbonyl groups of the cucurbit[6]uril molecule (O(11), O(21), and O(31)). Both CB[6] portals are linked to the praseodymium(III) aqua nitrate cations. The praseodymium : cucurbit[6]uril ratio in **1** is 2 : 1. The inner cavity of the cavitand is occupied by the nitrate anion coordinated to the praseodymium atom, which is located above one of the CB[6] portals, as well as by the water molecule coordinated to the praseodymium atom, which is located above another portal. The guest water molecule and the guest nitrate anion are

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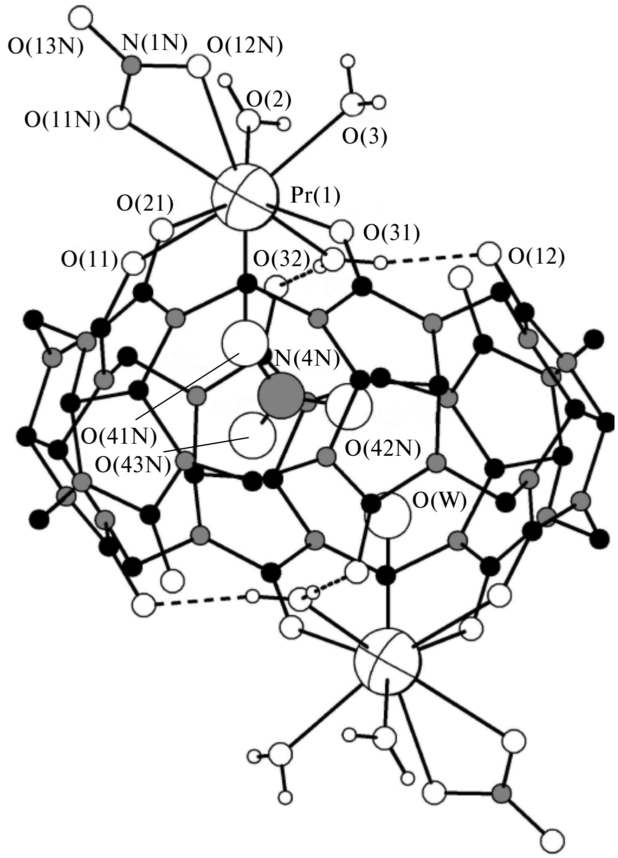

Fig. 1. Cationic praseodymium(III) complex $[\{Pr(NO_3)_2(H_2O)_3\}\{Pr(NO_3)(H_2O)_4\}(C_{36}H_{36}N_{24}O_{12})]^{3+}$ in the crystal structure of **1**. The atomic numbering scheme is given for the crystallograpically independent praseodymium atoms, the oxygen atoms involved in the first and second coordination spheres of the metal atoms, and the nitrogen atoms of the nitrate anions. The hydrogen bonds are indicated by dashed lines. The hydrogen atoms of the CB[6] molecules are omitted. Only one alternative position of the water molecule and one position of the nitrate anion encapsulated by CB[6] are shown; the atoms are represented by large circles.

Table 1. The M—O bond lengths in molecules **1** and **2**

Bond	d/Å		
	1	**2**	
		Nd(1)	Nd(2)
M—O(CB[6])	2.413(2)— 2.546(3)	2.437(1)— 2.486(0)	—
M—O(H_2O)	2.426(3)— 2.535(3)	2.481(2)— 2.529(1)	—
M—O(NO_3)	2.535(3)— 2.660(3)	2.521(1)— 2.586(1)	2.570(2)— 2.642(1)

disordered over two equivalent positions at different CB[6] portals. Figure 1 shows only one alternative position for the water molecule and one alternative position for the nitrate anion. Therefore, the oxygen atom can belong to both the nitrate anion (O(41N)) and the water molecule (O(W)). The Pr—O(41N) distance is 2.535(2) Å. The praseodymium atom at one of the portals is additionally coordinated by one bidentate nitrate anion, one monodentate nitrate anion, and three water molecules, whereas the praseodymium atom at another portal is additionally coordinated by one bidentate nitrate anion and four water molecules. In both cases, the coordination number of praseodymium is 9. The composition of complex **1** corresponds to the formula $[\{Pr(NO_3)_2(H_2O)_3\}\{Pr(NO_3)(H_2O)_4\}(C_{36}H_{36}N_{24}O_{12})](NO_3)_3 \cdot 4H_2O$. The Pr—O bond lengths in molecule **1** (Table 1) are in good agreement with the analogous bond lengths in other known lanthanide complexes with cucurbit[6]uril.[14—17] One of the water molecules coordinated to the praseodymium atom additionally forms two hydrogen bonds with the carbonyl groups of CB[6] with the following distances: O(1)...O(12), 2.760(3) Å (H...O, 1.95(3) Å); O(1)...O(32), 2.774(4) Å (H...O, 1.96(2) Å).

Figure 2 shows the packing of the cationic praseodymium complexes with CB[6] in the crystal structure of **1** projected along the *a* axis. It can be seen that yet another water molecule coordinated to the praseodymium atom forms a hydrogen bond with the carbonyl group of another CB[6] molecule. The O(3)...O(12) distance is 2.821(1) Å, and the corresponding H...O distance is 2.01(6) Å. Therefore, the structure contains directed chains formed through hydrogen bonding. The chains are linked by hydrogen bonds to the water molecules of crystallization and the additional nitrate ions located in the channels.

Earlier, we have synthesized and structurally characterized complexes with Gd^{3+} and Sm^{3+} cations, $[\{Gd(NO_3)(H_2O)_5\}_2(C_{36}H_{36}N_{24}O_{12})](NO_3)_4 \cdot 6.5H_2O$ and $[\{Sm(NO_3)(H_2O)_5\}_2(C_{36}H_{36}N_{24}O_{12})](NO_3)_4 \cdot 6.5H_2O$ (see Refs 15 and 16), respectively, with the metal : cucurbit[6]uril ratio of 2 : 1. The complexes have an island structure. As opposed to compound **1**, the CB[6] molecules in these complexes act as bidentate rather than tridentate ligands, the total coordination number of lanthanide remaining 9. The samarium complex was prepared by slow evaporation of a solution containing lanthanide nitrate and cucurbit[6]uril in air, whereas the CB[6] complex with gadolinium was synthesized under conditions similar to those used for the synthesis of compound **1** (heating in a sealed tube to 120 °C). Therefore, under conditions of hydrothermal synthesis of lanthanide complexes, cucurbit[6]uril can serve as both a bi- and tridentate ligand.

In the case of tridentate coordination of cucurbit[6]uril, the lanthanide atom is located much closer to the plane of the portal of the CB[6] molecule compared to complexes in which CB[6] is coordinated in a bidentate

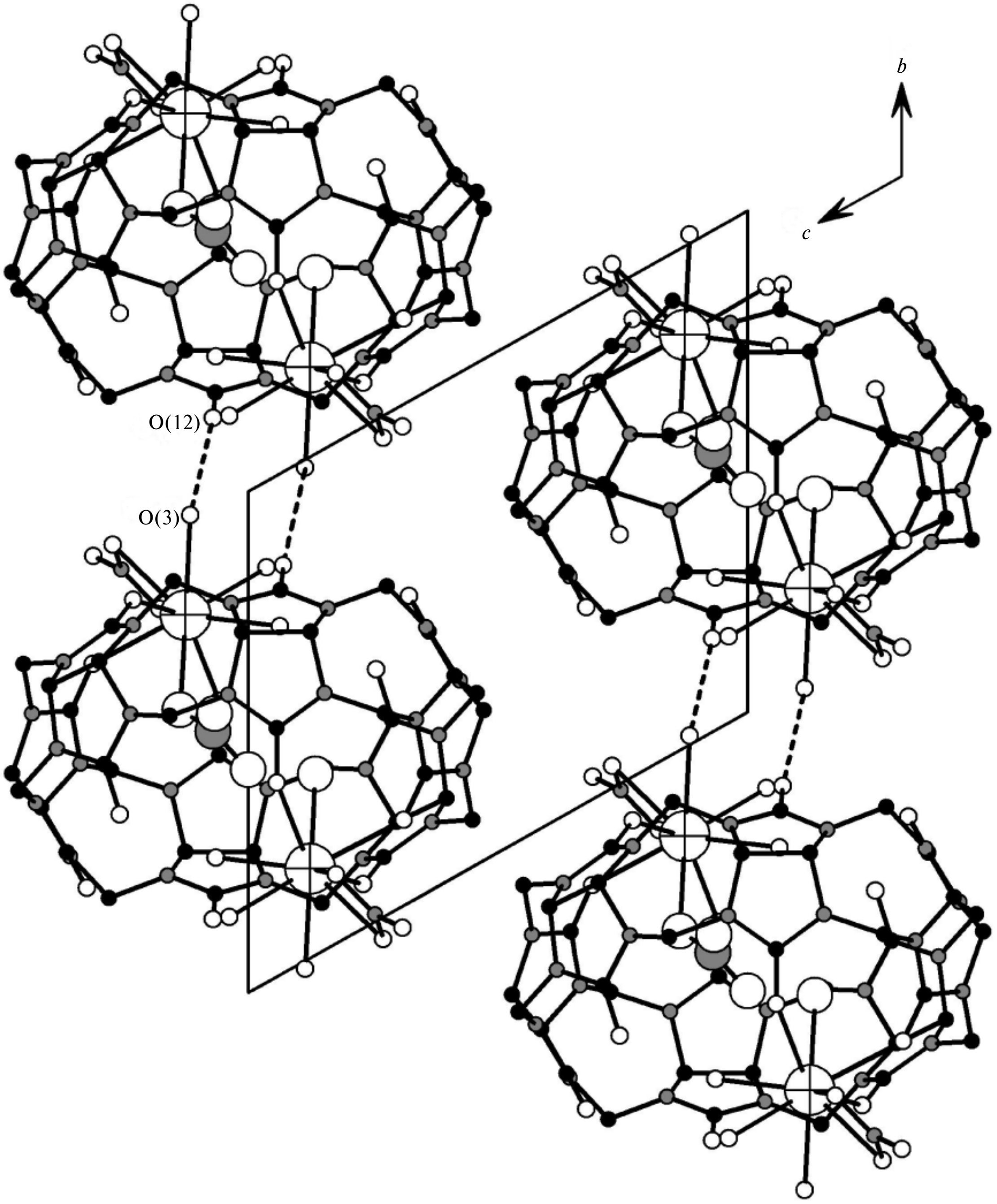

Fig. 2. Crystal packing in the structure of **1** projected onto the *bc* plane. The hydrogen atoms, the water molecules of crystallization, and the additional nitrate anions are omitted. The atoms of the water molecules and the nitrate anions encapsulated by CB[6] are represented by large circles. The formation of directed chains formed through hydrogen bonding is shown. The atomic numbering scheme is given for the crystallograpically independent oxygen atoms involved in the chains.

fashion. The distances between the metal atom and the plane of the portal in compound **1** is 0.86 Å, whereas the corresponding distances in the gadolinium and samarium complexes are 1.92 and 1.88 Å, respectively. The inner cavity of CB[6] in the gadolinium and samarium complexes, unlike that in compound **1**, is occupied by disordered water molecules, which are not coordinated to the lanthanide atoms. The maximum van der Waals diameter of the complex cation also changes (18.00 Å for **1**; 19.70 and 19.42 Å for $[\{Gd(NO_3)(H_2O)_5\}_2(C_{36}H_{36}N_{24}O_{12})]^{4+}$ and $[\{Sm(NO_3)(H_2O)_5\}_2(C_{36}H_{36}N_{24}O_{12})]^{4+}$, respectively).

In the structure of **1**, a substantial ellipsoidal distortion of the CB[6] molecule is observed. This distortion is generally caused by coordination to metal atoms or inclusion of guest molecules into the inner cavity. The degree of distortion is characterized by the difference in the distances between the opposite carbon atoms of CH groups.[18] In the ideal case, for example, in the structure of the supramolecular adduct $[InCl_2(H_2O)_4]_3Cl_3 \cdot (C_{36}H_{36}N_{24}O_{12}) \cdot 4H_2O$,[19] in which the cucurbit[6]uril molecule is not coordinated to the metal atom, does not encapsulate guest molecules, and occupies the position with the highest possible symmetry 6/mmm, this distance is 10.16 Å. In the structure of **1**, the distances between the opposite carbon atoms of the CH groups vary from 9.30 to 11.16 Å. This is the maximum deformation of the cavitand (Δ_{CH} = 1.86 Å) of all the cucurbit[6]uril-containing compounds retrieved from the Cambridge Structural Database (October 2004 release).

An analogous substantial distortion of the cucurbit[6]uril molecule (Δ_{CH} = 1.55 Å) was observed in the $[\{Th(H_2O)_5Cl\}_2(C_{36}H_{36}N_{24}O_{12})]Cl_6 \cdot 13H_2O$ complex, which we have prepared earlier[16] by evaporation of a hydrochloric acid solution of thorium chloride and cucurbit[6]uril. The CB[6] molecule is linked to the thorium complexes by both sides, each portal of cucurbit[6]uril also acting as a tridentate ligand and being coordinated to the metal atom through three CO groups. In addition to the CO groups of the portals, each Th^{4+} cation is coordinated by five aqua ligands and the chloride anion, which are located in the cavity of CB[6]. The bidentate coordination of CB[6] to the metal atoms does not lead to such strong distortions of the macrocycle. For the samarium and gadolinium complexes, Δ_{CH} is 0.71 and 0.68 Å, respectively. The cavity of CB[6] in the latter complex encapsulates the pyridine molecule. The distortions due to inclusion of different guest molecules into the cavity of uncoordinated cucurbit[6]uril are also smaller than those in **1**. The maximum distortion upon the inclusion of the 4-methylpyridinium cation, whose van der Waals size is comparable with the cavity size, is 1.31 Å.[18]

The neodymium complex with cucurbit[6]uril **2** was prepared under conditions analogous to those used for the synthesis of **1** (heating in a sealed tube at 120 °C). However, the concentration of a solution of neodymium nitrate with respect to metal was increased to 1.4 mol L^{-1}. The crystal structure of compound **2** can be described as a pseudohexagonal packing of the polymeric chains $[\{Nd(NO_3)(H_2O)_4\}_2(NO_3@C_{36}H_{36}N_{24}O_{12})]^{3+}{}_{\infty}$ consisting of CB[6] molecules, which are linked to the neodymium cations through the carbonyl groups. A fragment of the chain is shown in Fig. 3. Each CB[6] molecule is coordinated to four neodymium atoms, and each neodymium atom is coordinated by two CB[6] molecules (by one carbonyl group of one CB[6] molecule and two carbonyl groups of another CB[6] molecule). In addition to the carbonyl groups of the cucurbit[6]uril molecules, the lanthanide cations are coordinated by four water molecules and the bidentate nitrate anion. Therefore, the coordination number of neodymium is 9. The Nd(1)—O bond lengths in molecule **2** (see Table 1) agree well with the analogous bond lengths in other known lanthanide complexes with cucurbit[6]uril.[14—17] The water molecules coordinated to the neodymium atom form hydrogen bonds with the portal oxygen atoms of both CB[6] molecules, which are coordinated to the neodymium atom, as well as with the oxygen atoms of the water molecules coordinated to the adjacent neodymium atom. The hydrogen bond network is shown in Fig. 3. The O...O distances are

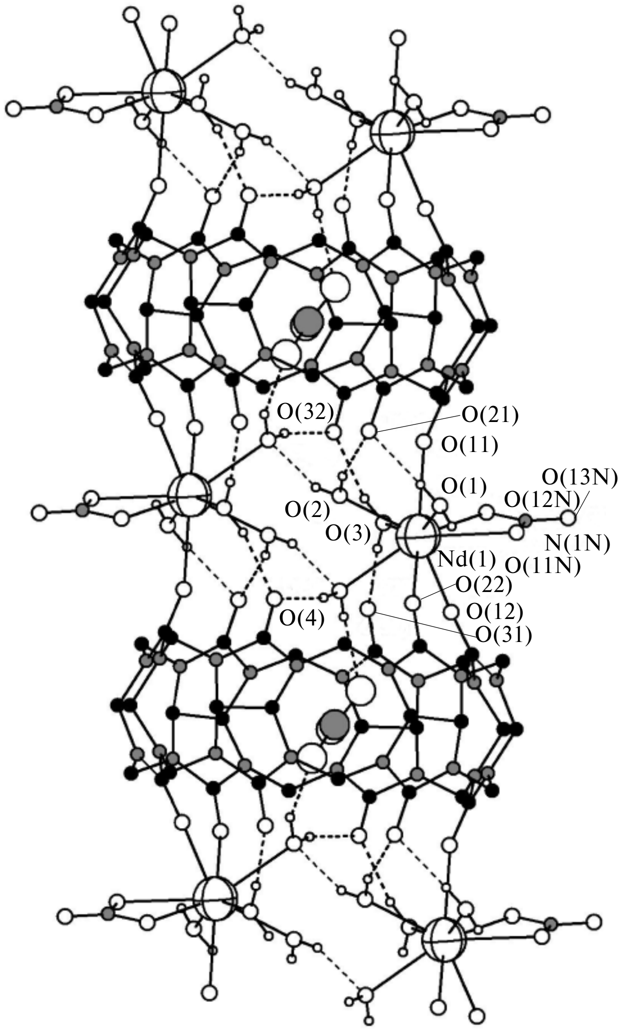

Fig. 3. Fragment of the infinite polymeric chain $[\{Nd(NO_3)(H_2O)_4\}_2(NO_3@C_{36}H_{36}N_{24}O_{12})]^{3+}{}_{\infty}$ in the structure of **2**. The atomic numbering scheme is given for the crystallographically independent neodymium atoms, the oxygen atoms involved in the first and second coordination spheres of the metal atoms, and the nitrogen atoms of the nitrate anions. The hydrogen bonds are indicated by dashed lines. The atoms of the nitrate anions encapsulated by the CB[6] molecules are represented by large circles; only one alternative position of the nitrate anion is shown. The hydrogen atoms of the CB[6] molecules are omitted.

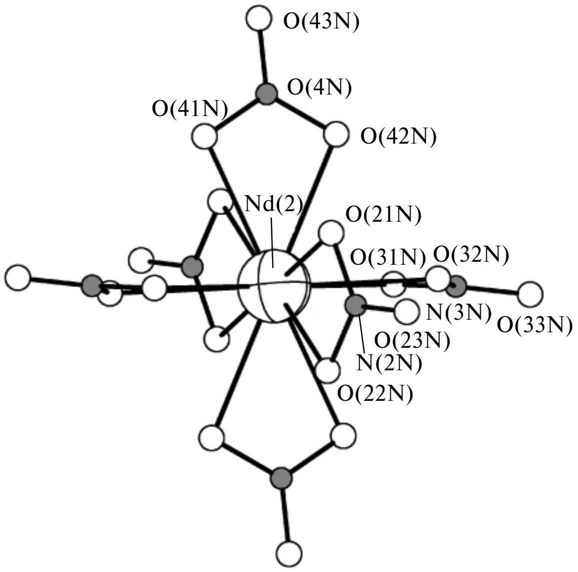

Fig. 4. Complex anion $[Nd(NO_3)_6]^{3-}$ in the structure of **2**. The atomic numbering scheme for the crystallograpically independent atoms is given.

in the range of 2.74—2.80 Å, and the H...O distances are in the range of 1.91—1.98 Å. The inner cavity of the cavitand is occupied by the nitrate anion, which is not coordinated to the metal atom and is disordered over two positions; the shortest distance between the oxygen atoms of the free nitrate anion and the nearest neodymium cation is 4.34 Å. The nitrate anion is linked to one of the water molecules coordinated to the neodymium atom by a short hydrogen bond (O...O, 2.66 Å; H...O, 1.87 Å). Compound **2** is the first example of encapsulation of the free nitrate anion, which is not coordinated to the metal atom, into the inner cavity of the CB[6] molecule. The angle between the plane of the nitrate anion and the planes of the portals is 57.8°. The deformation of the cavitand Δ_{CH} is 0.71 Å.

The complex anions $[Nd(NO_3)_6]^{3-}$ are located between the $[\{Nd(NO_3)(H_2O)_4\}_2(NO_3@C_{36}H_{36}N_{24}O_{12})]^{3+}{}_{\infty}$ chains. Therefore, the structure contains two types of neodymium complexes (coordinated and uncoordinated by cucurbit[6]uril). The total metal/ligand ratio is 3 : 1. The structure of the complex anion is shown in Fig. 4. The Nd(2) atom is coordinated by six bidentate nitrate

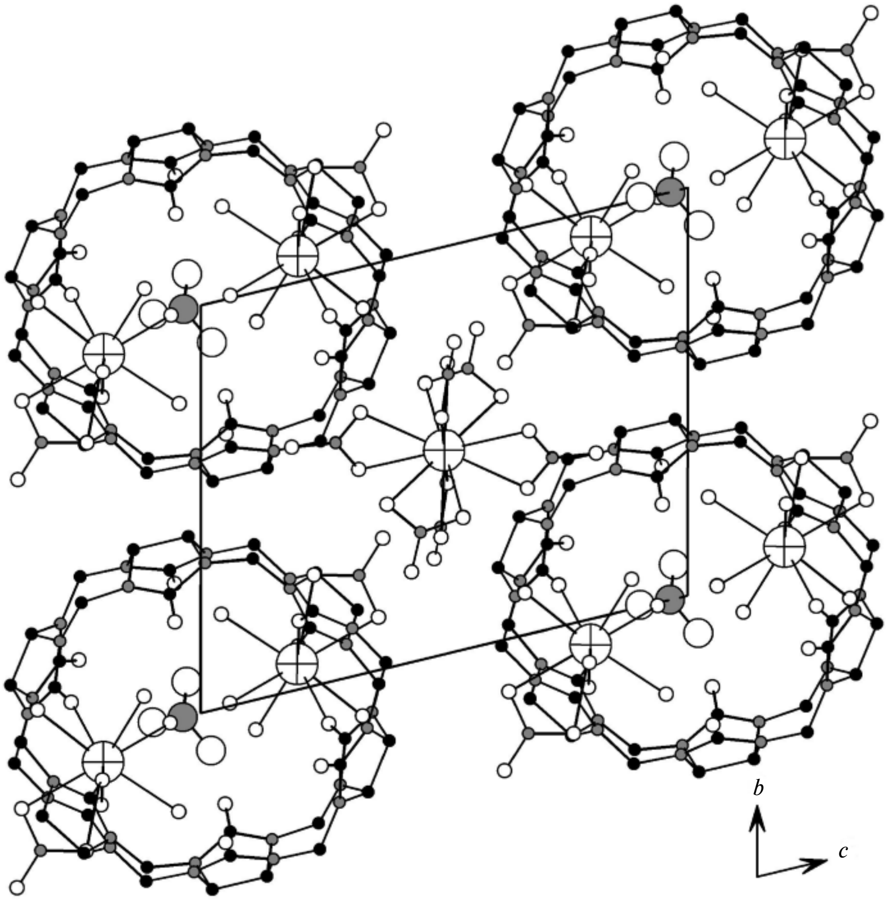

Fig. 5. Crystal packing in the structure of **2** projected onto the *ac* plane. The hydrogen atoms are omitted. The atoms of the nitrate anions encapsulated by the CB[6] molecules are represented by large circles.

anions so that its coordination number is 12. The angle between the plane of each nitrate anion and the plane of the adjacent anion is ~90°. This coordination environment is typical of neodymium.[20—22] The Nd(2)—O distances in $[Nd(NO_3)_6]^{3-}$ (see Table 1) agree well with the data published in the literature.[21—23]

The crystal packing of the structure of **2** is presented in Fig. 5. The polymeric chains are packed in a pseudohexagonal fashion. The free complex anions $[Nd(NO_3)_6]^{3-}$ are located between the chains. The chains adjacent along the unit cell edge are shifted with respect to each other along the *a* axis so that the neodymium complexes $[Nd(NO_3)(H_2O)_4]^{2+}$ of one chain face the CB[6] molecules of another chain. The chains adjacent along the unit cell diagonal are not shifted relative to one another, and the Nd(1) atoms in these chains lie in one plane with the Nd(2) atoms of the free complex anions $[Nd(NO_3)_6]^{3-}$.

The structure of **2** is similar to those of the divalent calcium complexes with cucurbit[6]uril $\{Ca(HSO_4)_2\}_2(C_{36}H_{36}N_{24}O_{12}) \cdot 13H_2O$ (see Refs 1 and 22) and $[\{Ca(H_2O)_3(HSO_4)(CH_3OH)\}_2(C_{36}N_{24}O_{12}H_{36})](HSO_4)_2 \cdot 4H_2O$.[6] This structure can also be described as a pseudohexagonal packing of infinite polymeric chains consisting of CB[6] molecules, which are linked to the calcium cations through the carbonyl groups. Each cucurbit[6]uril molecule in the calcium complexes, like those in **2**, is coordinated to four metal cations, and each metal cation is coordinated by two CB[6] molecules (by one carbonyl group of one cucurbit[6]uril molecule and two carbonyl groups of another CB[6] molecule).

Unlike the earlier synthesized cucurbit[6]uril complexes with lanthanide cations[14—17] having an island structure, compound **2** has a polymeric chain structure and is the first lanthanide complex with cucurbit[6]uril belonging to coordination polymers. Complexes having island structures with the metal : ligand ratio of 1 : 1 can be isolated from solutions containing metal at a concentration varying from 0.025 to 0.1 mol L^{-1}. At higher concentrations (0.5—1 mol L^{-1}), the metal : ligand ratio in the resulting complexes is 2 : 1. A further increase in the lanthanide concentration to 1.4 mol L^{-1} leads to the forma-

Table 2. Crystallographic parameters of **1** and **2** and details of X-ray diffraction study

Parameter	**1**	**2**
Crystal dimensions/mm	0.42×0.18×0.08	0.25×0.18×0.16
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell parameters		
a/Å	11.5504(4)	10.6350(2)
b/Å	11.7307(2)	12.0238(2)
c/Å	13.2094(2)	14.5642(3)
α/deg	116.038(1)	71.326(1)
β/deg	98.403(1)	71.616(1)
γ/deg	102.927(1)	69.388(1)
V/Å^3	1505.14(6)	1607.67(5)
Z	1	1
M/g mol^{-1}	1842.90	2131.83
d_{calc}/g cm^{-3}	2.033	2.202
λ(Mo-Kα)/Å	0.71073	0.71073
μ/mm^{-1}	1.739	2.533
2θ Angle range/deg	≤51.4	≤63
Number of parameters in refinement	561	580
Number of reflections	8	44
R_{int}	0.0157	0.0152
Total number of reflections	10302	14519
Number of reflections with $I > 2\sigma(I)$	5237	8653
R_1	0.0234	0.0240
wR_2	0.0608	0.0588
Number of all independent reflections	5573	10239
R_1	0.0257	0.0295
wR_2	0.0620	0.0601
GOOF	1.065	1.044
Residual electron density/e Å^3 (min/max)*	2.094/−0.608	−1.612/−0.713

* In the vicinity of the heavy atoms.

tion of compound **2** having a polymeric chain structure with the metal : ligand ratio of 3 : 1. In the structure of **2**, water molecules of crystallization were not revealed, which is on the whole not typical of adducts of metal complexes with cucurbit[6]uril characterized by large hydration numbers.

Experimental

The starting praseodymium and neodymium nitrates of analytical grade were used without additional purification. Cucurbit[6]uril was synthesized according to a known procedure[23] from glyoxal, carbamide, and paraformaldehyde in an acidic medium followed by recrystallization from hydrochloric acid. Elemental analysis was performed at the Vorozhtsov Novosibirsk Institute of Organic Chemistry of the Siberian Branch of the Russian Academy of Sciences. The IR spectra were recorded in KBr pellets on a Scimitar FTS 2000 Fourier-transform spectrometer in the 400—4000 cm^{-1} region.

Cucurbit[6]uril{(mononitratotetraaquapraseodymium(III))(dinitratotriaquapraseodymium(III))} trinitrate tetrahydrate, [{Pr(NO$_3$)$_2$(H$_2$O)$_3$}{Pr(NO$_3$)(H$_2$O)$_4$}(C$_{36}$H$_{36}$N$_{24}$O$_{12}$)](NO$_3$)$_3$·4H$_2$O (1). A weighed sample (0.010 g) of cucurbit[6]uril decahydrate ($C_{36}H_{36}N_{24}O_{12} \cdot 10H_2O$), praseodymium(III) nitrate hexahydrate ($Pr(NO_3)_3 \cdot 6H_2O$) (0.402 g), and water (1.5 mL) were placed in a glass tube (concentration with respect to metal was 0.6 mol L^{-1}). The tube was sealed and heated in the following mode: 1) heating from room temperature to 120 °C for 5 h; 2) storage at 120 °C for 5 h; 3) slow cooling to room temperature for 48 h. Needle-like colorless crystals of **1** were isolated from the opened tube after cooling. The yield was 0.013 g (83% based on consumed cucurbit[6]uril). Found (%): C, 23.51; H, 3.28; N, 22.18. $C_{36}H_{58}N_{30}O_{41}Pr_2$. Calculated (%): C, 23.39; H, 3.16; N, 22.73. IR (KBr), ν/cm^{-1}: 3416 (s), 1735 (s), 1713 (s), 1665 (s), 1495 (s), 1418 (s), 1384 (s), 1328 (s), 1293 (s), 1263 (s), 1241 (s), 1191 (s), 1147 (m), 1042 (m), 1023 (w), 985 (m), 966 (s), 822 (s), 806 (s), 762 (s), 682 (m), 634 (m).

Cucurbit[6]uril{nitrate clathrate bis(mononitratotetraaquaneodymium(III))} hexanitratoneodymate(III), [{Nd(NO$_3$)(H$_2$O)$_4$}$_2$(NO$_3$@C$_{36}$H$_{36}$N$_{24}$O$_{12}$)][Nd(NO$_3$)$_6$] (2). A weighed sample (0.010 g) of cucurbit[6]uril decahydrate ($C_{36}H_{36}N_{24}O_{12} \cdot 10H_2O$), neodymium(III) nitrate hexahydrate ($Nd(NO_3)_3 \cdot 6H_2O$) (0.475 g), and water (1 mL) were placed in a glass tube (concentration with respect to metal was 1.4 mol L^{-1}). The tube was sealed and heated in the following mode: 1) heating from room temperature to 120 °C for 5 h; 2) storage at 120 °C for 1 h; 3) slow cooling to room temperature for 48 h. Colorless crystals of **2** were isolated as skewed parallelepipeds from the opened tube after cooling. The yield was 0.014 g (77% based on consumed cucurbit[6]uril). Found (%): C, 20.71; H, 2.89; N, 21.96. $C_{36}H_{52}N_{33}Nd_3O_{47}$. Calculated (%): C, 20.28; H, 2.46; N, 21.68. IR (KBr), ν/cm^{-1}: 3420 (s), 1737 (s), 1713 (s), 1665 (s), 1494 (s), 1418 (s), 1384 (s), 1327 (s), 1293 (s), 1263 (s), 1241 (s), 1191 (s), 1146 (m), 1041 (m), 1023 (sh), 985 (m), 966 (s), 822 (s), 801 (s), 763 (s), 682 (m), 634 (m).

X-ray diffraction study of single crystals of **1** and **2** was carried out on a four-circle area-detector Bruker Nonius X8 Apex CCD diffractometer[24] at 150(2) K. Absorption corrections were applied using the SADABS program[24] (T_{min}/T_{max} were 0.5830/0.6675 for **1** and 0.5700/0.6874 for **2**). The structures were solved by direct methods and refined by the full-matrix least-squares method with anisotropic displacement parameters (except for the hydrogen atoms) with the use of the SHELXTL complex package.[24] The hydrogen atoms of the cucurbit[6]uril molecules were placed in geometrically calculated positions and refined using a riding model. The positions of the hydrogen atoms of the water molecules were located in difference electron density maps.

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References

1. W. A. Freeman, *Acta Crystallogr.*, 1984, **40B**, 382.
2. Y. M. Jeon, J. Kim, D. Whang, and K. Kim, *J. Am. Chem. Soc.*, 1999, **118**, 9790.
3. J. Heo, J. Kim, D. Whang, and K. Kim, *Inorg. Chim. Acta.*, 2000, **297**, 307.
4. J. Heo, S.-Y. Kim, D. Whang, and K. Kim, *Angew. Chem., Int. Ed. Engl.*, 1999, **38**, 641.
5. D. Whang, J. Heo, J. H. Park, and K. Kim, *Angew. Chem., Int. Ed. Engl.*, 1998. **37**, 78.
6. D. G. Samsonenko, A. A. Sharonova, M. N. Sokolov, A. V. Virovets, and V. P. Fedin, *Koord. Khim.,* 2001, **27**, 12 [*Russ. J. Coord. Chem.*, 2001, **27**, 12 (Engl. Transl.)].
7. O. A. Geras´ko, D. G. Samsonenko, and V. P. Fedin, *Usp. Khim.*, 2002, **71**, 840 [*Russ. Chem. Rev.*, 2002, **71**, 741 (Engl. Transl.)].
8. M. Elhabiri, R. Scopelliti, J.-C. G. Bunzli, and C. Piguet, *J. Am. Chem. Soc.*, 1999, **121**, 10747.
9. J.-C. G. Bunzli, in *Lanthanide Probes in Life, Chemical and Earth Sciences*, Eds J.-C. G. Bunzli and G. R. Choppin, Elsevier, Amsterdam, 1989, p. 219.
10. N. Kaltsoyannis and P. Scott, in *The f elements*, Eds S. G. Davies, R. G. Compton, J. Evans, and L. F. Gladden, Oxford University Press, New York, 1999, p. 56.
11. J.-C. G. Bunzli and J. A. Harrowfield, *Lanthanide Ions and Calixarenes*, in *Calixarenes: A Versatile Class of Macrocyclic Compounds*, Eds J. Vicens and V. Bohmer, Kluwer, Boston, 1991, p. 317.
12. A. Drljaca, M. J. Hardie, J. A. Johnson, C. L. Raston, and H. R. Webb, *Chem. Commun.*, 1999, 1135.
13. J. L. Atwood, G. W. Orr, N. C. Means, F. Hamada, H. Zhang, S. G. Bott, and K. D. Robinson, *Inorg. Chem.*, 1992, **31**, 603.
14. D. G. Samsonenko, J. Lipkowski, O. A. Gerasko, A. V. Virovets, M. N. Sokolov, V. P. Fedin, J. Platas, R. Hernandez-Molina, and A. Mederos, *Eur. J. Inorg. Chem.*, 2002, **9**, 2380.
15. A. A. Tripol´skaya, E. A. Mainicheva, T. V. Mit´kina, O. A. Geras´ko, D. Yu. Naumov, and V. P. Fedin, *Koord. Khim.*, 2005, **31**, 810 [*Russ. J. Coord. Chem.*, 2005, **31**, 768 (Engl. Transl.)].
16. D. G. Samsonenko, M. N. Sokolov, O. A. Geras´ko, A. V. Virovets, Ya. Lipkovski, D. Fenske, and V. P. Fedin, *Izv.*

Akad. Nauk, Ser. Khim., 2003, 2020 [*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 2132].

17. D. G. Samsonenko, O. A. Geras´ko, Ya. Lipkovski, A. V. Virovets, and V. P. Fedin, *Izv. Akad. Nauk, Ser. Khim.*, 2002, **51**, 1763 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 1915].
18. D. G. Samsonenko, A. V. Virovets, Ya. Lipkovski, O. A. Geras´ko, and V. P. Fedin, *Zh. Strukt. Khim.,* 2002, **43**, 715 [*Russ. J. Struct. Chem.*, 2002, **43**, 664 (Engl. Transl.)].
19. D. G. Samsonenko, M. N. Sokolov, A. V. Virovets, N. V. Pervukhina, and V. P. Fedin, *Eur. J. Inorg. Chem.*, 2001, 167.
20. S.-Y. Niu, Z.-Z. Yang, Q.-C. Yang, B. Yang, J.-Q. Cao, and G.-D. Yang, *Gaodeng Xuexiao Huaxue Xuebao* (Chin.), 1998, **19**, 179 [*Chem. J. Chin. Uni.*, 1998, **19**, 179 (Engl. Transl.)].
21. N. P. Chatterton, D. M. L. Goodgame D. A. Grachvogel, I. Hussain, A. J. P. White, and D. J. Williams, *Inorg. Chem.*, 2001, **40**, 312.
22. W. A. Freeman, W. L. Mock, and N.-Y. Shih, *J. Am. Chem. Soc.*, 1981, **103**, 7367.
23. J.-C. G. Bunzli, B. Klein, D. Wessner, K. J. Schenk, G. Chapuis, G. Bombieri, and G. de Paoli, *Inorg. Chim. Acta.*, 1981, **54**, 43.
24. *APEX2 (Version 1.08), SAINT (Version 7.03), SADABS (Version 2.11), and SHELXTL (Version 6.12). Bruker Advanced X-ray Solutions*, Bruker AXS Inc., Madison, Wisconsin, USA, 2004.

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