

Syntheses and crystal structures of Sm^{III} and Th^{IV} complexes with macrocyclic cavitand cucurbituril

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Slow evaporation of solutions of samarium nitrate and thorium chloride in hydrochloric acid containing the macrocyclic cavitand cucurbituril (C₃₆H₃₆N₂₄O₁₂) afforded crystals of the [Sm(H₂O)₅(NO₃)₂](C₃₆H₃₆N₂₄O₁₂)(NO₃)₄·6.5H₂O and [Th(H₂O)₅Cl]₂(C₃₆H₃₆N₂₄O₁₂)Cl₆·13H₂O complexes, respectively. The [Sm(C₃₆H₃₆N₂₄O₁₂)(H₂O)₅(SO₄)][Sm(H₂O)₅(SO₄)₂]·17H₂O complex was generated upon heating (130 °C) of a mixture of samarium sulfate, cucurbituril, and water in a sealed tube. X-ray diffraction analysis demonstrated that the metal atoms in these complexes are bound to the portal oxygen atoms of the cucurbituril molecules. In addition, the portal oxygen atoms of cucurbituril are linked to the coordinated H₂O molecules *via* hydrogen bonds.

Key words: samarium(III), thorium(IV), cucurbituril, complexes, crystal structure, X-ray diffraction analysis.

Recent studies^{1–7} demonstrated that the barrel-shaped organic macrocyclic cavitand cucurbituril (C₃₆H₃₆N₂₄O₁₂), which consists of six glycoluril fragments linked by methylene bridges, can serve as a polydentate ligand in complexes with oxophilic metals due to the presence of 12 polarized carbonyl groups. The use of cucurbituril as a polydentate ligand proved to be efficient for isolation of kinetically labile lanthanide(III) complexes from aqueous solutions.^{8,9} Cucurbituril is similar in size to such macrocycles as α -cyclodextrin or 18-crown-6, whose high selectivity with respect to 4f element cations allows one to consider these compounds as promising reagents for nuclear waste separation and disposal.¹⁰ At the same time, cucurbituril bears a higher negative charge on the donor oxygen atoms of the portals,^{11,12} which is responsible for higher stability of its compounds with positively charged metal ions. Since cucurbituril is a readily accessible compound highly stable both in acidic and alkaline media, it is a convenient starting reagent for the preparation of various supramolecular compounds.

Cucurbituril complexes with the La³⁺, Ce³⁺, Sm³⁺, Gd³⁺, Ho³⁺, and Yb³⁺ cations with metal : cucurbituril ratios of 1 : 1, 2 : 2, and 2 : 3 have been synthesized and structurally characterized.⁸ In these complexes, the cucurbituril molecule is coordinated to the lanthanide cations as a bi- or tetradentate ligand through its portal oxygen atoms. The uncoordinated oxygen atoms of the carbonyl groups are involved in hydrogen bonding with the metal-coordinated H₂O molecules.

In the present study, we synthesized samarium(III) and thorium(IV) compounds with cucurbituril, *viz.*, [Sm(C₃₆H₃₆N₂₄O₁₂)(H₂O)₅(SO₄)][Sm(H₂O)₅(SO₄)₂]·17H₂O (**1**), [{Sm(H₂O)₅(NO₃)₂}(C₃₆H₃₆N₂₄O₁₂)](NO₃)₄·6.5H₂O (**2**), and [Th(H₂O)₅Cl]₂(C₃₆H₃₆N₂₄O₁₂)Cl₆·13H₂O (**3**), and established their crystal structures.

Results and Discussion

The samarium(III) complex with cucurbituril [Sm(C₃₆H₃₆N₂₄O₁₂)(H₂O)₅(SO₄)][Sm(H₂O)₅(SO₄)₂]·17H₂O (**1**) was prepared as colorless air-unstable crystals by heating a mixture of samarium sulfate Sm₂(SO₄)₃, cucurbituril, and water in a sealed tube at 130 °C followed by slow cooling of the reaction mixture. The crystal structure contains two crystallographically independent Sm³⁺ cations,

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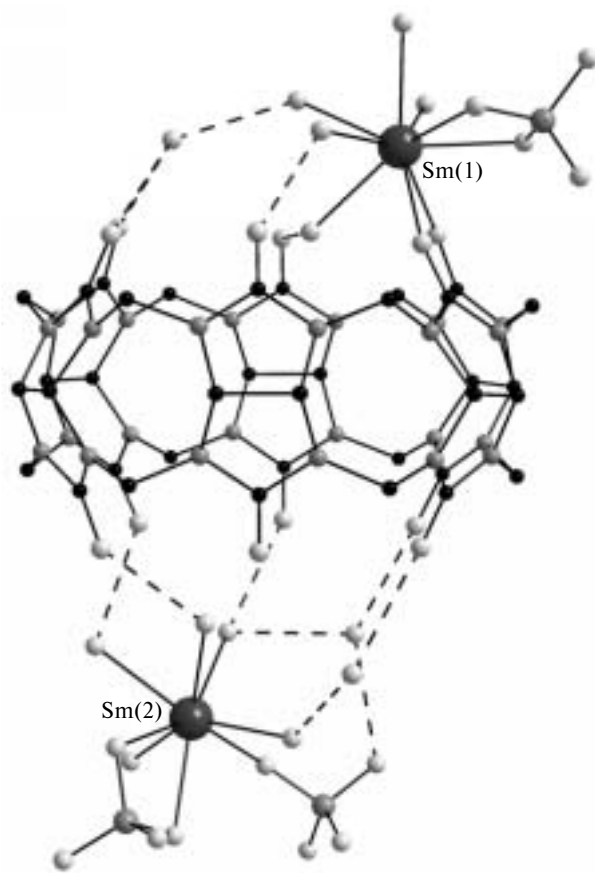


Fig. 1. Structure of supermolecule 1. Hydrogen bonds are indicated by dashed lines.

which serve different functions (Fig. 1). One of these cations (Sm(1)) is coordinated by two CO groups of the macrocycle (Sm—O, 2.428(4) and 2.510(5) Å), five H₂O molecules, two of which form hydrogen bonds with two other CO groups of the portal (O...O, 2.693 and 2.830 Å), and one bidentate sulfate anion giving rise to the cationic complex [Sm(C₃₆H₃₆N₂₄O₁₂)(H₂O)₅(SO₄)]⁺. Another metal atom (Sm(2)) is coordinated by five H₂O molecules, one bidentate sulfate anion, and one monodentate sulfate anion to form the anionic complex [Sm(H₂O)₅(SO₄)₂][−]. Both complexes, *viz.*, cationic and anionic, are linked to each other through hydrogen bonds between the CO groups of the open portal of the cucurbituril molecule and the H₂O ligands of the anionic complex (aver. O...O, 2.815 Å) to form a neutral supramolecular associate (metal : cucurbituril ratio is 2 : 1) in which both portals of cucurbituril are closed by the samarium(III) sulfate aqua complexes. The supermolecule also contains three water molecules of crystallization, which are involved in hydrogen bonding between the metal-coordinated water molecules and the oxygen atoms of cucurbituril (see Fig. 1).

The coordination number of Sm(1) is nine, and its coordination polyhedron is a distorted monocapped square antiprism in which the short edge is occupied by the sulfate anion. The coordination number of Sm(2) is eight, and its coordination polyhedron is a distorted trigonal dodecahedron in which the short edge is also occupied by the sulfate anion coordinated in a bidentate fashion. Interestingly, all sulfate groups in NH₄Sm(SO₄)₂·4H₂O serve as bridges to form the layered structure instead of the discrete [Sm(SO₄)₂(H₂O)₄][−] anions.¹³ The tendency of the sulfate anion in lanthanide complexes to serve as a bridging ligand has a general character.¹⁴ Therefore, the structure of 1 characterized by another mode of coordination of the ligand is worthy of notice.

The neutral supermolecules are packed one above the other in a head-to-tail fashion to form chains extended along the vectors $\pm(\mathbf{a} + \mathbf{b})$, the adjacent chains being opposite to each other, and the wide region of one chain fitting the narrow region of another chain (Fig. 2). The cavities between the supermolecules are occupied by the water molecules of crystallization, which are involved in an extensive hydrogen bond system with the participation of all structural units of the crystal.

The samarium cucurbituril complex with composition [{Sm(H₂O)₅(NO₃)₂}(C₃₆H₃₆N₂₄O₁₂)](NO₃)₄·6.5H₂O (2) containing the nitrate anion coordinated to the samarium atom was prepared by slow evaporation of a solution of samarium nitrate and cucurbituril in hydrochloric acid (0.04 M HCl was used to increase the solubility of cucurbituril) as colorless air-unstable crystals. In this complex, the metal : cucurbituril ratio is also 2 : 1, and both portals of the cucurbituril molecule are coordinated through the oxygen atoms of the carbonyl groups (two groups of each portal) to the metal cations (Sm(1)—O, 2.395(3) and 2.490(3) Å; Sm(2)—O, 2.380(3) and 2.472(3) Å). In the crystal structure, there are two such crystallographically independent cationic complexes. The structure of one of these complexes is shown in Fig. 3. Each Sm³⁺ cation is coordinated by two CO groups of the portal of the macrocycle as well as by five H₂O ligands and one bidentate nitrate anion. Two aqua ligands are involved in hydrogen bonding with two other CO groups of the portal (*cf.* the O...O distances of 2.825 and 2.795 Å for Sm(1) and Sm(2), respectively). The coordination number of the Sm³⁺ cation is nine, and its coordination polyhedron is a distorted monocapped square antiprism, whose shortest edge is occupied by the nitrate anion. The packing of the cationic complexes in the structure of compound 2 is shown in Fig. 4. The centers of the cucurbituril molecules occupy two different sites in inversion centers (crystallographic positions 1b (0, 0, 1/2) and 1e (1/2, 1/2, 0)) to form a body-centered sublattice. The cavities between the complexes are occupied by the water molecules of crystallization and additional nitrate anions

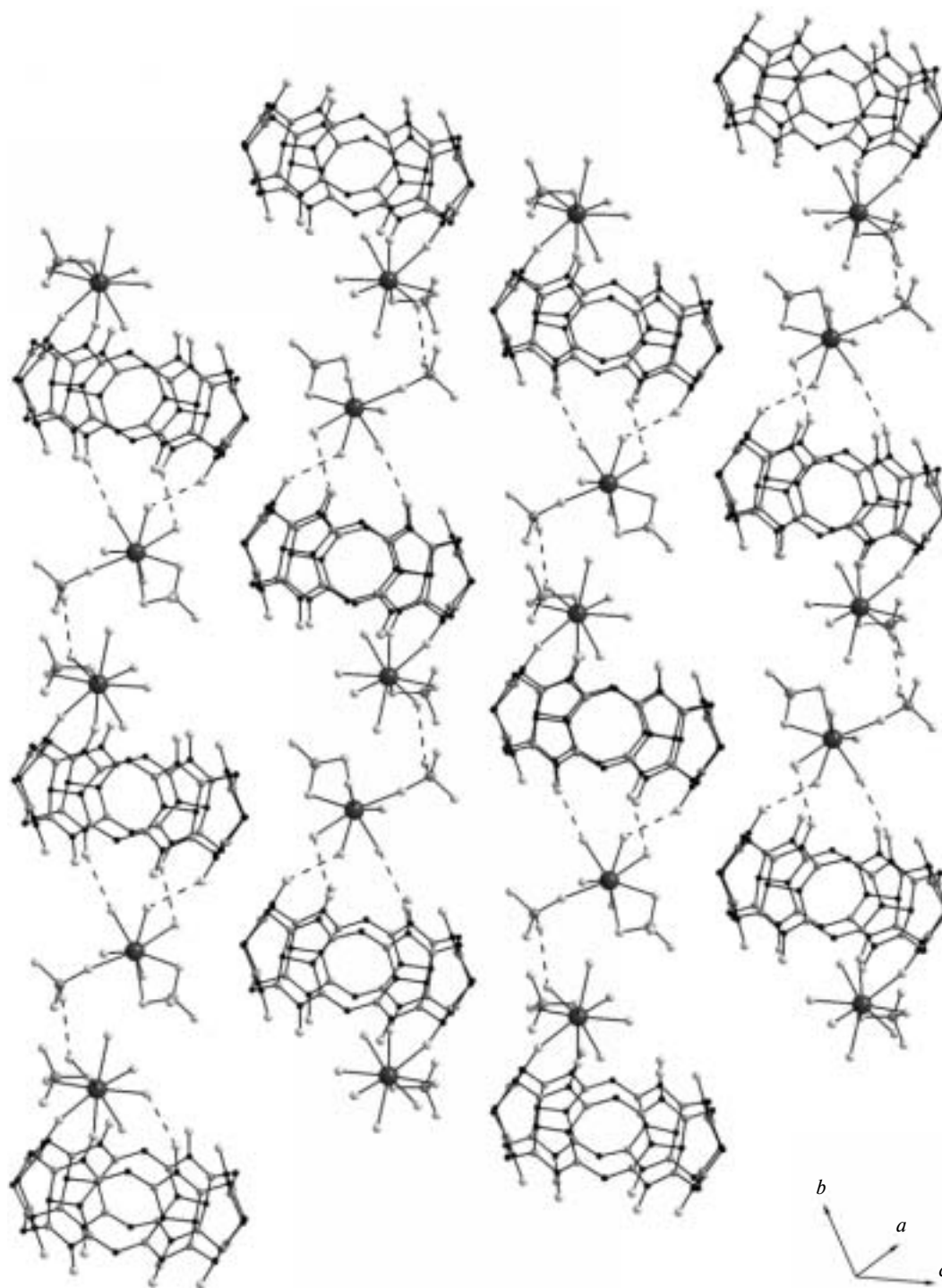


Fig. 2. Packing of chains in the crystal structure of **1**. Water molecules of solvation are omitted.

through which all structural units of the crystal are linked by an extensive hydrogen bond system.

Samarium cucurbituril complexes **1**, **2**, and $[\{\text{Sm}(\text{H}_2\text{O})_4\}_2(\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})_3]\text{Br}_6 \cdot 44\text{H}_2\text{O}$ (**4**)⁹ clearly demonstrate the effect of the counterion in the starting lanthanide salts, *viz.*, sulfate for compound **1**, nitrate for **2**,

and bromide for **4**, on the composition and structure of the lanthanide complexes with cucurbituril. The presence of the oxygen-containing SO_4^{2-} and NO_3^- ligands in aqueous solutions leads to their coordination by highly oxophilic rare-earth metals even in a weakly acidic solution of hydrochloric acid (in the case of nitrate complex **2**).

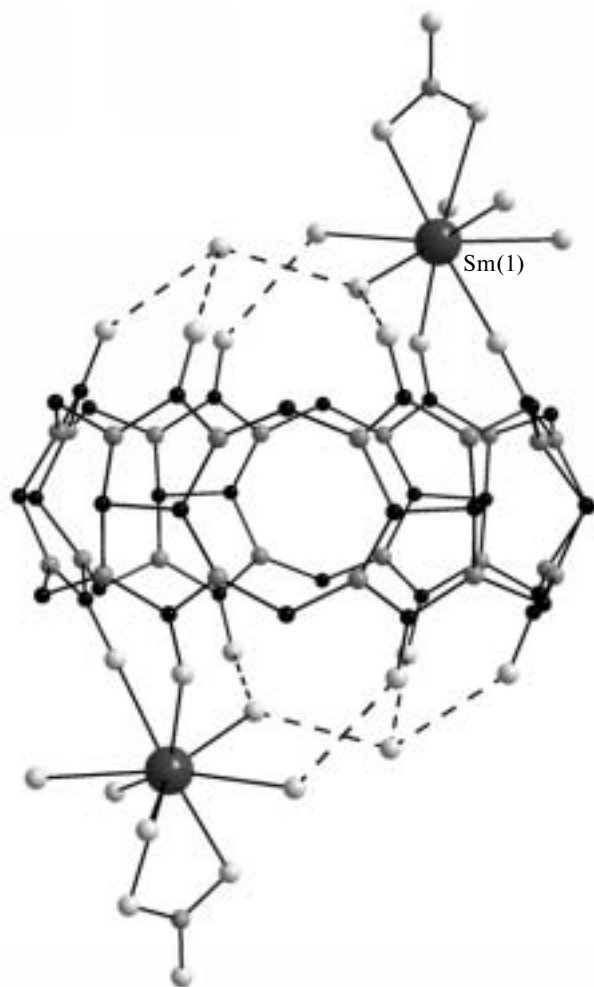


Fig. 3. Structure of one of two crystallographically independent cationic complexes $[\{\text{Sm}(\text{H}_2\text{O})_5(\text{NO}_3)_2\}(\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})]^{4+}$ in **2**.

These ligands successfully compete with cucurbituril for a site in the coordination sphere about the metal atom up to complete displacement of cucurbituril to the outer coordination sphere (Sm(2) atom in compound **1**). The use of lanthanide bromides as the starting reagents does not lead to the formation of compounds containing the Ln—Br bonds, like in compound **4**, the isostructural gadolinium complex $[\{\text{Gd}(\text{H}_2\text{O})_4\}_2(\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})_3]\text{Br}_6 \cdot 45\text{H}_2\text{O}$, and the sandwich cerium complex $[\{\text{Ce}(\text{H}_2\text{O})_5\}_2(\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})_2]\text{Br}_6 \cdot 26\text{H}_2\text{O}$.⁸

The thorium(IV) cucurbituril complex with composition $[\{\text{Th}(\text{H}_2\text{O})_5\text{Cl}\}_2(\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})]\text{Cl}_6 \cdot 13\text{H}_2\text{O}$ (**3**) was prepared as colorless crystals by slow evaporation of a solution (in 1 M HCl) of thorium(IV) chloride and cucurbituril. This is the first example of coordination of cucurbituril by actinide metals. The uranyl complex with cucurbituril with composition $\{[(\text{UO}_2)_4\text{O}_2\text{Cl}_4(\text{H}_2\text{O})_6](\text{H}_2\text{O} \cdot \text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})\} \cdot 4\text{H}_2\text{O}$ has been described in the literature.¹⁴ However, the macrocycle in this complex is linked to the chloro aqua complex

only by hydrogen bonds between the uranium-coordinated H_2O molecules and the oxygen atoms of the carbonyl groups of cucurbituril.¹⁵

The structure of the cationic thorium complex $[\{\text{Th}(\text{H}_2\text{O})_5\text{Cl}\}_2(\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})]^{6+}$ in **3** is shown in Fig. 5; the metal : cucurbituril ratio is 2 : 1. The cucurbituril molecule serves as a hexadentate ligand coordinated to the thorium cations through the oxygen atoms of the carbonyl groups (three groups of each portal; the average Th—O distance is 2.422 Å). Each Th^{4+} cation is coordinated by three CO groups of the portal of the macrocycle, five H_2O ligands, and one chloride anion. The coordination number of the Th^{4+} cation is nine, and its coordination polyhedron is a monocapped square antiprism in which the chlorine atom occupies the cap position. It should be noted that weak coordination of Cl^- to $\text{Th}^{4+}(\text{aq})$ occurs in an aqueous solution. For $\text{ThCl}_3^+(\text{aq})$, the stability constant $K = 2.24$ at the ionic strength $I = 0.5 \mu$.¹⁶

In complex **3**, both chloride anions coordinated to the Th^{4+} cations in the vicinity of opposite portals are located in the cavity of the cucurbituril molecule ($\text{Cl} \cdots \text{Cl}$, 3.657(1) Å; the sum of the van der Waals radii of two chlorine atoms is 3.6 Å).¹⁷ The inclusion of guest molecules in the cavity of the molecule is a characteristic feature of cucurbituril. Many guest—host complexes of cucurbituril in which various organic and inorganic molecules or ions serve as guests were described in the literature.^{1,7,11,18–20} However, the presence of simultaneously two anions in the cavity was found only in the strontium(II) complex with cucurbit[8]uril* $[\{\text{Sr}(\text{H}_2\text{O})_{12}\}(\text{Sr}(\text{H}_2\text{O})_3(\text{NO}_3)_2)_2(\text{C}_{48}\text{H}_{48}\text{N}_{32}\text{O}_{16})](\text{NO}_3)_4 \cdot 8\text{H}_2\text{O}$. The larger cavity of cucurbit[8]uril is occupied by two nitrate anions coordinated to the strontium(II) cations located at the opposite portals of the macrocycle.²¹ The inclusion of two chloride anions in the cavity of complex **3** leads to distortion of the cucurbituril molecule, e.g., to contraction along one diameter and extension along another diameter by ~ 1 Å compared to the non-distorted cucurbituril molecule.²²

In the crystal of complex **3**, the molecules are linked in chains *via* hydrogen bonds between the aqua ligands of one $[\{\text{Th}(\text{H}_2\text{O})_5\text{Cl}\}_2(\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})]^{6+}$ complex and the oxygen atoms of the CO groups of the cucurbituril molecule of another complex ($\text{O} \cdots \text{O}$, 2.869 and 2.878 Å). The packing of the cationic complexes is shown in Fig. 6. The centers of the cucurbituril molecules occupy the crystallographic positions $2a$ (0, 0, 0) and $2d$ (0, 1/2, 1/2) with the symmetry $2/m$ (C_{2h}) to form the C lattice. The water molecules of crystallization and chloride anions, which are involved in an extensive hydrogen bond system, are located between these chains.

* The $\text{C}_{48}\text{H}_{48}\text{N}_{32}\text{O}_{16}$ molecule consists of eight glycoluril fragments.

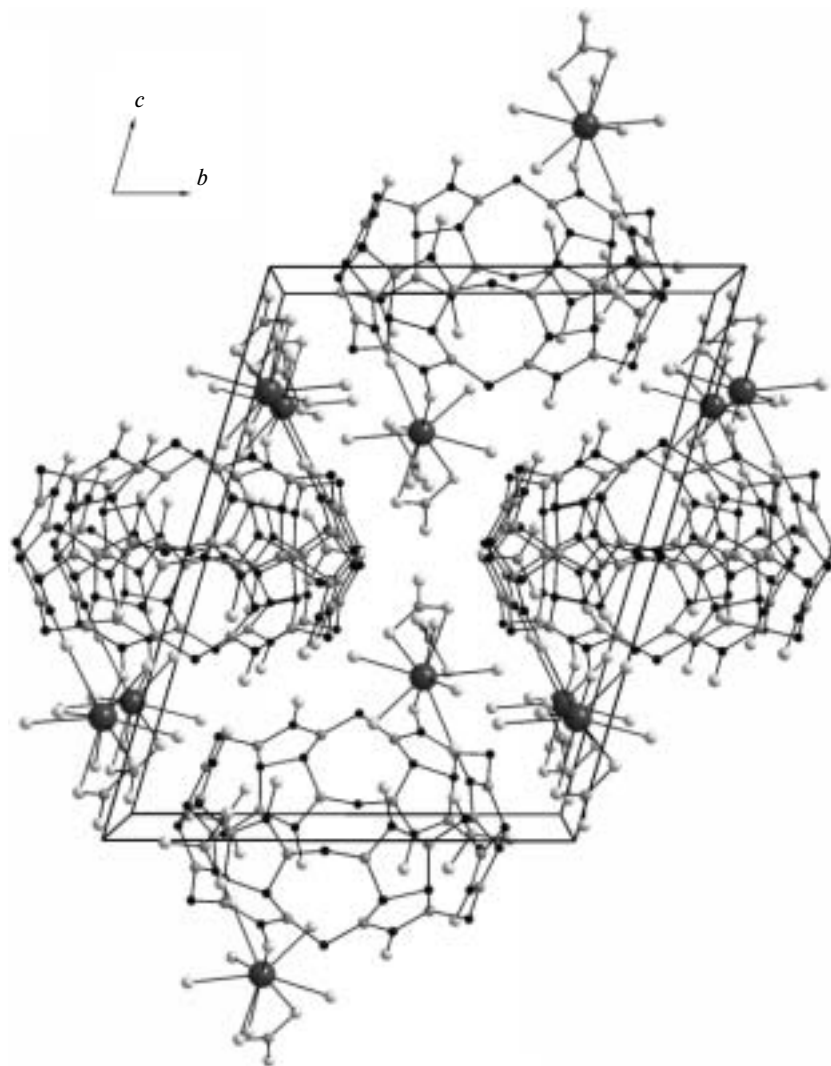


Fig. 4. Packing of the cationic complexes in the crystal structure of **2**. Water molecules of solvation and nitrate anions are omitted.

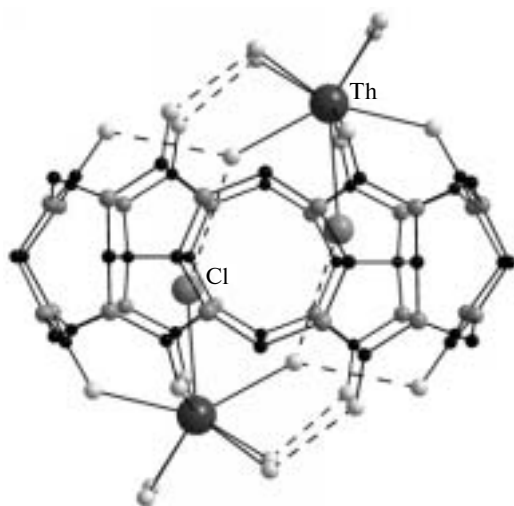


Fig. 5. Structure of the $[\{\text{Th}(\text{H}_2\text{O})_5\text{Cl}\}_2(\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})]^{6+}$ cationic complex in **3**.

Experimental

The starting samarium nitrate and sulfate (analytical grade) were used without additional purification. Cucurbituril was prepared according to a modified procedure^{23,24} from glyoxal, carbamide, and paraformaldehyde in an acidic medium followed by recrystallization from HCl. Thorium chloride was synthesized according to a known procedure.²⁵ Elemental analysis was carried out at the N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry of the Siberian Branch of the Russian Academy of Sciences.

Crystal hydrate of monosulfatopentaaquacucurbiturilsamarium(III) disulfatopentaaquasamarate(III), $[\text{Sm}(\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})(\text{H}_2\text{O})_5(\text{SO}_4)][\text{Sm}(\text{H}_2\text{O})_5(\text{SO}_4)_2] \cdot 17\text{H}_2\text{O}$ (1**).** A mixture of $\text{Sm}_2(\text{SO}_4)_3$ (0.067 g), cucurbituril ($\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12} \cdot 10\text{H}_2\text{O}$) (0.020 g), and H_2O (0.50 mL) was heated in a sealed glass tube at 130 °C for one day. After cooling, the tube was opened and colorless crystals of **1** were picked up. The yield of **1** was 0.022 g (62% with respect to cucurbituril). Found (%): C, 20.81; H, 4.56; N, 16.30; S, 4.62.

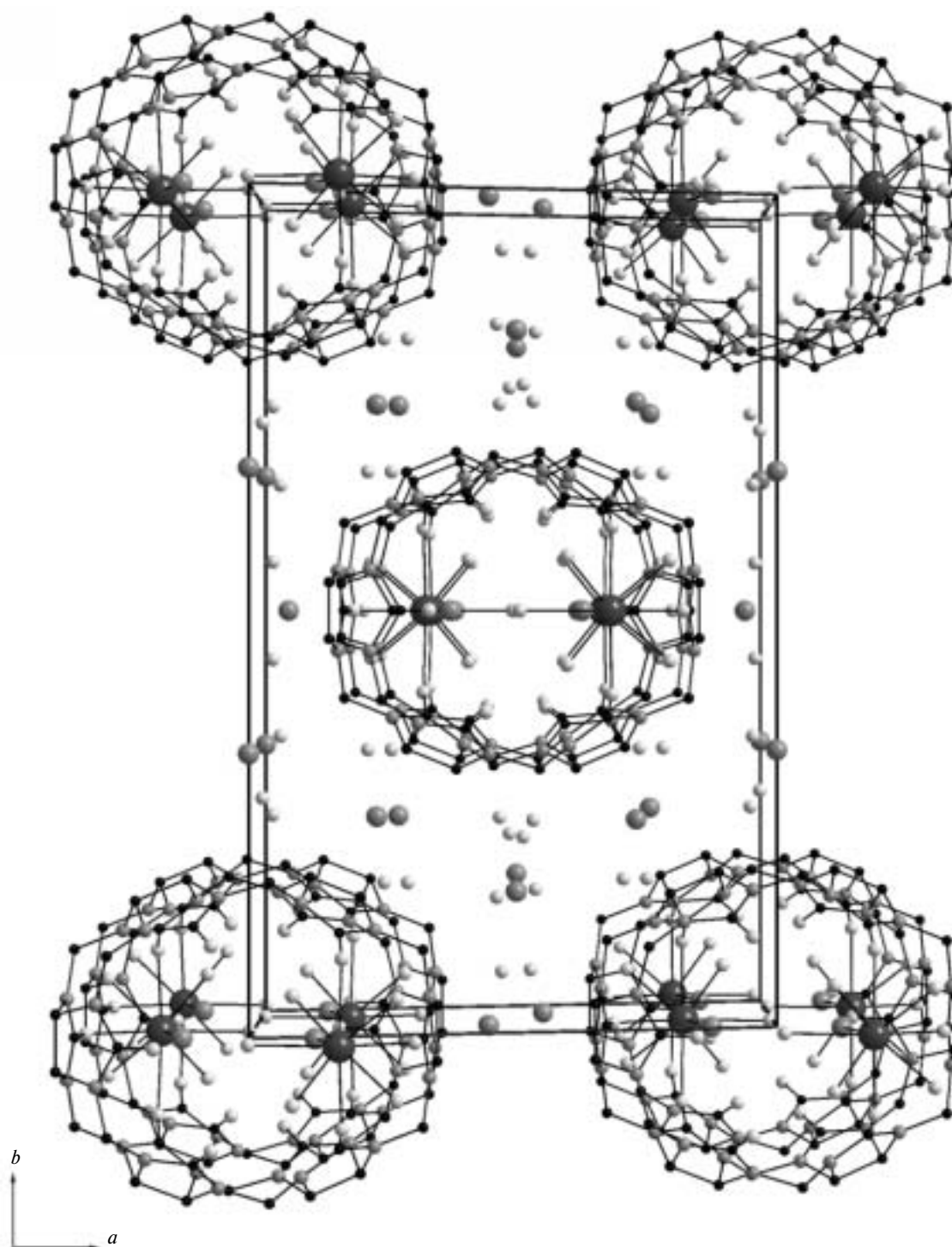


Fig. 6. Packing of the cationic complexes in the crystal structure of 3.

$C_{36}H_{90}N_{24}O_{51}S_3Sm_2$. Calculated (%): C, 20.87; H, 4.38; N, 16.22; S, 4.64.

Crystal hydrate of cucurbiturilbis[mono-nitratopentaaquasamarium(III)] tetranitrate, $[Sm(H_2O)_5(NO_3)_2(C_{36}H_{36}N_{24}O_{12})](NO_3)_4 \cdot 6.5H_2O$ (2). A mixture of $Sm(NO_3)_3 \cdot 5H_2O$ (0.90 g), cucurbituril

$(C_{36}H_{36}N_{24}O_{12} \cdot 10H_2O)$ (0.021 g), 1.0 M HCl (0.125 mL), and H_2O (3.0 mL) was heated for ~10 min until the mixture was almost completely dissolved and then filtered. The solution was allowed to evaporate slowly in air at ~20 °C. Colorless crystals of 2 were isolated from the solution after several hours. The yield was 0.023 g (66% with respect to cucurbituril). Found (%):

C, 21.95; H, 3.50; N, 21.40. $C_{36}H_{69}N_{30}O_{46.5}Sm_2$. Calculated (%): C, 21.98; H, 3.54; N, 21.36.

Crystal hydrate of cucurbiturilbis[monochloropentaquathorium(IV)] hexachloride, $[(Th(H_2O)_5Cl)_2(C_{36}H_{36}N_{24}O_{12})Cl_6 \cdot 13H_2O]$ (3). A mixture of $ThCl_4 \cdot 8H_2O$ (0.10 g), cucurbituril ($C_{36}H_{36}N_{24}O_{12} \cdot 10H_2O$) (0.021 g), and 1.0 M HCl (10 mL) was heated for ~15 min until the mixture was almost completely dissolved and then filtered. The solution was allowed to evaporate slowly in air at $-20^\circ C$. Colorless parallelepiped-like crystals **3** were isolated from the solution after 3 days. The yield was 0.022 g (57% with respect to cucurbituril). Found (%): C, 20.05; H, 3.75; N, 15.51; Cl, 13.15. $C_{36}H_{82}Cl_8N_{24}O_{35}Th_2$. Calculated (%): C, 20.03; H, 3.83; N, 15.57; Cl, 13.14.

X-ray diffraction study. The crystallographic characteristics and details of X-ray diffraction study are given in Table 1. Single crystals of complexes **1**–**3** were taken directly from the mother liquor. The crystal of **1** was protected by applying mineral oil to its surface. The crystals of **2** and **3** were sealed in glass tubes. The

structures were solved by direct methods and refined by the full-matrix least-squared method with anisotropic thermal parameters (except for the hydrogen atoms and oxygen atoms of the disordered water molecules) using the SHELX-97 program package.²⁶ The hydrogen atoms of the cucurbituril molecule were placed in the geometrically calculated positions and refined using a rigid-body model. The hydrogen atoms of the water molecules were not located. For the crystal of complex **1**, the intensities of three check reflections showed an almost linear decrease (reaching 9.9%) in the course of X-ray data collection, and the corrections for radiation damage were applied. In the refinement of the structure of complex **2**, restrictions were imposed on the anisotropic thermal parameters of the oxygen atoms of two water molecules (O(5W) and O(6W)). In the refinement of the structure of complex **3**, restrictions were imposed on the anisotropic thermal parameters of the O(2W) and Cl(4) atoms. One of the chloride anions in **3** is disordered over two positions together with the water molecule of crystallization with the relative weights of 0.697 (O(2W) and Cl(3)) and 0.303

Table 1. Principal crystallographic characteristics and details of X-ray diffraction studies

Parameter	1	2	3
Molecular formula	$C_{36}H_{90}N_{24}O_{51}S_3Sm_2$	$C_{36}H_{69}N_{30}O_{46.5}Sm_2$	$C_{36}H_{82}Cl_8N_{24}O_{35}Th_2$
Molecular weight	2072.20	1966.91	2158.94
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$C2/m$
Unit cell parameters			
$a/\text{\AA}$	12.5299(11)	13.4336(2)	15.2480(1)
$b/\text{\AA}$	17.3701(15)	14.5085(2)	23.4560(1)
$c/\text{\AA}$	17.926(3)	18.3580(3)	10.5830(1)
α/deg	94.516(10)	73.544(1)	106.1620(4)
β/deg	91.942(9)	87.5233(8)	—
γ/deg	108.232(8)	87.7516(6)	—
$V/\text{\AA}^3$	3687.1(7)	3426.87(9)	3635.49(4)
Z	2	2	2
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.866	1.906	1.972
T/K	200(2)	150(2)	150(2)
Diffractometer	STOE STADI4	Nonius KappaCCD	Nonius KappaCCD
$\lambda/\text{\AA}$	0.71073 (Mo-Ka)	0.71073 (Mo-Ka)	0.71073 (Mo-Ka)
$2\theta_{\text{max}}/\text{deg}$	50.00	60.16	69.92
Crystal dimensions/mm	$0.50 \times 0.41 \times 0.33$	$0.44 \times 0.32 \times 0.25$	$0.43 \times 0.30 \times 0.28$
μ/mm^{-1}	1.790	1.830	4.483
$T_{\text{min}}/T_{\text{max}}$	0.838/0.999	—	—
Measured reflections	13427	34919	20656
Independent reflections	12974	19760	8099
R_{int}	0.0549	0.0334	0.0281
Reflections with $I > 2\sigma(I)$	10103	15804	7488
Refinable parameters	1064	1045	250
Number of restrictions	0	12	12
R factors for reflections with $I > 2\sigma(I)$			
R_1	0.0474	0.0476	0.0407
wR_2	0.1100	0.1088	0.1088
R factors for all reflections			
R_1	0.0745	0.0673	0.0453
wR_2	0.1281	0.1234	0.1106
GOOF	1.217	1.044	1.069
Residual electron density (min/max/ $e \cdot \text{\AA}^{-3}$)	−0.812/1.422	−1.773/3.980	−1.297/8.534

(O(1W) and Cl(4)). The atomic coordinates of compounds **1–3** were deposited with the Cambridge Structural Database and can be obtained from the authors.

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