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# Synthesis and crystal structure of the nanosized supramolecular $Sm^{III}$ complex with macrocyclic cavitand cucurbituril $\{[Sm(H_2O)_4]_2(C_{36}H_{36}N_{24}O_{12})_3\}Br_6 \cdot 44H_2O$

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The supramolecular compound $\{[Sm(H_2O)_4]_2(Cuc)_3\}Br_6 \cdot 44H_2O$ (Cuc = $C_{36}H_{36}N_{24}O_{12}$) was synthesized. Its crystal and molecular structure was established by X-ray diffraction analysis. The binuclear complex cation $\{(Cuc)[Sm(H_2O)_4](Cuc)[Sm(H_2O)_4](Cuc)\}^{6+}$ built from the alternating cucurbituril molecules ($C_{36}H_{36}N_{24}O_{12}$) and the $[Sm(H_2O)_4]^{3+}$ aqua ions is a triple-decker nanosized (33 Å) sandwich.

**Key words:** samarium, aqua complex, cucurbituril, supramolecular compound, crystal structure, X-ray diffraction analysis.

Cucurbituril (Cuc) is a trivial name of the compound of composition $C_{36}H_{36}N_{24}O_{12}$, which was prepared by Behrend *et al.* in 1905 by condensation of formaldehyde with glycoluril.[1] Cucurbituril closely resembles in shape an oblate barrel having an inner cavity with a van der Waals diameter of ~5.5 Å.[2,3] Pure cucurbituril is insoluble in water and organic solvents. However, due to the presence of the polarized carbonyl groups at the barrel portals, cucurbituril can serve as a polydentate ligand and form complexes with oxophilic metals. Cucurbituril and alkali metal ions give highly ordered hybrid materials containing large pores and/or channels with controlled sizes and shapes. Thus, crystallization of aqueous solutions of alkali metal (Na, K, Rb, Cs) or alkaline metal (Ca) salts with cucurbituril afforded unique supramolecular compounds having molecular[4,5] or polymeric[6—10] structures. It is believed that such supramolecular compounds containing large pores or channels can find use in separation processes, supramolecular catalysis, and optoelectronics.

In the present study, we report the synthesis and crystal structure of the first cucurbituril complex with 4f-elements of composition $\{[Sm(H_2O)_4]_2(C_{36}H_{36}N_{24}O_{12})_3\}Br_6 \cdot 44H_2O$ (**1**).

Slow evaporation of an aqueous solution of $SmBr_3$ and cucurbituril gave rise to complex **1** as small colorless crystals in 74% yield. The crystals lose a large portion of water of crystallization upon storage in air. According to the data from elemental analysis (C, H, N, Br), the loss of water is 19 $H_2O$ molecules per formula unit.

According to the results of X-ray diffraction study, the crystal structure of compound **1** consists of the triple-decker sandwiches $\{(Cuc)[Sm(H_2O)_4](Cuc)[Sm(H_2O)_4](Cuc)\}^{6+}$ (Cuc = $C_{36}H_{36}N_{24}O_{12}$) built from the alternating cucurbituril molecules and $Sm^{3+}$ cations. The shape of the complex can be approximated by a skewed cylinder with a van der

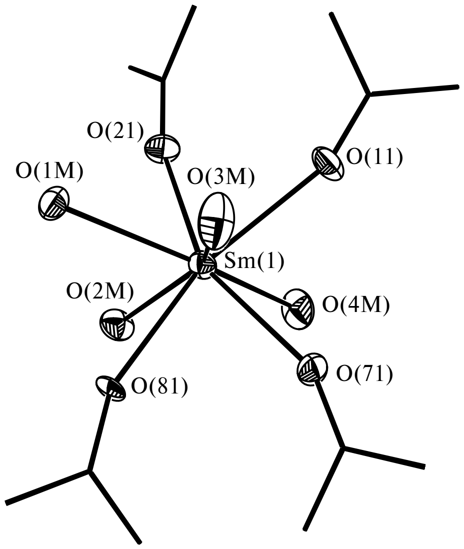

**Fig. 1.** Coordination environment about the $Sm^{3+}$ cation in the sandwich cucurbituril complex $\{(Cuc)[Sm(H_2O)_4](Cuc)[Sm(H_2O)_4](Cuc)\}^{6+}$.

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**Table 1.** The Sm—O bond angles and bond angles at the Sm atom in compound **1**

| Bond | *d*/Å | Angle | ω/deg | Angle | ω/deg |
|---|---|---|---|---|---|
| Sm(1)—O(1M) | 2.454(6) | O(2M)—Sm(1)—O(1M) | 82.6(2) | O(21)—Sm(1)—O(2M) | 73.6(2) |
| Sm(1)—O(2M) | 2.421(7) | O(2M)—Sm(1)—O(4M) | 73.1(2) | O(21)—Sm(1)—O(4M) | 87.4(2) |
| Sm(1)—O(3M) | 2.387(7) | O(3M)—Sm(1)—O(1M) | 71.7(2) | O(21)—Sm(1)—O(11) | 76.4(2) |
| Sm(1)—O(4M) | 2.423(7) | O(3M)—Sm(1)—O(2M) | 147.8(2) | O(21)—Sm(1)—O(71) | 153.6(2) |
| Sm(1)—O(11) | 2.407(7) | O(3M)—Sm(1)—O(4M) | 136.2(2) | O(71)—Sm(1)—O(1M) | 133.3(2) |
| Sm(1)—O(21) | 2.402(7) | O(3M)—Sm(1)—O(11) | 73.8(2) | O(71)—Sm(1)—O(2M) | 115.0(2) |
| Sm(1)—O(71) | 2.405(7) | O(3M)—Sm(1)—O(21) | 113.8(3) | O(71)—Sm(1)—O(4M) | 72.7(2) |
| Sm(1)—O(81) | 2.388(7) | O(3M)—Sm(1)—O(71) | 73.0(2) | O(71)—Sm(1)—O(11) | 81.7(2) |
| | | O(3M)—Sm(1)—O(81) | 83.6(3) | O(81)—Sm(1)—O(1M) | 71.1(2) |
| | | O(4M)—Sm(1)—O(1M) | 151.2(2) | O(81)—Sm(1)—O(2M) | 69.7(2) |
| | | O(11)—Sm(1)—O(1M) | 115.9(2) | O(81)—Sm(1)—O(4M) | 112.9(2) |
| | | O(11)—Sm(1)—O(2M) | 136.7(2) | O(81)—Sm(1)—O(11) | 151.7(2) |
| | | O(11)—Sm(1)—O(4M) | 75.0(2) | O(81)—Sm(1)—O(21) | 129.5(2) |
| | | O(21)—Sm(1)—O(1M) | 70.8(2) | O(81)—Sm(1)—O(71) | 75.5(2) |

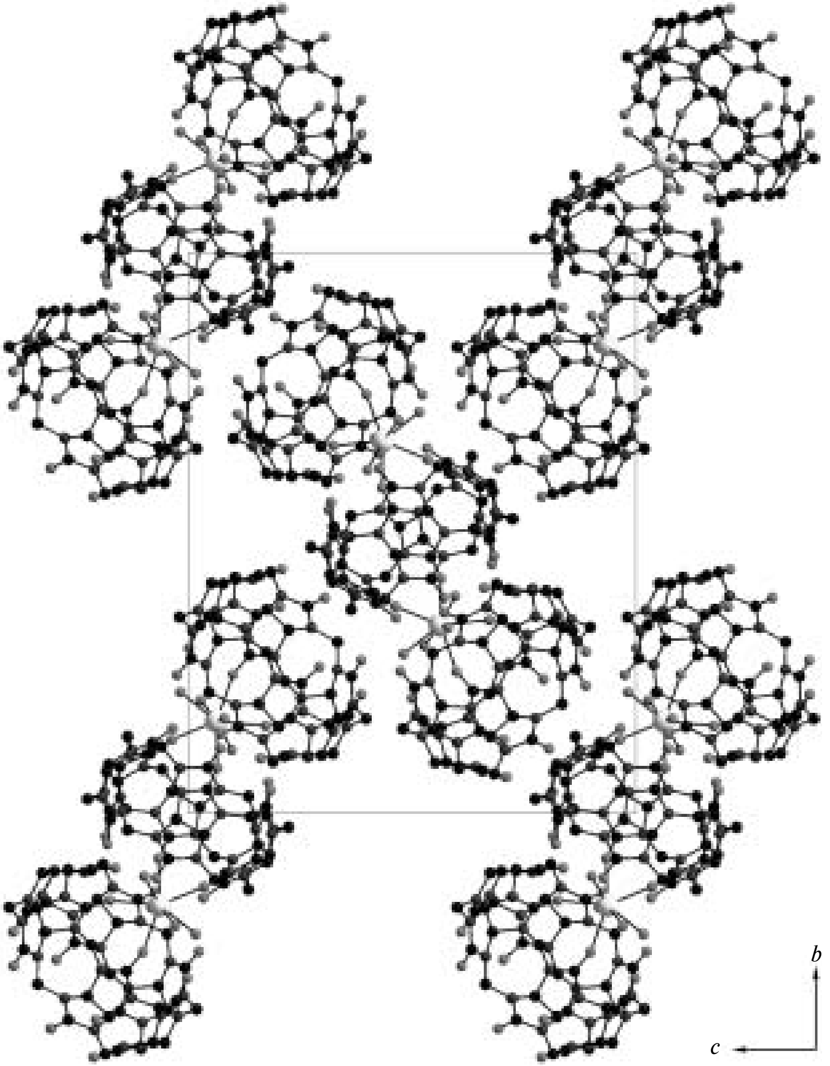

**Fig. 2.** Packing of the supramolecular adducts in the crystal of **1** projected onto the *bc* plane. The water molecules of solvation and bromide anions are omitted.

Waals diameter of approximately 15 Å and a height of approximately 28 Å. The longest distance between the most remote O atoms of the terminal cucurbituril molecules is 30.11 Å (taking into account twice the van der Waals radius of the O atom, this distance is 33 Å).

Each samarium(III) cation is coordinated by four aqua ligands ($\bar{d}_{\text{Sm—O}}$ = 2.421 Å) and two cucurbituril molecules ($\bar{d}_{\text{Sm—O}}$ = 2.401 Å), the latter being coordinated in a bidentate fashion. Samarium has a coordination number 8. The coordination polyhedron is a slightly distorted square antiprism (Fig. 1). The principal bond lengths and bond angles of triple-decker complex **1** are given in Table 1.

The packing of the triple-decker sandwich complexes in the crystal of **1** is shown in Fig. 2. The centers of the sandwiches are located on inversion centers to form a body-centered packing (crystallographic position *2b*: 1/2, 0, 0; 0, 1/2, 1/2). The complexes are packed in stacks along the crystallographic axis *a*. In each stack, the sandwich complexes are related by crystallographic translations, which are responsible for the their parellel arrangement. The sandwiches from the adjacent stacks are almost perpendicular to each other. The stacks are shifted with respect to one another by one-half of the translation along the axis *a* and form walls of quadrangular channels. The cavities between the triple-decker sandwich complexes are occupied by the water molecules of crystallization and bromide anions.

The calculations performed with the use of the KPACK program[11] demonstrated that the sandwich complexes comprise 46.0% of the unit-cell volume, whereas the water molecules of crystallization and bromide anions occupy 18.0% of the unit-cell volume. The total packing coefficient for the crystal structure of compound **1** is 64.0%. The sandwich complexes are embedded in a hydrate "coat" formed by the water molecules involved in a continuous uninterrupted complex system of hydrogen bonds.

## Experimental

Commercially available samarium bromide (analytical grade) and cucurbituril decahydrate (Merck) were used without additional purification. Elemental analysis was carried out at the N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry of the Siberian Division of the Russian Academy of Sciences.

**Tris(cucurbituril)bis(tetraaquasamarium) haxabromide 44 crystal hydrate (1).** A mixture of cucurbituril ($C_{36}H_{36}N_{24}O_{12}$) (0.050 g), samarium bromide ($SmBr_3$) (0.175 g), and water (13 mL) was heated until the cucurbituril was almost completely dissolved (~15 min). Then the reaction mixture was filtered and slowly evaporated in air at room temperature. Colorless crystals of complex **1** precipitated from the solution during 7—10 days. According to the results of X-ray diffraction analysis, complex **1** has the composition $\{[Sm(H_2O)_4]_2(C_{36}H_{36}N_{24}O_{12})_3\}Br_6 \cdot 44H_2O$. After drying in air for one day, crystals of **1** lost 19 water molecules per formula unit. The yield was 0.046 g (74%). Found (%): C, 29.67; H, 3.90; N, 22.95; Br, 10.86. $C_{108}H_{174}Br_6N_{72}O_{69}Sm_2$. Calculated (%): C, 29.72; H, 4.02; N, 23.10; Br, 10.98.

**X-ray diffraction study.** A single crystal of complex **1** of dimensions 0.27×0.21×0.16 mm was taken directly from the mother liquor and sealed in a glass tube. The X-ray diffraction data were collected at 150(2) K on a four-circle automated Enraf—Nonius KappaCCD diffractometer equipped with a two-dimensional detector. The crystals belong to the monoclinic system, $a$ = 16.5687(2), $b$ = 27.0517(3), $c$ = 21.9073(4) Å, $\beta$ = 100.5037(6)°, $V$ = 9654.6(2) Å$^3$, $M$ = 4707.66, $d$ = 1.619 g cm$^{-3}$, $\lambda$(Mo-K$\alpha$) = 0.71073 Å, space group $P2_1/n$ (No. 14), $Z$ = 2, $\mu$ = 1.956 mm$^{-1}$. The frames were integrated and the X-ray data were processed using the Denzo,[12] Scalepack,[12] and maXus program packages.[13] A total of 59512 reflections were measured in the angle range $2\theta \le 50.02°$ ($R_{\text{int}}$ = 0.0898, $R_{\text{sigma}}$ = 0.0784) of which 16991 reflections were independent (14082 with $F_0 > 4\sigma(F_0)$). The structure was solved by direct methods and refined by the full-matrix least-squares method with anisotropic thermal parameters using the SHELX-97 program package.[14] Analysis of the experimental data showed that the high-angle reflections were of low quality. Because of this, only reflections with resolution >1 Å (37833 reflections in the angle range $6.8 \le 2\theta \le 41.62°$, $R_{\text{int}}$ = 0.0576) were included in the refinement. The criterion GOOF was 1.124. The residual maximum and minimum electron densities were 2.088 and –0.772 e/Å$^3$ (in the vicinity of the disordered water molecules of crystallization and bromide anions), respectively, $R_1$ = 0.0731 and $wR_2$ = 0.1777 for 8964 reflections with $F_0 > 4\sigma(F_0)$, $R_1$ = 0.0841 and $wR_2$ = 0.1832 for all independent reflections (10065) used in the calculations. The hydrogen atoms of the cucurbituril molecules were placed in geometrically calculated positions. The hydrogen atoms of the water molecules were not located. The bromide anions and some water molecules of solvation are strongly disordered and have large thermal motion. Because of this, restrictions were imposed on their atomic displacement parameters in the course of refinement. The atomic coordinates were deposited with the Cambridge Structural Database and can be obtained from the authors.

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