Synthesis and crystal structures of sumpramolecular compounds of cucurbit[*n*]urils (*n* = 6, 8) with polynuclear strontium aqua complexes*

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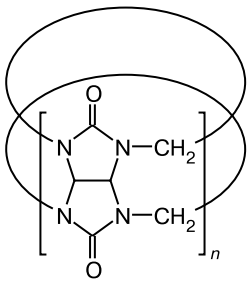
Crystals of the $\{[Sr_4(H_2O)_{12}(NO_3)_4](C_{36}H_{36}N_{24}O_{12})\}(NO_3)_4 \cdot 3H_2O$ and $\{[Sr_2(H_2O)_{12}][Sr(H_2O)_3(NO_3)_2]_2(C_{48}H_{48}N_{32}O_{16})\}(NO_3)_4 \cdot 8H_2O$ were prepared by slow concentration of aqueous solutions containing strontium nitrate and macrocyclic cavitands, *viz.*, cucurbit[6]uril and cucurbit[8]uril ($[C_6H_6N_4O_2]_n$, n = 6 and 8), respectively. According to the results of X-ray diffraction analysis, the crystal structures of these supramolecular compounds are built from polymeric chains, which consist of the alternating cucurbit[*n*]uril molecules and Sr^{2+} cations linked through the bridging aqua ligands and nitrate anions. The supramolecular compound of cucurbit[8]uril provides the first example of compounds in which this macrocycle is bound to metal aqua complexes.

Key words: aqua complexes, strontium, cucurbit[6]uril, cucurbit[8]uril, supramolecular compounds, crystal structure, X-ray diffraction analysis.

Cucurbit[*n*]urils is a trivial name of organic macrocyclic compounds synthesized by condensation of formaldehyde with glycoluril.[1—5]

Compounds with n = 5—10 have been synthesized and characterized. The cucurbituril molecules resemble in shape a barrel containing oxygen atoms of carbonyl groups (portals) in the planes of the bottom and lid. Having a large inner cavity, cucurbiturils are cavitands and can serve as hosts, which form inclusion compounds with guest molecules of suitable size.[2,3,6—8] Due to the presence of polarized carbonyl groups, cucurbiturils can also form complexes and supramolecular associates with metal aqua complexes. Hence, these macrocyclic compounds can serve as large building blocks for the construction of supramolecular compounds. Recently, compounds of this type with cucurbit[6]uril ($C_{36}H_{36}N_{24}O_{12}$) have been synthesized. Metal aqua complexes are bound to the macrocycle both *via* the coordination of the oxygen atoms of the portals of cucurbituril to metal cations (in the case of Na, K, Rb, Cs,[9—12] Ca,[1,13] and lanthanides[14]) and hydrogen bonds between the oxygen atoms of the portals and the aqua ligands (in the case of Al and In[15] and cluster aqua complexes of transition metals[16—19]). The presence of large pores and/or channel with controlled sizes and shapes in such hybrid organic-inorganic compounds is of interest for the construction of porous materials, which find application in the separation and supramolecular catalysis. Cucurbiturils in which the number of glycoluril fragments is other than six became available quite recently.[4,5] Ealrier, supramolecular compounds of these cucurbiturils with metal aqua complexes have been unknown.



Cucurbit[*n*]uril

In the present study, we synthesized supramolecular compounds of cucurbit[*n*]urils (n = 6, 8) with polynuclear strontium aqua complexes, *viz.*, the compounds of cucurbit[6]uril $\{[Sr_4(H_2O)_{12}(NO_3)_4](C_{36}H_{36}N_{24}O_{12})\}(NO_3)_4 \cdot 3H_2O$ (**1**) and the first compound of cucurbit[8]uril with the metal aqua complex

* Dedicated to Academician I. P. Beletskaya on the occasion of her anniversary.

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$\{[Sr_2(H_2O)_{12}][Sr(H_2O)_3(NO_3)_2]_2(C_{48}H_{48}N_{32}O_{16})\}(NO_3)_4 \cdot 8H_2O$ (**2**), and characterized their structures by X-ray diffraction analysis.

Results and Discussion

Cucurbiturils are virtually insoluble in water. The solubility of these compounds noticeably increases in solutions of $Sr(NO_3)_2$ on heating. Colorless crystals of complexes **1** and **2** were prepared in 56 and 67% yields, respectively, by slow concentration of aqueous solutions of strontium nitrate with cucurbit[6]uril and cucurbit[8]uril, respectively. The IR spectra of complexes **1** and **2** have vibration bands of cucurbiturils, nitrate anions, and H_2O molecules.

According to the results of X-ray diffraction study, the crystal structures of compounds **1** and **2** consist of the infinite $[\{[Sr_4(H_2O)_{12}(NO_3)_4](C_{36}H_{36}N_{24}O_{12})\}^{4+}]_\infty$ and $[\{[Sr_2(H_2O)_{12}][Sr(H_2O)_3(NO_3)_2]_2(C_{48}H_{48}N_{32}O_{16})\}^{4+}]_\infty$ polymeric chains, respectively. The cavities between these chains are occupied by water molecules of crystallization and nitrate anions. The fragment of the polymeric chain of complex **1** consisting of the alternating cucurbit[6]uril molecules and strontium cations is shown in Fig. 1. Each cucurbit[6]uril molecule is bound to four strontium cations (two cations per each portal). Each strontium cation is bound to one cucurbit[6]uril molecule. Four Sr^{2+} cations in this supramolecular compound are virtually in a single plane (the average deviation of the Sr^{2+} cations from the plane is 0.28 Å) to form two pairs, which are linked to each other through the bridging nitrate anion. In these pairs, the Sr^{2+} cations are linked through three bridging aqua ligands. Four Sr atoms have different coordination environments (Fig. 2).

The bridging mode of coordination of the NO_3^- anion with all three oxygen atoms of the nitrate anion being involved in the coordination to the adjacent metal cations

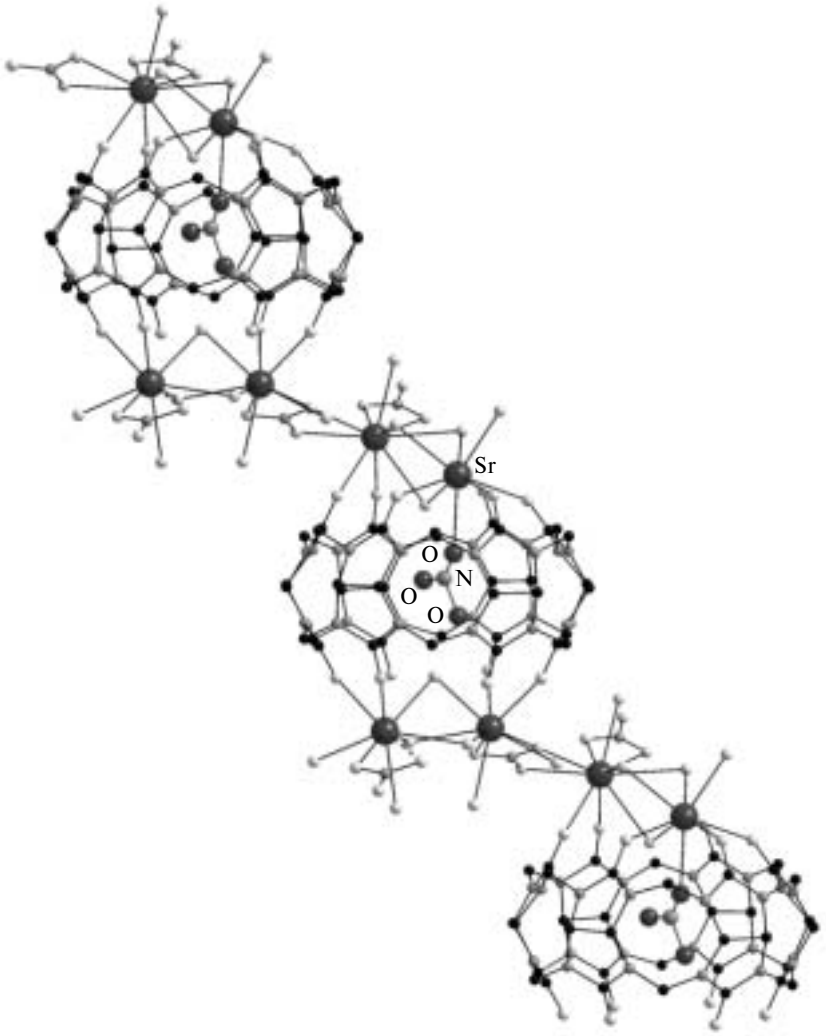

Fig. 1. Fragment of the $[\{[Sr_4(H_2O)_{12}(NO_3)_4](C_{36}H_{36}N_{24}O_{12})\}^{4+}]_\infty$ polymeric chain in complex **1**. The nitrogen and oxygen atoms of the NO_3^- ligand incorporated into the cavity of cucurbit[6]uril are represented by lager spheres.

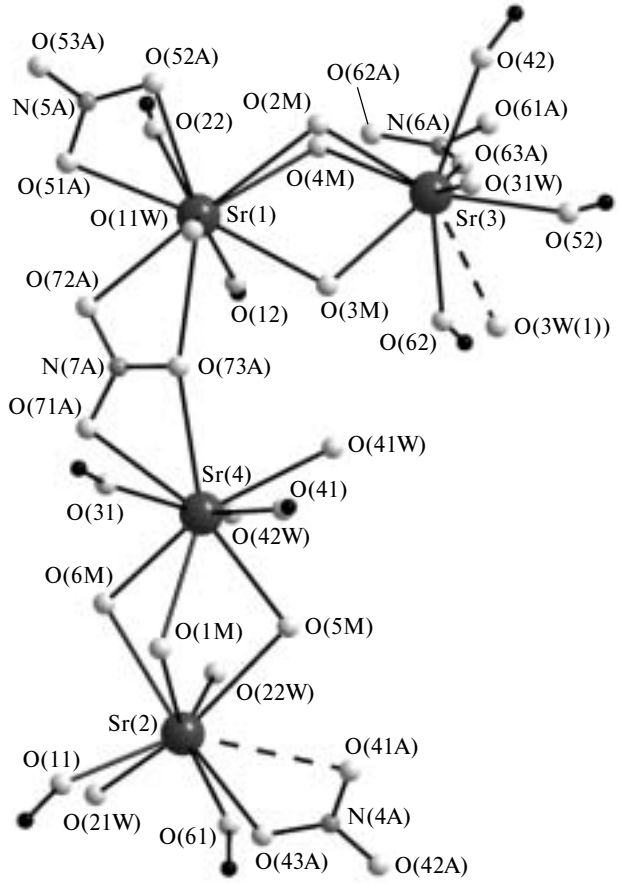

Fig. 2. Coordination environment about the Sr atoms in complex **1**. Additional short contacts between the strontium atoms and the oxygen atoms of the NO_3^- ligand and water molecule are shown by dashed lines.

(one of three oxygen atoms being coordinated to both cations) is observed in complexes of early lanthanides (La, Ce, Pr).[20,21] In addition to complex **1** synthesized by us, there is one more example of this mode of coordination of the μ_2-bridging NO_3^- ligand to the strontium cation, *viz.*, the binuclear nitrate acetate complex $[Sr_2(AcO)_2(NO_3)_2(H_2O)_3]$.[22]

In compound **1**, the strontium cations are coordinated by the carbonyl groups of the cucurbit[6]uril molecules (the Sr(1), Sr(2), and Sr(4) atoms are coordinated by two groups each, and the Sr(3) atom is coordinated by three groups) and also by the aqua ligands and nitrate anions. The coordination numbers of the Sr(1), Sr(2), Sr(3), and Sr(4) atoms are 10, 8+1, 8+1, and 9, respectively. The average Sr—O distance with the terminal water molecules is 2.61 Å (Table 1), which is almost equal to the average bond length (2.62 Å) in the eight-coordinate strontium aqua complex $[Sr(H_2O)_8]^{2+}$.[23] The Sr(2) and Sr(3) atoms form additional short contacts. The Sr(2) atom forms a contact with the second oxygen atom of the coordinated NO_3^- ligand (Sr(2)—O(41A), 3.078(16) Å), and the Sr(3) atom forms a contact with the oxygen atom

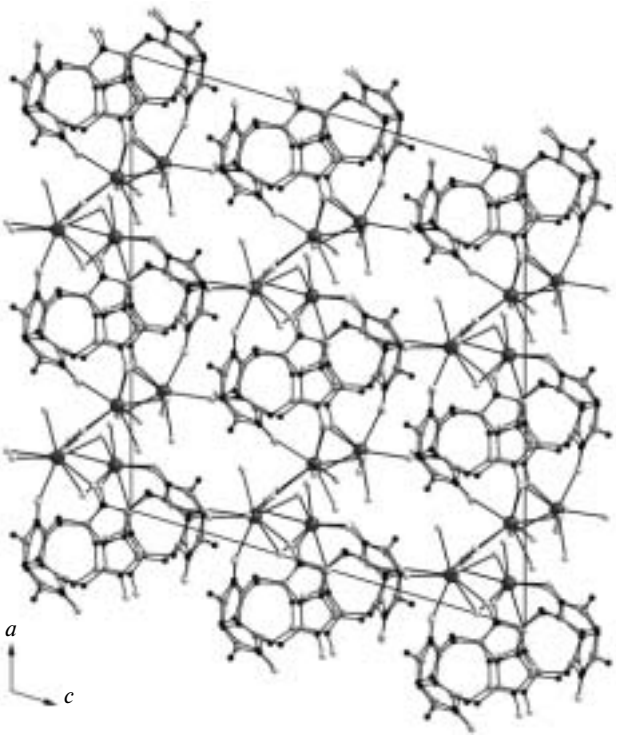

Fig. 3. Packing of the polymeric chains in the structure of **1** projected onto the *ac* plane. The water molecules of solvation and nitrate anions are omitted for clarity.

of the water molecule (Sr(3)—O(3W(1)), 3.01(5) Å). The nitrate anion coordinated to the Sr(3) atom is located in the plane of the cucurbit[6]uril molecule. Decamethylcucurbit[5]uril,[24] which is composed of five methyl-substituted glycoluril fragments and has a smaller inner cavity than that in cucurbit[6]uril, provides the only example of the inclusion of the nitrate anion into the cavity of the cucurbituril molecule.

The molecular packing in the structure of **1** is shown in Fig. 3 (projection onto the *ac* plane). The polymeric supramolecular chains form a system of intersecting lines, whose alignment is described by the following rules: $\pm(\boldsymbol{a} + \boldsymbol{b})$ and $\pm(\boldsymbol{a} - \boldsymbol{b})$. The equally oriented lines form a system of planes parallel to the *ab* plane. These planes alternate along the *c* axis at intervals of one-half of the translation. Within these planes, the distances between the centers of the cucurbit[6]uril molecules along the *a* and *b* axes are equal to the lengths of the corresponding translation vectors. The water molecules of crystallization and additional nitrate anions are located between the polymeric chains.

The fragment of the polymeric supramolecular chain $[\{[Sr_2(H_2O)_{12}][Sr(H_2O)_3(NO_3)_2]_2(C_{48}H_{48}N_{32}O_{16})\}^{4+}]_\infty$ of complex **2** is shown in Fig. 4. Each cucurbit[8]uril molecule is bound to four strontium cations (two cations per each portal). The strontium atoms linked to the portal of the larger macrocycle (in **2**) are more remote from each

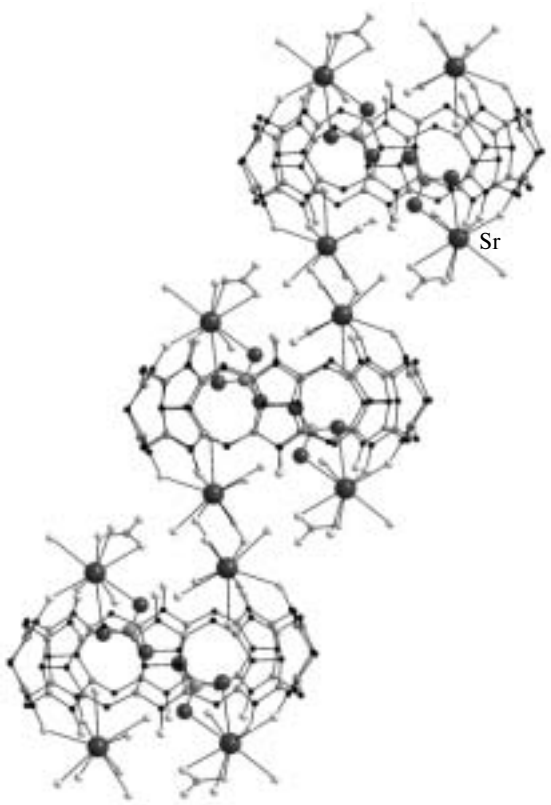

Fig. 4. Fragment of the $[\{[Sr_2(H_2O)_{12}][Sr(H_2O)_3(NO_3)_2]_2(C_{48}H_{48}N_{32}O_{16})\}^{4+}]_\infty$ polymeric chain in complex **2**. The nitrogen and oxygen atoms of the NO_3^- ligands incorporated into the cavity of cucurbit[8]uril are represented by lager spheres.

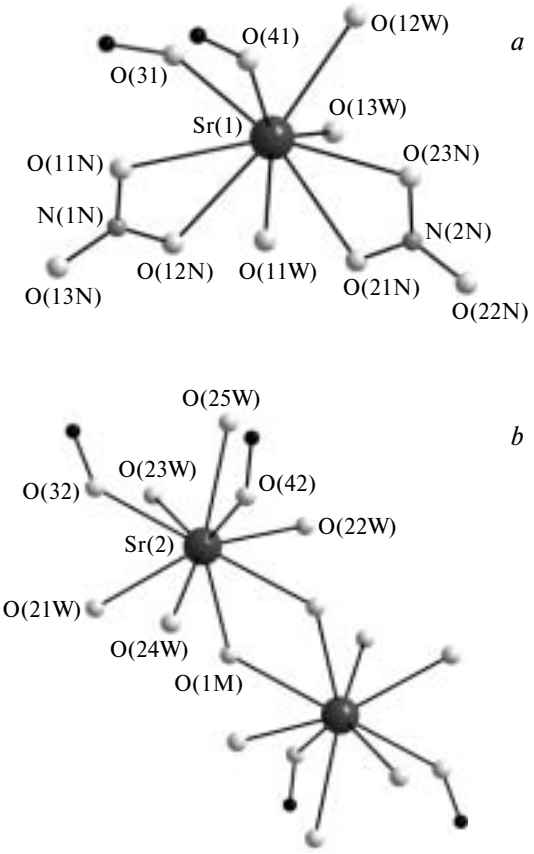

Fig. 5. Coordination environments about the Sr(1) (*a*) and Sr(2) (*b*) atoms in complex **2** (Tables 2 and 3).

other than those in the structure of **1** and are not linked to each other through the bridging ligands. The polymeric chain is formed by the bonds between the bridging water molecules O(1M) and the Sr(2) cations coordinated to the CO groups of the lower portal of one cucurbit[8]uril molecule and the upper portal of another cucurbit[8]uril molecule.

The structure of complex **2** contains two types of strontium atoms (Sr(1) and Sr(2)). The coordination numbers of both Sr atoms are 9. The coordination environments about the Sr(1) and Sr(2) atoms are shown in Fig. 5. Each strontium cation is coordinated by two carbonyl groups of the cucurbit[8]uril molecule. In addition, the Sr(1) atom is coordinated to three water molecules and two bidentate nitrate anions, and the Sr(2) atom is coordinated to seven water molecules two of which serve as bridges.

Since the cavity in cucurbit[8]uril is much larger than that in cucurbit[6]uril (the volumes of the cavities are 479 and 164 Å^3, respectively[4]), it can involve two nitrate anions coordinated to the strontium cations located at opposite portals of cucurbit[8]uril. The nitrogen and oxygen atoms of the NO_3 groups incorporated into the cavity are located in parallel planes at a distance of ~4 Å from each other. The presence of two nitrate anions in the cavity leads to a distortion of the cavitand molecule. The difference between its largest and smallest diameters (*i.e.*, the distances between the opposite carbon atoms of the CH groups of cucurbit[8]uril) is 0.93 Å. Analogous distortions are observed upon the incorporation of guest molecules into the cavities of cucurbituril molecules, particularly, when the van der Waals size of the guest molecule is comparable with the cavity of the host molecule. The differences between the largest and smallest diameters are 1.31 and 1.47 Å for cucurbit[6]uril (which involves the methylpyridinium cation)[25] and cucurbit[8]uril (which includes two bulky organic molecules),[8] respectively.

The molecular packing in the structure of **2** is shown in Fig. 6 (projection onto the *bc* plane). The centers of the cucurbit[8]uril molecules occupy the crystallographic positions 2*a* (0, 0, 0; 0, 1/2, 1/2) with the symmetry $\bar{1}$ to form a one-layer hexagonal packing in which the layers alternate along the *a* axis. The layers are composed of the polymeric chains alternating along the *b* axis. The chains are shifted with respect to each other by one-half of the crystallographic translation along the *c* axis, so that the wide region of one chain fits the narrow region of the adjacent chain. The channels with variable diameters ex-

Table 1. Selected bond lengths and bond angles in compound **1**

Bond	*d*/Å	Angle	ω/deg	Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
Sr(1)—O(2M)	2.93(2)	O(2M)—Sr(1)—Sr(3)	40.8(4)	O(72A)—Sr(1)—O(3M)	114.9(4)	O(43A)—Sr(2)—O(6M)	145.0(5)	O(5M)—Sr(4)—O(6M)	78.5(4)
Sr(1)—O(3M)	2.688(14)	O(3M)—Sr(1)—Sr(3)	37.5(3)	O(72A)—Sr(1)—O(4M)	131.4(5)	O(43A)—Sr(2)—O(41A)	43.6(4)	O(5M)—Sr(4)—O(41W)	78.3(4)
Sr(1)—O(4M)	2.88(2)	O(3M)—Sr(1)—O(2M)	62.9(4)	O(72A)—Sr(1)—O(52A)	115.1(5)	O(2M)—Sr(3)—O(3W(1))	113.5(11)	O(5M)—Sr(4)—O(71A)	139.4(4)
Sr(1)—O(11W)	2.635(15)	O(3M)—Sr(1)—O(4M)	72.1(5)	O(72A)—Sr(1)—O(73A)	47.4(4)	O(3M)—Sr(3)—O(2M)	66.2(5)	O(5M)—Sr(4)—O(73A)	146.9(4)
Sr(1)—O(12)	2.603(13)	O(3M)—Sr(1)—O(52A)	123.4(5)	O(73A)—Sr(1)—O(2M)	128.2(4)	O(3M)—Sr(3)—O(62)	70.6(4)	O(6M)—Sr(4)—O(71A)	69.7(4)
Sr(1)—O(22)	2.507(13)	O(3M)—Sr(1)—O(73A)	68.8(4)	O(73A)—Sr(1)—O(4M)	124.3(5)	O(3M)—Sr(3)—O(3W(1))	67.9(11)	O(41W)—Sr(4)—Sr(2)	118.0(3)
Sr(1)—O(51A)	2.677(15)	O(4M)—Sr(1)—Sr(3)	36.9(4)	O(73A)—Sr(1)—O(52A)	141.4(4)	O(4M)—Sr(3)—O(2M)	61.3(8)	O(41W)—Sr(4)—O(1M)	132.7(6)
Sr(1)—O(52A)	2.763(16)	O(4M)—Sr(1)—O(2M)	55.5(6)	O(1M)—Sr(2)—O(5M)	63.1(5)	O(4M)—Sr(3)—O(3M)	78.5(6)	O(41W)—Sr(4)—O(6M)	140.2(5)
Sr(1)—O(72A)	2.682(14)	O(11W)—Sr(1)—O(2M)	72.0(6)	O(1M)—Sr(2)—O(6M)	60.6(6)	O(4M)—Sr(3)—O(42)	88.3(5)	O(41W)—Sr(4)—O(71A)	111.0(4)
Sr(1)—O(73A)	2.738(11)	O(11W)—Sr(1)—O(3M)	75.7(4)	O(1M)—Sr(2)—O(41A)	111.2(5)	O(4M)—Sr(3)—O(62)	95.2(6)	O(41W)—Sr(4)—O(73A)	71.9(4)
Sr(2)—Sr(4)	4.128(3)	O(11W)—Sr(1)—O(4M)	126.5(6)	O(5M)—Sr(2)—O(6M)	76.7(4)	O(4M)—Sr(3)—O(3W(1))	143.7(11)	O(42W)—Sr(4)—O(1M)	115.4(5)
Sr(2)—O(1M)	2.695(15)	O(11W)—Sr(1)—O(51A)	71.8(5)	O(5M)—Sr(2)—O(41A)	60.5(4)	O(31W)—Sr(3)—O(2M)	72.2(7)	O(42W)—Sr(4)—O(5M)	69.7(4)
Sr(2)—O(5M)	2.740(14)	O(11W)—Sr(1)—O(52A)	70.5(5)	O(6M)—Sr(2)—O(41A)	132.1(4)	O(31W)—Sr(3)—O(3M)	86.1(6)	O(42W)—Sr(4)—O(6M)	68.7(5)
Sr(2)—O(6M)	2.741(15)	O(11W)—Sr(1)—O(72A)	100.6(5)	O(21W)—Sr(2)—O(1M)	134.3(7)	O(31W)—Sr(3)—O(4M)	133.4(8)	O(42W)—Sr(4)—O(41W)	73.0(5)
Sr(2)—O(21W)	2.598(17)	O(11W)—Sr(1)—O(73A)	79.2(4)	O(21W)—Sr(2)—O(5M)	147.1(6)	O(31W)—Sr(3)—O(42)	81.2(6)	O(42W)—Sr(4)—O(71A)	75.5(5)
Sr(2)—O(22W)	2.590(17)	O(12)—Sr(1)—O(2M)	114.4(5)	O(21W)—Sr(2)—O(6M)	89.5(6)	O(31W)—Sr(3)—O(62)	120.7(7)	O(42W)—Sr(4)—O(73A)	87.7(4)
Sr(2)—O(11)[a]	2.575(14)	O(12)—Sr(1)—O(3M)	76.8(4)	O(21W)—Sr(2)—O(41A)	114.5(5)	O(31W)—Sr(3)—O(63A)	147.3(7)	O(31)[a]—Sr(4)—O(1M)	75.0(5)
Sr(2)—O(61)[a]	2.487(14)	O(12)—Sr(1)—O(4M)	64.2(5)	O(21W)—Sr(2)—O(43A)	72.5(6)	O(31W)—Sr(3)—O(3W(1))	59.1(12)	O(31)[a]—Sr(4)—O(5M)	137.2(4)
Sr(2)—O(41A)	3.078(16)	O(12)—Sr(1)—O(11W)	143.9(5)	O(22W)—Sr(2)—O(1M)	120.4(5)	O(42)—Sr(3)—O(2M)	80.8(5)	O(31)[a]—Sr(4)—O(6M)	91.9(4)
Sr(3)—O(2M)	2.747(18)	O(12)—Sr(1)—O(51A)	131.0(5)	O(22W)—Sr(2)—O(5M)	73.9(6)	O(42)—Sr(3)—O(3M)	146.9(4)	O(31)[a]—Sr(4)—O(41W)	126.6(5)
Sr(3)—O(3M)	2.628(13)	O(12)—Sr(1)—O(52A)	145.3(5)	O(22W)—Sr(2)—O(6M)	71.2(6)	O(42)—Sr(3)—O(62)	141.5(4)	O(31)[a]—Sr(4)—O(42W)	144.6(4)
Sr(3)—O(4M)	2.558(19)	O(12)—Sr(1)—O(72A)	70.8(4)	O(22W)—Sr(2)—O(21W)	73.4(7)	O(42)—Sr(3)—O(3W(1))	127.5(11)	O(31)[a]—Sr(4)—O(41)[a]	79.0(4)
Sr(3)—O(31W)	2.55(2)	O(12)—Sr(1)—O(73A)	69.3(4)	O(22W)—Sr(2)—O(41A)	76.8(6)	O(52)—Sr(3)—O(2M)	146.6(6)	O(31)[a]—Sr(4)—O(71A)	70.0(4)
Sr(3)—O(42)	2.592(13)	O(22)—Sr(1)—O(2M)	99.8(6)	O(22W)—Sr(2)—O(43A)	74.8(6)	O(52)—Sr(3)—O(3M)	129.6(4)	O(31)[a]—Sr(4)—O(73A)	74.3(4)
Sr(3)—O(52)	2.475(12)	O(22)—Sr(1)—O(3M)	136.6(5)	O(11)[a]—Sr(2)—O(1M)	75.5(5)	O(52)—Sr(3)—O(4M)	142.3(7)	O(41)[a]—Sr(4)—O(1M)	82.0(5)
Sr(3)—O(62)	2.632(14)	O(22)—Sr(1)—O(4M)	65.9(5)	O(11)[a]—Sr(2)—O(5M)	138.6(4)	O(52)—Sr(3)—O(31W)	79.3(6)	O(41)[a]—Sr(4)—O(5M)	83.4(4)
Sr(3)—O(63A)	2.55(2)	O(22)—Sr(1)—O(11W)	140.0(5)	O(11)[a]—Sr(2)—O(6M)	84.5(4)	O(52)—Sr(3)—O(42)	77.8(4)	O(41)[a]—Sr(4)—O(6M)	142.0(5)
Sr(3)—O(3W(1))	3.01(5)	O(22)—Sr(1)—O(12)	75.7(4)	O(11)[a]—Sr(2)—O(21W)	67.3(5)	O(52)—Sr(3)—O(62)	76.2(4)	O(41)[a]—Sr(4)—O(41W)	65.5(4)
Sr(4)—O(1M)	2.735(14)	O(22)—Sr(1)—O(51A)	74.1(5)	O(11)[a]—Sr(2)—O(22W)	133.7(6)	O(52)—Sr(3)—O(63A)	74.8(6)	O(41)[a]—Sr(4)—O(42W)	134.2(4)
Sr(4)—O(5M)	2.625(13)	O(22)—Sr(1)—O(52A)	70.8(5)	O(11)[a]—Sr(2)—O(41A)	142.2(4)	O(52)—Sr(3)—O(3W(1))	63.1(10)	O(41)[a]—Sr(4)—O(71A)	137.0(4)
Sr(4)—O(6M)	2.747(15)	O(22)—Sr(1)—O(72A)	86.5(5)	O(11)[a]—Sr(2)—O(43A)	113.9(5)	O(62)—Sr(3)—O(2M)	133.9(5)	O(41)[a]—Sr(4)—O(73A)	96.8(4)
Sr(4)—O(41W)	2.642(15)	O(22)—Sr(1)—O(73A)	128.8(4)	O(61)[a]—Sr(2)—O(1M)	83.0(5)	O(62)—Sr(3)—O(3W(1))	61.6(11)	O(73A)—Sr(4)—O(1M)	148.9(5)
Sr(4)—O(42W)	2.620(14)	O(51A)—Sr(1)—O(2M)	108.2(5)	O(61)[a]—Sr(2)—O(5M)	95.8(4)	O(63A)—Sr(3)—O(2M)	123.1(7)	O(73A)—Sr(4)—O(6M)	116.4(4)
Sr(4)—O(31)[a]	2.469(12)	O(51A)—Sr(1)—O(3M)	147.4(5)	O(61)[a]—Sr(2)—O(6M)	142.5(5)	O(63A)—Sr(3)—O(3M)	125.9(6)	O(73A)—Sr(4)—O(71A)	47.0(4)
Sr(4)—O(41)[a]	2.615(13)	O(51A)—Sr(1)—O(4M)	131.2(5)	O(61)[a]—Sr(2)—O(21W)	112.4(6)	O(63A)—Sr(3)—O(4M)	67.6(8)	Sr(2)—O(1M)—Sr(4)	98.9(5)
Sr(4)—O(71A)	2.799(16)	O(51A)—Sr(1)—O(52A)	46.0(4)	O(61)[a]—Sr(2)—O(22W)	142.6(6)	O(63A)—Sr(3)—O(42)	74.2(6)	Sr(3)—O(2M)—Sr(1)	94.9(7)
Sr(4)—O(73A)	2.676(11)	O(51A)—Sr(1)—O(72A)	69.7(4)	O(61)[a]—Sr(2)—O(11)[a]	77.3(4)	O(63A)—Sr(3)—O(62)	71.9(7)	Sr(3)—O(3M)—Sr(1)	103.9(5)
		O(51A)—Sr(1)—O(73A)	102.3(4)	O(61)[a]—Sr(2)—O(41A)	67.2(5)	O(63A)—Sr(3)—O(3W(1))	122.5(11)	Sr(3)—O(4M)—Sr(1)	100.5(8)
		O(52A)—Sr(1)—O(2M)	64.1(5)	O(61)[a]—Sr(2)—O(43A)	72.4(5)	O(1M)—Sr(4)—O(6M)	60.1(5)	Sr(4)—O(5M)—Sr(2)	100.6(4)
		O(52A)—Sr(1)—O(4M)	93.5(5)	O(43A)—Sr(2)—O(1M)	150.1(6)	O(1M)—Sr(4)—O(71A)	116.2(6)	Sr(2)—O(6M)—Sr(4)	97.6(5)
		O(72A)—Sr(1)—O(2M)	172.6(5)	O(43A)—Sr(2)—O(5M)	102.1(4)	O(5M)—Sr(4)—O(1M)	64.1(5)		

[a] The atoms are generated from the basis atoms by the symmetry operation $x + 1/2$, $y + 1/2$, z.

tended along the *c* axis are located between the layers formed by the polymeric chains. The channels can be occupied by water molecules of crystallization and additional nitrate anions.

Both structures are stabilized by complex networks of hydrogen bonds involving the oxygen atoms of the cucurbituril and water molecules and the nitrate anions. Such networks of hydrogen bonds involving all structural units of crystals are very characteristic of this type of compounds.[13—19]

The chemistry of polynuclear alkaline-earth complexes (particularly, in aqueous solutions) remains poorly known.[26—30] The results of the present study of supramolecular compounds **1** and **2** provide the first evidence that macrocyclic cavitands, *viz.*, cucurbit[*n*]urils, can be used for both the extraction of strontium from aqueous solutions and preparation of crystals of polynuclear strontium aqua complexes. The characteristic feature of these compounds is that the metal atoms have high coordination numbers (8, 9, and 10).

Table 2. Selected bond lengths in compound **2**

Bond	*d*/Å	Bond	*d*/Å
Sr(1)—O(11W)	2.689(6)	Sr(2)—O(21W)	2.686(7)
Sr(1)—O(12W)	2.611(7)	Sr(2)—O(22W)	2.707(7)
Sr(1)—O(13W)	2.615(6)	Sr(2)—O(23W)	2.753(6)
Sr(1)—O(11N)	2.844(6)	Sr(2)—O(24W)	2.604(7)
Sr(1)—O(12N)	2.642(7)	Sr(2)—O(25W)	2.622(6)
Sr(1)—O(21N)	2.694(6)	Sr(2)—O(1M)[a]	2.678(5)
Sr(1)—O(23N)	2.625(6)	Sr(2)—O(1M)	2.723(6)
Sr(1)—O(31)	2.549(5)	Sr(2)—O(32)	2.584(6)
Sr(1)—O(41)	2.527(6)	Sr(2)—O(42)	2.649(6)

[a] The atoms are generated from the basis atoms by the symmetry operation $-x, -y + 1, -z + 2$.

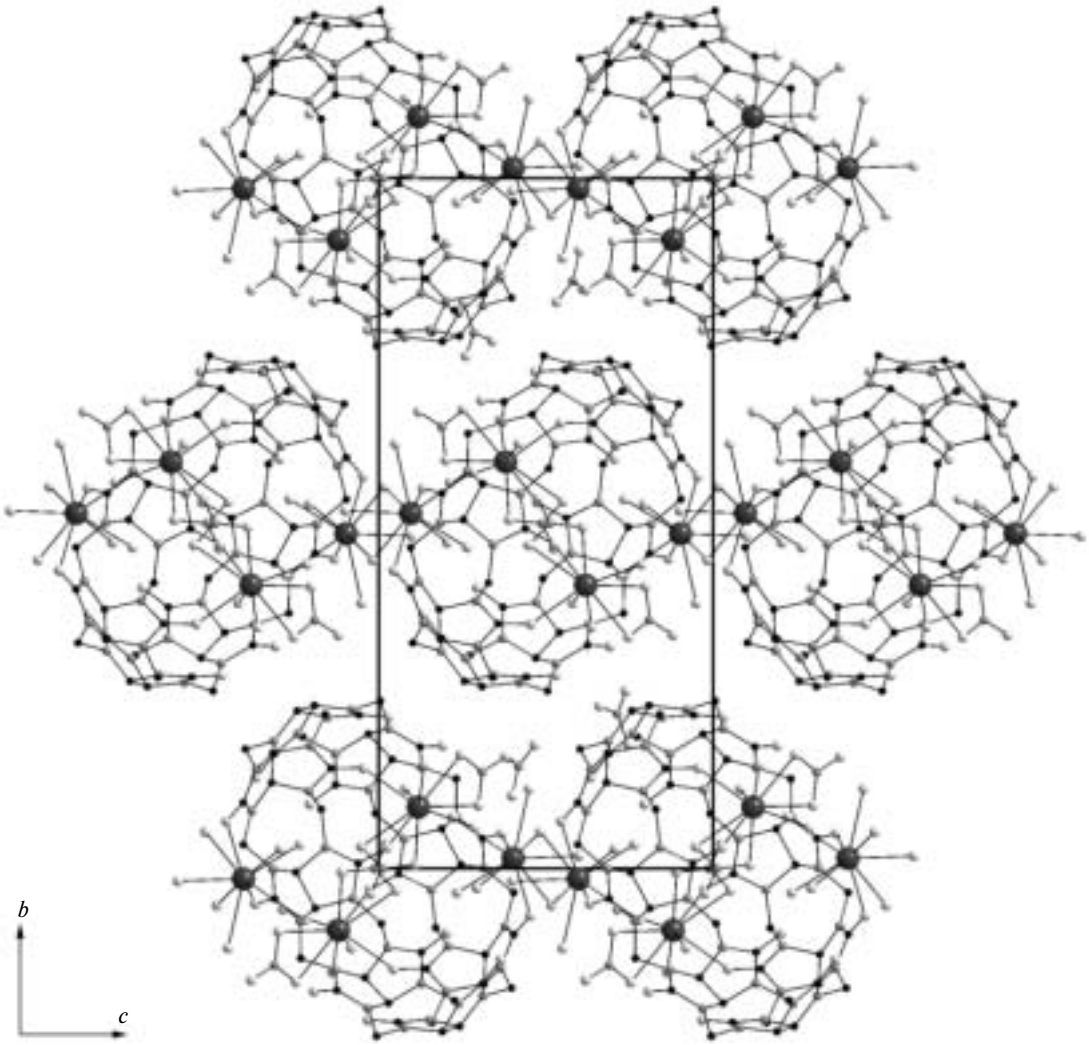

Fig. 6. Packing of the polymeric chains in the structure of **2** projected onto the *bc* plane. The water molecules of solvation and nitrate anions are omitted for clarity.

Table 3. Selected bond angles in compound **2**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
O(11W)—Sr(1)—O(11N)	67.59(18)	O(31)—Sr(1)—O(12N)	81.5(2)	O(25W)—Sr(2)—O(22W)	69.4(2)
O(11W)—Sr(1)—O(21N)	67.67(19)	O(31)—Sr(1)—O(21N)	139.27(18)	O(25W)—Sr(2)—O(23W)	68.9(2)
O(12W)—Sr(1)—O(11W)	127.8(2)	O(31)—Sr(1)—O(23N)	154.94(19)	O(25W)—Sr(2)—O(1M)[a]	140.41(19)
O(12W)—Sr(1)—O(13W)	72.7(2)	O(41)—Sr(1)—O(11W)	76.23(18)	O(25W)—Sr(2)—O(1M)	106.87(19)
O(12W)—Sr(1)—O(11N)	134.3(2)	O(41)—Sr(1)—O(12W)	70.9(2)	O(25W)—Sr(2)—O(42)	67.51(19)
O(12W)—Sr(1)—O(12N)	161.8(2)	O(41)—Sr(1)—O(13W)	142.6(2)	O(1M)[a]—Sr(2)—O(21W)	68.3(2)
O(12W)—Sr(1)—O(21N)	110.5(2)	O(41)—Sr(1)—O(11N)	73.46(17)	O(1M)[a]—Sr(2)—O(22W)	72.52(18)
O(12W)—Sr(1)—O(23N)	73.1(2)	O(41)—Sr(1)—O(12N)	118.19(19)	O(1M)[a]—Sr(2)—O(23W)	92.01(19)
O(13W)—Sr(1)—O(11W)	135.57(19)	O(41)—Sr(1)—O(21N)	134.22(19)	O(1M)—Sr(2)—O(23W)	138.95(18)
O(13W)—Sr(1)—O(11N)	130.7(2)	O(41)—Sr(1)—O(23N)	94.38(19)	O(1M)[a]—Sr(2)—O(1M)	64.8(2)
O(13W)—Sr(1)—O(12N)	94.8(2)	O(41)—Sr(1)—O(31)	86.27(18)	O(32)—Sr(2)—O(21W)	66.7(2)
O(13W)—Sr(1)—O(21N)	68.1(2)	O(21W)—Sr(2)—O(22W)	125.2(2)	O(32)—Sr(2)—O(22W)	139.29(18)
O(13W)—Sr(1)—O(23N)	83.1(2)	O(21W)—Sr(2)—O(23W)	68.7(2)	O(32)—Sr(2)—O(23W)	73.98(19)
O(12N)—Sr(1)—O(11W)	70.4(2)	O(21W)—Sr(2)—O(1M)	124.3(2)	O(32)—Sr(2)—O(24W)	81.6(2)
O(12N)—Sr(1)—O(11N)	46.18(18)	O(22W)—Sr(2)—O(23W)	76.1(2)	O(32)—Sr(2)—O(25W)	74.5(2)
O(12N)—Sr(1)—O(21N)	75.2(2)	O(22W)—Sr(2)—O(1M)	65.07(18)	O(32)—Sr(2)—O(1M)[a]	134.92(18)
O(21N)—Sr(1)—O(11N)	114.73(18)	O(24W)—Sr(2)—O(21W)	74.5(2)	O(32)—Sr(2)—O(1M)	146.26(18)
O(23N)—Sr(1)—O(11W)	70.2(2)	O(24W)—Sr(2)—O(22W)	137.5(2)	O(32)—Sr(2)—O(42)	81.56(18)
O(23N)—Sr(1)—O(11N)	137.7(2)	O(24W)—Sr(2)—O(23W)	141.5(2)	O(42)—Sr(2)—O(21W)	133.8(2)
O(23N)—Sr(1)—O(12N)	119.4(2)	O(24W)—Sr(2)—O(25W)	132.0(2)	O(42)—Sr(2)—O(22W)	100.82(19)
O(23N)—Sr(1)—O(21N)	47.80(19)	O(24W)—Sr(2)—O(1M)[a]	84.54(19)	O(42)—Sr(2)—O(23W)	134.25(19)
O(31)—Sr(1)—O(11W)	133.65(18)	O(24W)—Sr(2)—O(1M)	72.9(2)	O(42)—Sr(2)—O(1M)[a]	131.33(17)
O(31)—Sr(1)—O(12W)	83.6(2)	O(24W)—Sr(2)—O(42)	68.26(19)	O(42)—Sr(2)—O(1M)	68.82(17)
O(31)—Sr(1)—O(13W)	81.31(19)	O(25W)—Sr(2)—O(21W)	128.5(2)	Sr(2)[a]—O(1M)—Sr(2)	115.2(2)
O(31)—Sr(1)—O(11N)	66.34(17)				

[a] The atoms are generated from the basis atoms by the symmetry operation $-x, -y + 1, -z + 2$.

In conclusion, it should be noted that ^{90}Sr is one of the most toxic radionuclides produced upon radioactive decay of ^{235}U and ^{239}Pu. Studies of nuclear weapons led to a wide distribution of radioactive ^{90}Sr. The concentration of this isotope increased substantially after the Chernobyl catastrophe. Crown ethers, other polyethers, and poly(ethylene glycols) were proposed for the binding of strontium.[31] However, a search for new ligands suitable for this purpose remains an urgent problem. Macrocyclic cucurbit[*n*]urils also hold promise for the binding of strontium radioisotopes in the course of reprocessing of wastes from nuclear power stations. Cucurbit[*n*]urils are rather readily accessible and are quite stable both in strongly acidic and strongly alkaline media.

Experimental

The starting strontium nitrate (analytical grade) and commercial cucurbit[6]uril as decahydrate (Merck) were used without additional purification. Cucurbit[8]uril was prepared according to a procedure described earlier.[5] 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. The IR spectra were recorded on a Bruker IFS-85 Fourier spectrometer in KBr pellets.

Cucurbit[6]uril(dodecaaquatetranitratotetrastrontium) tetranitrate trihydrate (1). A mixture of cucurbit[6]uril ($C_{36}H_{36}N_{24}O_{12} \cdot 10H_2O$) (0.060 g), strontium nitrate ($Sr(NO_3)_2 \cdot 4H_2O$) (1.40 g), and water (6 mL) was heated for ~15 min until cucurbit[6]uril was almost completely dissolved. Then the reaction mixture was filtered and allowed to slowly evaporate in air at ~20 °C. Colorless crystals of complex **1** precipitated from the solution during 3—4 days. According to the results of X-ray diffraction analysis, complex **1** has the composition $[Sr_4(H_2O)_{12}(NO_3)_4(C_{36}H_{36}N_{24}O_{12})](NO_3)_4 \cdot 3H_2O$. After drying in air for one day, crystals of **1** lost three water molecules per formula unit. The yield was 0.060 g (56% with respect to cucurbit[6]uril). Found (%): C, 21.15; H, 3.03; N, 21.32. $C_{36}H_{60}N_{32}O_{48}Sr_4$. Calculated (%): C, 21.00; H, 2.94; N, 21.76. IR, ν/cm^{-1}: 3430 s, 1733 s, 1653 m, 1486 s, 1384 s, 1237 s, 1191 s, 1149 m, 967 s, 820 s, 801 s, 760 m, 678 m, 634 w.

Cucurbit[8]uril(octadecaaquatetranitratotetrastrontium) tetranitrate octahydrate (2). A mixture of cucurbit[8]uril ($C_{48}H_{48}N_{32}O_{16} \cdot 30H_2O \cdot 2.5HCl$) (0.020 g), strontium nitrate ($Sr(NO_3)_2 \cdot 4H_2O$) (0.70 g), and water (3 mL) was heated for ~15 min until cucurbit[8]uril was almost completely dissolved. Then the reaction mixture was filtered and allowed to slowly evaporate in air at ~20 °C for 3—4 days. The colorless crystalline compound that precipitated was filtered off and dried in air for one day. The yield was 0.018 g (67% with respect to cucurbit[8]uril). Found (%): C, 21.55; H, 3.95; N, 20.87. $C_{48}H_{100}N_{40}O_{66}Sr_4$. Calculated (%): C, 21.81; H, 3.81; N, 21.19. IR, ν/cm^{-1}: 3420 s, 1735 s, 1640 m, 1485 s, 1390 s, 1240 s,

Table 4. Principal crystallographic characteristics and details of X-ray diffraction studies

Parameter	**1**	**2**
Molecular formula	$C_{36}H_{66}N_{32}O_{51}Sr_4$	$C_{48}H_{100}N_{40}O_{66}Sr_4$
Molecular weight	2113.69	2644.16
Crystal system	Monoclinic	Monoclinic
Space group	*Cc*	$P2_1/c$
a/Å	23.640(4)	14.577(3)
b/Å	14.632(3)	25.932(2)
c/Å	21.214(5)	12.7977(10)
β/deg	106.725(18)	101.661(11)
V/Å^3	7027(2)	4737.7(11)
Z	4	2
ρ_{calc}/g cm^{-3}	1.998	1.854
T/K	203(2)	200(2)
Diffractometer	STOE STADI4	
λ/Å	0.71073 (Mo-Kα)	
$2\theta_{max}$/deg	50.12	50.04
Crystal dimensions/mm	0.55×0.40×0.35	0.80×0.78×0.40
μ/mm^{-1}	3.161	2.378
T_{min}/T_{max}	0.992/0.741	0.523/1.000
Measured reflections	6406	8695
Independent reflections	6406	8350
R_{int}	0	0.0437
Reflections with $I > 2\sigma(I)$	4494	5983
Refinable parameters	1097	679
Number of restrictions	452	0
R factors for reflections with $I > 2\sigma(I)$		
R_1	0.0717	0.0752
wR_2	0.1301	0.1725
R factors for all reflections		
R_1	0.1364	0.1211
wR_2	0.1716	0.2047
Figure of merit based on F^2	1.123	1.106
Residual electron density/$e \cdot$Å^{-3} (d_{min}/d_{max})	−0.897/1.200	−1.956/2.300

1195 s, 1155 m, 970 s, 810 m, 801 s, 760 m, 680 m, 675 m, 640 w, 620 w.

X-ray diffraction study. The crystallographic characteristics and details of X-ray diffraction studies of compounds **1** and **2** are given in Table 4. The X-ray diffraction data were collected at low temperature from colorless single crystals sealed in thin-walled glass capillaries. The intensities of reflections were measured with the use of the standard θ/2θ scan technique in the ranges of $-28 \le h \le 26$, $0 \le k \le 17$, $0 \le l \le 25$ for the crystal of **1** and $-0 \le h \le 17$, $-30 \le k \le 0$, $-15 \le l \le 14$ for the crystal of **2**. The absorption corrections were applied using azimuthal scanning curves. The structures were solved by direct methods and refined by the full-matrix least-squared method with anisotropic thermal parameters (except for the disordered oxygen atoms of the water molecules of crystallization in the structure of **1** and one nitrate anion in the structure of **2**) with the use of the SHELX-97 program package. In the refinement, restrictions were imposed on thermal parameters of some light atoms. The hydrogen atoms of the cucurbituril molecules were placed in the geometrically calculated positions and refined using a rigid-body model. The hydrogen atoms of the water molecules were not located. The atomic coordinates of compounds **1** and **2** were deposited with the Cambridge Structural Database and can be obtained from the authors.

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