Synthesis and crystal structure of a supramolecular adduct of trinuclear molybdenum oxocluster with macrocyclic cavitand cucurbit[5]uril containing the included ionic associate $Na^+...Cl...Na^+$

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The compound of composition $[\{Mo_3O_4(H_2O)_6Cl_3\}_2(Na_2Cl\subset C_{30}H_{30}N_{20}O_{10})]Cl_3 \cdot 14H_2O$ (**1**) was prepared by evaporation of a hydrochloric acid solution containing NaCl, the trinuclear aqua complex $[Mo_3O_4(H_2O)_9]^{4+}$, and the macrocyclic cavitand cucurbit[5]uril ($C_{30}H_{30}N_{20}O_{10}$). X-ray diffraction analysis demonstrated that the cucurbit[5]uril molecule is closed on both sides by the cluster cations through hydrogen bonding between the CO groups of the cucurbit[5]uril portals and the aqua ligands of the oxo cluster. The inner cavity of the supramolecular adduct includes an unusual ionic associate $Na^+...Cl...Na^+$. The sodium cations are coordinated by five carbonyl oxygen atoms of each portal of the macrocycle. Compound **1** is the first structurally characterized complex, in which the macrocyclic cucurbit[5]uril ligand is directly coordinated to the alkali metal cation.

Key words: cluster compounds, molybdenum, cucurbit[5]uril, supramolecular adduct, crystal structure.

The supramolecular approach to isolation of polynuclear metal aqua complexes from aqueous solutions, which has been developed in our earlier studies[1—7] based on the use of organic macrocyclic cavitand cucurbituril, allowed us to synthesize and structurally characterize a wide range of supramolecular adducts of triangular thio and seleno molybdenum and tungsten cluster complexes M_3Q_4 with cucurbit[6]uril (CB[6]). The macrocyclic cavitand cucurbit[6]uril ($C_{6n}H_{6n}N_{4n}O_{2n}$, $n = 6$) consisting of six glycoluril fragments linked by methylene bridges is the most well studied of cucurbit[*n*]urils (CB[*n*]) with different numbers of such fragments ($n = 5$—10) and has a barrel-like shape, whose portals are formed by carbonyl groups.[8] Six water molecules coordinated to the metal atoms of the cluster complex $[M_3Q_4(H_2O)_{9-x}Cl_x]^{(4-x)+}$ (M = Mo, W; Q = S, Se; $x = 1$—3) are almost in a single plane and match well in size and symmetry with six carbonyl groups of each portal of CB[6]. In addition, the cationic aqua cluster complexes have strong acid properties and serve as donors of hydrogen bonds, whereas the oxygen atoms of the polarized carbonyl groups of cucurbituril act as acceptors of hydrogen bonds. This geometric and functional (donor—acceptor of hydrogen bonds) complementarity is responsible for an extensive hydrogen bond network between the cavitand molecules and the triangular aqua complexes and gives rise to stable poorly soluble supramolecular compounds. The cluster : cucurbituril ratio in these compounds is 1 : 1, if only one cucurbituril portal is closed by the cluster complex, and is 2 : 1, if both portals are closed.

Like thio and seleno analogs, the trinuclear molybdenum oxo cluster $[Mo_3O_4(H_2O)_6Cl_3]^+$ forms the supramolecular complex with cucurbit[6]uril, $\{[Mo_3O_4(H_2O)_6Cl_3]_2(C_{36}H_{36}N_{24}O_{12})\}Cl_2 \cdot 14H_2O$, in which the macrocyclic molecule is linked to two cluster cations through hydrogen bonds.[9] However, the smaller size of the oxo cluster compared to the sizes of chalcogenide clusters results in the shift of the cluster cation to the end of the portal and inclination of the plane of the Mo_3 triangle with respect to the plane of the portal by 18.5°.

In the present study, we synthesized a new supramolecular complex of the trinuclear molybdenum oxo cluster with the smaller macrocyclic cavitand, *viz.*, cucurbit[5]uril (CB[5]), containing an unusual ionic associate $Na^+...Cl...Na^+$ in the inner cavity. The compound $[\{Mo_3O_4(H_2O)_6Cl_3\}_2(Na_2Cl\subset C_{30}H_{30}N_{20}O_{10})]Cl_3 \cdot 14H_2O$ (**1**) was characterized by X-ray diffraction.

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Results and Discussion

Cucurbit[n]urils with other than six glycoluril fragments have became accessible rather recently.[10—12] No supramolecular compounds of cucurbit[5]uril with metal aqua complexes have been structurally characterized, although the existence in solution of decamethylcucurbit[5]uril (CB[5] derivative, in which all hydrogen atoms of the CH groups of the glycoluril fragments are replaced with the Me groups) complexes with alkali and alkaline-earth metals and with Pb^{2+} and Cd^{2+} cations was confirmed by calorimetry and potentiometric titration.[13]

The compound of composition $[\{Mo_3O_4(H_2O)_6Cl_3\}_2(Na_2Cl\subset C_{30}H_{30}N_{20}O_{10})]Cl_3\cdot 14H_2O$ (**1**) was prepared as red-brown crystals by slow evaporation of a hydrochloric acid solution containing NaCl, the trinuclear aqua complex $[Mo_3O_4(H_2O)_9]^{4+}$, and cucurbit[5]uril at room temperature. The IR spectrum of complex **1** confirms that the molecule contains CB[5], the trinuclear molybdenum cluster complex, and water molecules of crystallization. X-ray diffraction study demonstrated that the ratio of cucurbit[5]uril to the molybdenum oxo cluster complex is 1 : 2, and both portals of the macrocycle are closed by the cluster anions $[Mo_3O_4(H_2O)_6Cl_3]^+$ as lids (Fig. 1).

The average Mo—Mo, Mo—(μ_2-O), Mo—(μ_3-O), Mo—Cl, and Mo—OH_2 distances are 2.504(4), 1.910(8), 2.045(6), 2.444(10), and 2.143(16) Å, respectively, which agree well with the data for $\{[Mo_3O_4(H_2O)_6Cl_3]_2(C_{36}H_{36}N_{24}O_{12})\}Cl_2\cdot 14H_2O$ (**2**) studied earlier.[9] Six aqua ligands of the oxo cluster are in *cis* positions with respect to the μ_3-O atom and form six hydrogen bonds with five carbonyl oxygen atoms of the CB[5] portals (Fig. 2). The O...O distances are in the range of 2.614(6)—2.778(7) Å (aver., 2.68(7) Å). The oxo cluster in compound **1**, unlike that in the complex with

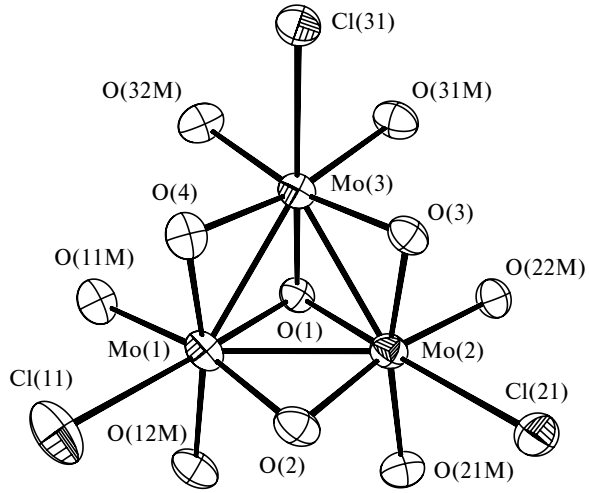

Fig. 1. Structure of the cationic complex $[Mo_3O_4(H_2O)_6Cl_3]^+$ in compound **1**.

CB[6] prepared earlier, is virtually parallel to the portal of cucurbit[5]uril (angle of inclination of the Mo_3 triangle with respect to the plane of the portal is 2.2°). This is accounted for by the smaller diameter of the CB[5] portals compared to the CB[6] portals, resulting in the better geometric complementarity between the portal oxygen atoms of CB[5] and the coordinated water molecules of the aqua complex $[Mo_3O_4(H_2O)_6Cl_3]^+$ (diameter of the CB[5] portal in molecule **1** is 5.04 Å, whereas the diameter of the CB[6] portal in molecule **2** is 6.98 Å, the diameter of the circle enclosing six aqua ligands of the oxo cluster is 5.74 Å).

Compound **1** is an interesting example of supramolecular complexes in which both portals of cucurbituril are closed by cluster complexes ("two lids on the barrel" type[14]). The inner cavity of the nanosized (van der Waals sizes are 15×20 Å) supramolecular adduct includes an

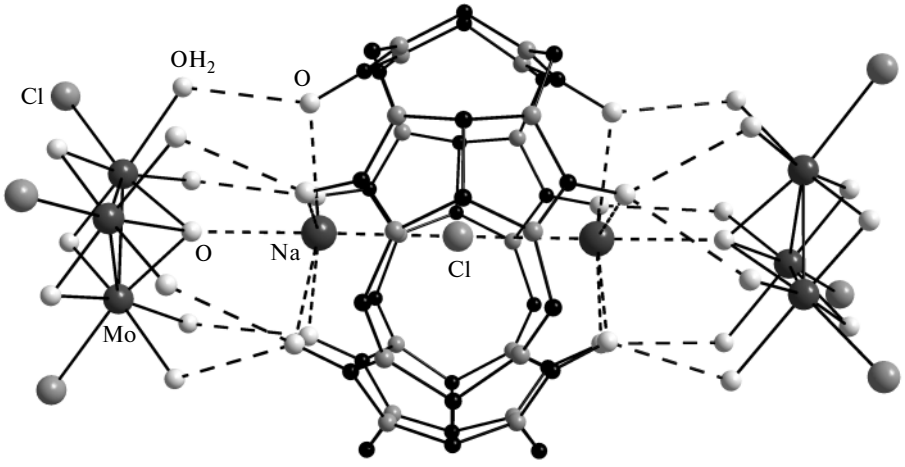

Fig. 2. Structure of the cationic supramolecular complex $[\{Mo_3O_4(H_2O)_6Cl_3\}_2(Na_2Cl\subset C_{30}H_{30}N_{20}O_{10})]^{3+}$ (Na...Cl and Na...O contacts and hydrogen bonds are indicated by dashed lines).

Table 1. Selected bond lengths (*d*) and bond angles (ω) in the crystal structure of **1**

Bond	*d*/Å	Bond	*d*/Å	Parameter	Value
Mo(1)—Mo(2)	2.4992(7)	Mo(2)—O(3)	1.906(3)	Bond	*d*/Å
Mo(1)—Mo(3)	2.5068(6)	Mo(2)—Cl(21)	2.4461(14)	Na(1)—O(11)	2.684(5)
Mo(2)—Mo(3)	2.5046(6)	Mo(2)—O(21M)	2.159(4)	Na(1)—O(12)[b]	2.484(5)
Mo(1)—O(1)	2.046(3)	Mo(2)—O(22M)[a]	2.156(4)	Na(1)—O(21)	2.485(5)
Mo(1)—O(2)	1.912(4)	Mo(3)—O(1)	2.038(4)	Na(1)—O(22)[b]	2.535(5)
Mo(1)—O(4)	1.913(4)	Mo(3)—O(3)	1.916(3)	Na(1)—O(31)	2.470(5)
Mo(1)—Cl(11)	2.4534(16)	Mo(3)—O(4)	1.916(4)	Na(1)—Cl(1)	2.712(2)
Mo(1)—O(11M)	2.148(4)	Mo(3)—Cl(31)	2.4333(13)	Angle	ω/deg
Mo(1)—O(12M)	2.143(4)	Mo(3)—O(31M)	2.131(4)	Na(1)—Cl(1)—Na(1′)[b]	178.52(14)
Mo(2)—O(1)	2.050(4)	Mo(3)—O(32M)	2.118(4)	O(1)—Na(1)—Cl(1)	179.08(14)
Mo(2)—O(2)	1.894(4)	Na(1)—O(1)	2.488(4)		

[a] The atomic numbering scheme is given in Fig. 1.
[b] The primed atoms are generated by the symmetry operation $x + 1$, $y + 1$, z.

unusual ionic associate $Na^+...Cl...Na^+$. All five carbonyl oxygen atoms of each CB[5] portal coordinate the sodium cation (see Fig. 2). The sodium cations lie almost in the plane of the portals (deviations from the plane are within 0.2 Å).

Supramolecular complex **1** is the first structurally characterized compound in which the alkali metal ion is coordinated by the oxygen atoms of the CB[5] portals. This coordination of the alkali metal cations is characteristic of cucurbit[6]uril,[5] the larger size of the CB[6] portals allowing two metal atoms (Na,[15] K,[16] or Rb[17]) to be coordinated to each portal giving rise to four M—O bonds (two bonds with each metal atom). The Na—O distances in compound **1** (Table 1) are slightly longer than those in the sodium complex with CB[6] of composition $[\{Na_4(H_2O)_{10}\}(C_4H_8O{\subset}C_{36}H_{36}N_{24}O_{12})](SO_4)_2 \cdot 10H_2O$ [15] (2.484(5)—2.684(5) and 2.275(4)—2.461(4) Å, respectively). The coordination environment of the sodium cations (Fig. 3) is formed, in addition to the carbonyl oxygen atoms of the CB[5] portals, by the bridging μ_3-O ligand of the molybdenum oxo cluster and the chloride anion located in the cavity of the cucurbit[5]uril molecule. This gives rise to the ...(μ_3-O)—Na—Cl—Na—(μ_3-O)... chains, in which all angles are close to 180° (see Table 1). The cationic supramolecular complex has the composition $[\{Mo_3O_4(H_2O)_6Cl_3\}_2(Na_2Cl{\subset}C_{30}H_{30}N_{20}O_{10})]^{3+}$ (see Fig. 2).

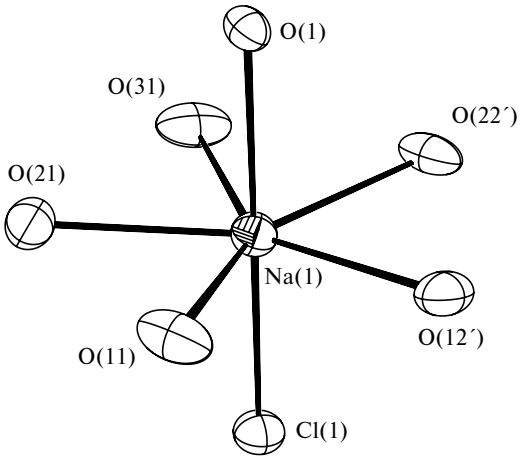

Fig. 3. Coordination environment of the Na^+ cation in compound **1**.

The Na—Cl distance in molecule **1** is 2.712(2) Å, which is shorter than the corresponding distance in solid NaCl (2.814 Å)[18] and is substantially longer than the experimental distance in the NaCl molecule in the gas phase (2.39 Å).[19] In the crystal structures containing the ...Na—Cl—Na... fragments (14 structures were found in the Cambridge Structural Database, October 2003 version[20]), the Na—Cl distances are in the range of 2.642—3.031 Å (aver., 2.822 Å). However, the coordination number of the chlorine atoms in most of these compounds, unlike that in complex **1**, is larger than two, and the sodium atoms are linked to each other by several bridging chlorine atoms.

The inclusion of the ionic associate $Na^+...Cl^-...Na^+$ in the inner cavity of cucurbit[5]uril is not unique. We have observed an analogous situation in the compound of composition $[Na_2Cl{\subset}C_{30}H_{30}N_{20}O_{10}]Cl \cdot xH_2O$ (**3**), which was prepared in a neutral medium in the absence of the oxo cluster and was characterized by preliminary data from single-crystal X-ray diffraction study (monoclinic symmetry, space group $C2/m$, a = 31.134(2) Å, b = 19.490(1) Å, c = 17.328(1) Å, β = 117.668(3)°).

Noteworthy is the high affinity of cucurbit[5]uril for sodium cations, because crystals of compounds **1** and **3** precipitated even from a solution, which was prepared with the use of cucurbit[7]uril containing an insignificant impurity of cucurbit[5]uril.

The behavior of cucurbit[*n*]urils as cavitands (hosts), which can include small guest molecules or ions, is asso-

ciated with the presence of a rather rigid intramolecular cavity. In compounds **1** and **3**, the guest chloride anion is located in the cavity of the CB[5] molecule. For cucurbit[5]uril, the supramolecular compound of the "macrocycle in macrocycle" type, {Cl⊂CB[5]⊂CB[10]}, is the only structurally characterized example of the inclusion of a guest.[21] In this compound, cucurbit[5]uril is included in cucurbit[10]uril, and the chlorine anion is located inside CB[5]. Compounds, in which a water molecule[22] or a nitric acid molecule[23] is present in the cavity of decamethylcucurbit[5]uril, were structurally characterized. The possibility of inclusion of N_2, O_2, methanol, and acetonitrile molecules in decamethylcucurbit[5]uril was proved by electrospray mass spectrometry.[24]

The packing of the molecular ions in the crystal of **1** is shown in Fig. 4. The cationic supramolecular complexes form a two-layer packing, in which the layers alternate along the *c* axis. The centers of the cucurbit[5]uril molecules occupy the crystallographic positions 2*a* (0, 0, *z*; 1/2, 1/2, $\bar{z}$; $z = 0.2557$) of symmetry 2 (C_2) and form a body-centered sublattice. The axes of the $Na^+—Cl^-—Na^+$ associates located inside the supramolecular complexes in one layer are parallel to each other, and the axes of these associates from the adjacent layers cross at a nearly right angle. Water molecules of crystallization and additional chlorine anions are located between the cationic supramolecular complexes. In the crystal of **1**, all structural units are involved in an extensive hydrogen bond network, which is very typical of such compounds.[5]

Experimental

Commercial sodium chloride of reagent grade was used without additional purification. The starting solution of $[Mo_3O_4(H_2O)_9]^{4+}$ in 2 *M* HCl was prepared according to a known procedure[25] from $Na_2MoO_4 \cdot 2H_2O$ and K_3MoCl_6 (both of analytical grade), purified on the cation-exchange resin DOWEX-50W2, and identified by UV-Vis spectroscopy (λ = 505 nm, $\varepsilon = 189\ M^{-1}\ cm^{-1}$) on an Ultraspec 3300pro instrument (200—1100 nm). Cucurbit[5]uril was prepared according to a

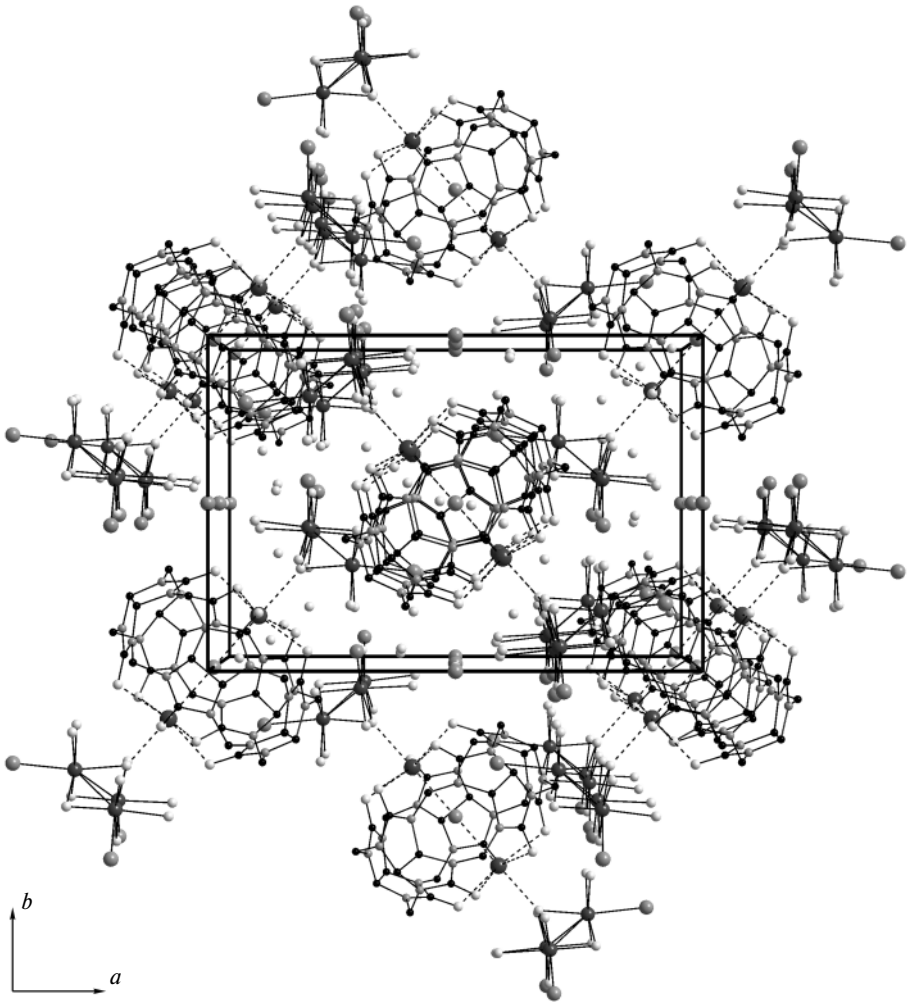

Fig. 4. Packing of the molecular fragments in the crystal of **1** (projection along the *c* axis).

procedure described earlier.[12] 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-transform spectrometer in KBr pellets.

[Bis{hexaaquatrichloro-μ_3-oxo-tri-μ_2-oxo-triangulotrimolybdenum(Mo—Mo)}-cucurbit[5]uril]monochlorodisodium trichloride tetradecahydrate, $[\{Mo_3O_4(H_2O)_6Cl_3\}_2(Na_2Cl\subset C_{30}H_{30}N_{20}O_{10})]Cl_3\cdot 14H_2O$ (1). A mixture of NaCl (0.030 g), a 0.02 *M* $[Mo_3O_4(H_2O)_9]^{4+}$ solution (3 mL) in 3 *M* HCl (0.06 mmol), CB[5] (0.020 g, 0.02 mmol), and water (6 mL) was slightly heated with stirring until the compounds were completely dissolved (~5 min) and allowed to slowly evaporate in air at ~20 °C. Dark red-brown crystals of compound **1** were isolated from the solution after 20 days. The yield was 0.020 g (40%). IR (ν/cm^{-1}): 3186 (s), 1710 (s), 1623 (m), 1502 (s), 1477 (s), 1415 (s), 1379 (s), 1336 (s), 1300 (s), 1282 (s), 1242 (s), 1192 (s), 1142 (s), 984 (m), 954 (s), 801 (s), 760 (s), 674 (m), 630 (m), 465 (m). Found (%): C, 15.05; H, 3.50; N, 11.55; Cl, 14.93. $C_{30}H_{82}Cl_{10}Mo_6N_{20}Na_2O_{44}$. Calculated (%): C, 14.99; H, 3.44; N, 11.66; Cl, 14.75.

X-ray diffraction study. X-ray diffraction data for compound **1** were collected from a single crystal of dimensions 0.19×0.10×0.10 mm at 150(2) K on a four-circle automated Bruker—Nonius X8Apex CCD diffractometer equipped with an area detector. The crystals belong to the orthorhombic system, a = 19.1293(13) Å, b = 12.9768(8) Å, c = 15.1839(11) Å, V = 3769.2(4) Å^3, M = 1709.56, d_{calc} = 2.118 g cm^{-3}, λ(Mo-Kα) = 0.71073 Å, space group $P2_12_12$ (No. 18), Z = 2. X-ray data collection, frame integration, and data processing were performed with the use of the APEX2[26] and SAINT[27] program packages. The absorption correction (μ = 1.445 mm^{-1}) was applied based on the intensities of equivalent reflections with the use of the SADABS program[28] (T_{min} = 0.7260, T_{max} = 0.8015). A total of 44325 reflections were measured in the angle range $2\theta \leq 61.36°$, of which 10705 reflections were independent (R_{int} = 0.0370). The structure was solved by direct methods using the XS program implemented in the SHELXTL program package[29] and refined anisotropically (except for the hydrogen atoms, disordered water molecules, and chloride ions) by the full-matrix least-squares method using the SHELXL program implemented in the SHELX-97 program package.[30] The goodness-of-fit was 1.032, the residual maximum and minimum electron densities were 2.485 and −1.760 e/Å^3 (in the vicinity of the disordered chloride anion), respectively; R_1 = 0.0487 and wR_2 = 0.1332 for 9138 reflections with $F_0 > 4\sigma(F_0)$, R_1 = 0.0601 and wR_2 = 0.1388 for all independent reflections used in calculations.

The positions of the hydrogen atoms of the cucurbit[5]uril molecules were calculated geometrically. The isotropic displacement parameters of the hydrogen atoms were taken equal to U_{eq} of the pivot nonhydrogen atoms. The hydrogen atoms of the water molecules were not localized. Some chloride anions and water molecules of crystallization are disordered. One of the chloride anions of the outer sphere, which are necessary for charge compensation of the cationic complex, was not revealed. Apparently, the missing chloride anion is strongly disordered and is located in cavities between the supramolecular complexes. The atomic coordinates were deposited with the Cambridge Structural Database and can be obtained from the authors.

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