494 *Russian Chemical Bulletin, International Edition, Vol. 50, No. 3, pp. 494—496, March, 2001*

Synthesis and the crystal structure of a supramolecular adduct of the $[Mo_3O_4(H_2O)_6Cl_3]^+$ cluster complex with macrocyclic cavitand cucurbituril

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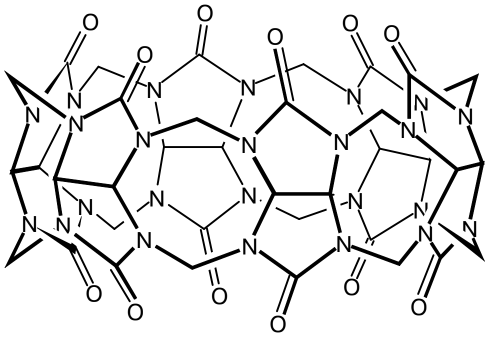
The crystalline supramolecular compound of composition $\{(C_{36}H_{36}N_{24}O_{12})[Mo_3O_4(H_2O)_6Cl_3]_2\}Cl_2 \cdot 14H_2O$ was obtained by slow concentration of a hydrochloric solution of the cluster aqua complex $[Mo_3O_4(H_2O)_9]^{4+}$ and macrocyclic cavitand cucurbituril ($C_{36}H_{36}N_{24}O_{12}$). The molecular and crystal structure of the supramolecular adduct was established by X-ray diffraction analysis.

Key words: cluster complexes, aqua complexes, molybdenum, cucurbituril, supramolecular compound, crystal structure, X-ray diffraction analysis.

This work was undertaken as part of our continuing studies on the synthesis of supramolecular compounds based on cucurbituril.[1—4] Cucurbituril ($C_{36}H_{36}N_{24}O_{12}$) is a barrel-shaped macrocyclic cavitand[5,6] (the point symmetry group is D_{6h}; the diameter of the inner cavity of the molecule is 5.5 Å) bounded by carbonyl groups ("portals").



Cucurbituril ($C_{36}H_{36}N_{24}O_{12}$)

It has been demonstrated[1—3] that the reactions of hydrochloric solutions of the chalcogenide cluster aqua complexes $[M_3Q_4(H_2O)_9]^{4+}$ (M = Mo or W; Q = S or Se) with cucurbituril afforded supramolecular adducts. In these adducts, the cucurbituril molecules are closed by one or two "caps" formed by the cluster complexes, which are held *via* geometrically and functionally complementary hydrogen bonds between the hydrogen atoms of the water molecules coordinated to the metal atom and the oxygen atoms of the carbonyl groups of cucurbituril. The cavities of the cucurbituril molecules in these aggregates are occupied by guest water molecules[1,2] or pyridinium cations.[2,3]

In the present study, we synthesized the supramolecular adduct of the $[Mo_3(\mu_3\text{-}O)(\mu_2\text{-}O)_3(H_2O)_6Cl_3]^+$ cluster complex with macrocyclic cavitand cucurbituril of composition $\{(C_{36}H_{36}N_{24}O_{12})[Mo_3O_4(H_2O)_6Cl_3]_2\}Cl_2 \cdot 14H_2O$ (**1**) and established its crystal structure.

Compound **1** was obtained as red-brown crystals upon slow concentration (~20 °C) of a hydrochloric solution of the $[Mo_3O_4(H_2O)_9]Cl_4$ complex and cucurbituril. We succeeded in preparing crystals suitable for X-ray diffraction study only upon addition of small amounts of glycerol.

As in the case of thio and seleno analogs, the oxo cluster forms a 2 : 1 adduct with cucurbituril through a system of hydrogen bonds. The adduct consists of the cucurbituril molecule whose portal is closed by two $[Mo_3O_4(H_2O)_6Cl_3]^+$ cluster cations as "caps" (Fig. 1). The packing of such supramolecular aggregates has a dominant role in the formation of the crystal structure of compound **1**. The cavity of the cucurbituril molecule is occupied by the guest water molecule, which is disordered over four positions (O(C(1)) and O(C(2))) and is linked to the water molecule located in the portal (O(W(1))) *via* hydrogen bonds (the average O...O distance is 2.67 Å). The Cl^- counterion and the water molecules of crystallization, which are partially disordered and have large thermal parameters, are located between the aggregates.

The "cap" (μ_3-O)-ligand (O(1)) in the $[Mo_3O_4(H_2O)_6Cl_3]^+$ cluster cation is directed toward the cavity of the cucurbituril molecule. The chloride anions are in *trans* positions with respect to this ligand. The water molecules in the *cis* positions each form six hydrogen bonds with the carbonyl groups of cucurbituril (the average O...O distance is 2.67 Å) and one hydrogen bond with

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 3, pp. 475—477, March, 2001.

1066-5285/01/5003-494 $25.00 © 2001 Plenum Publishing Corporation

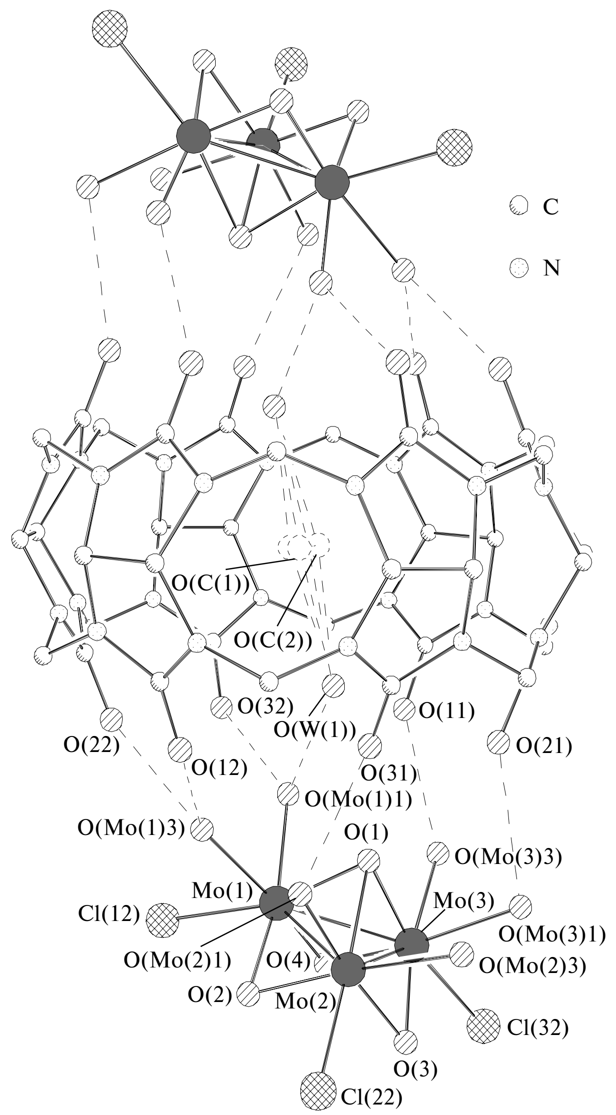


Fig. 1. Structure of the supramolecular adduct $\{[Mo_3O_4(H_2O)_6Cl_3]_2(C_{36}H_{36}N_{24}O_{12})(H_2O)_3\}^{2+}$. The disordered oxygen atoms of the water molecule and hydrogen bonds are indicated by dashed lines. The principal bond lengths: Mo—Mo, 2.5032(15)—2.5040(15) Å; Mo—(μ_3-O), 2.014(8)—2.044(8) Å; Mo—(μ_2-O), 1.895(8)—1.927(8) Å; Mo—OH_2, 2.119(8)—2.296(8) Å; Mo—Cl, 2.434(4)—2.459(3) Å.

the water molecule of solvation located in the vicinity of the plane of the portal (the O...O distance is 2.62(1) Å).

Complex **1** differs from adducts of cucurbituril with chalcogenide molybdenum[1,2] and tungsten[1—3] complexes in that the plane of the Mo_3 triangle in **1** is inclined to the plane of the portal of the cucurbituril molecule (the angle of inclination is 18.5°) and the cluster cation is shifted toward one end of the portal ring resulting in the nonequivalence of the existing hydrogen bonds. The O...O distances between the coordinated water molecules and the carbonyl groups of cucurbituril range from 2.61(1) for O(Mo(2)1)...O(31) to 2.76(1) Å for O(Mo(3)1)...O(21). It should also be noted that the hydrogen bonds in compound **1** are substantially shorter than those in adducts of chalcogenide complexes.[1—3] Apparently, these differences in the structure of the supramolecular adducts of cucurbituril with oxo- and chalcogen-bridged molybdenum clusters are associated with the smaller size of the Mo_3O_4 oxo cluster (the average Mo—Mo bond length is 2.504 Å) compared to the sizes of the M_3Q_4 chalcogenide clusters (2.74 Å for M = Mo and Q = S;[2] 2.78 Å for M = Mo and Q = Se;[1] and 2.72 Å for M = W and Q = S [2,3]) as well as with the higher acidity of the oxo complex. The displacement of the cluster cation toward the end of the portal ring is also observed in the adduct of cucurbituril with the binuclear Nb^{IV} complex of composition $\{[Nb_2S_4(H_2O)_8](C_{36}H_{36}N_{24}O_{12})\}Cl_4 \cdot 15H_2O$.[4]

The crystal packing of supramolecular adducts **1** is shown in Fig. 2. The $[Mo_3O_4(H_2O)_6Cl_3]^+$ cluster cations are located in general positions. One of the chloride ligands of the cluster complex (Cl(12)) forms Cl...Cl contacts with the adjacent cluster (the Cl...Cl distance is 3.483(7) Å; the sum of the van der Waals radii[7] is 3.62 Å). The centers of the cucurbituril molecules occupy the crystallographic positions *2b* (1/2, 0, 0; 1/2, 1/2, 1/2) with the symmetry $\bar{1}$ to form a single-layer pseudohexagonal packing. The layers are parallel to the plane *bc*. The distance between the centers of the cucurbituril molecules belonging to the adjacent layers is 12.219(2) Å (the unit cell parameter *a*). The distances between the centers of the cucurbituril molecules in the layer are 12.316(1) (the unit cell parameter *b*) and 15.135(3) Å. In the crystal, there is an extensive network of hydrogen bonds involving the oxygen atoms of the cucurbituril and water molecules and the chloride anions.

Thus, the reaction of the cluster aqua complex $[Mo_3O_4(H_2O)_9]^{4+}$ with cucurbituril afforded the supramolecular adduct. In this adduct, cucurbituril is closed by two cluster complexes as "caps," which are held through hydrogen bonds between the hydrogen atoms of the water molecules coordinated to the molybdenum atoms and the oxygen atoms of the carbonyl groups of the cavitand.

Experimental

The initial solution of $[Mo_3O_4(H_2O)_9]^{4+}$ in 2 *M* HCl was prepared from $Na_2MoO_4 \cdot 2H_2O$ (analytical grade) and K_3MoCl_6 (analytical grade) according to a known procedure.[8] The solution was purified on a Dowex-50Wx2 cation-exchange resin and identified based on the electronic absorption spectra (λ_{max} = 505 nm, ε = 189 mol^{-1} cm^{-1}) measured on a Specord M 40 instrument. Commercial cucurbituril (Merck) was used as a decahydrate without additional purification. Glycerol was of the reagent-grade purity.

Cucurbituril{bis[hexaaquatrichloro(μ_3-oxo)tri(μ_2-oxo)trimolybdenum (Mo—Mo)]} dichloride tetrahydrate (1). A mixture of 3 *M* HCl (3 mL) and cucurbituril (7 mg, 0.007 mmol) was added to a solution of $[Mo_3O_4(H_2O)_9]^{4+}$ (21 *mM*) in 2 *M* HCl (1 mL). The reaction mixture was slightly warmed on an electric hot plate until cucurbituril was almost completely dissolved. Then the mixture was filtered. Two drops of glycerol were added to the filtrate. The mixture was stirred and slowly concentrated in air at ~20 °C. After 10—15 days, dark red-brown crystals precipitated from the solution. The yield was 0.016 g (93%). Found (%):

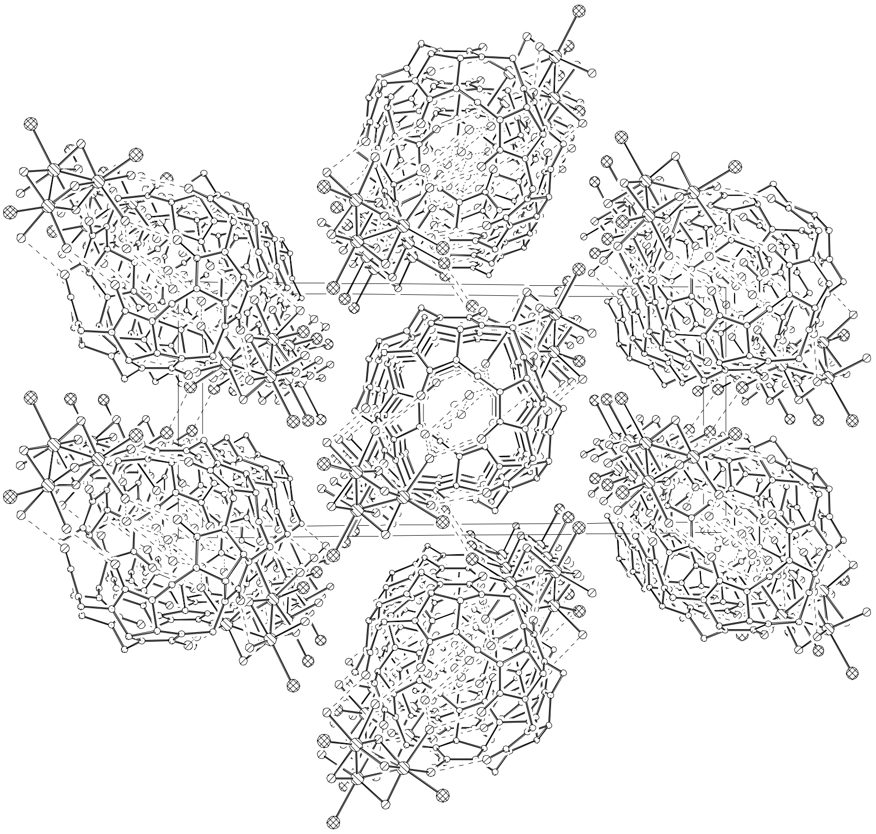


Fig. 2. Crystal packing of supramolecular adducts **1** projected along the axis *a*. Hydrogen bonds are indicated by dashed lines.

C, 17.77; H, 3.44; N, 13.66; Cl, 11.22. $C_{36}H_{88}Cl_8Mo_6N_{24}O_{46}$. Calculated (%): C, 17.63; H, 3.62; N, 13.71; Cl, 11.56.

X-ray diffraction study of a single crystal of adduct **1** of dimensions 0.32×0.26×0.19 mm was carried out on a four-circle automated STOE STADI4 diffractometer at 293(2) K; space group $P2_1/c$, a = 12.219(2), b = 12.316(1), c = 27.651(4) Å, β = 102.13(2)°, V = 4068.1(9) Å^3, M = 2452.54, d_{calc} = 2.002 g cm^{-3}, λ(MoKα) = 0.71073 Å, Z = 2, μ = 1.271 mm^{-1}. A total of 7502 reflections were measured by the $\theta/2\theta$ scanning technique in the angle range $2\theta \leq 50.24°$ of which 7248 reflections were independent. The intensities of three check reflections showed an almost linear decrease (reaching 25.9%) in the course of X-ray data collection. The corrections for radiation damage and absorption were applied using two azimuth scanning curves. The structure of **1** was solved by the direct method and refined by the full-matrix least-squares method with anisotropic thermal parameters for all nonhydrogen atoms (except for the O atom of one of the disordered water molecules) using the SHELX-97 program package;[9] GOF was 1.217; the residual maximum and minimum electron densities were 1.928 and −0.837 e/Å^3 (in the vicinity of heavy atoms), respectively; R_1 = 0.0781 and wR_2 = 0.1871 for 5236 reflections with $F > 4\sigma(F)$; R_1 = 0.1192 and wR_2 = 0.2117 for all independent reflections used in calculations. The hydrogen atoms of the cucurbituril molecules were placed in geometrically calculated positions. The hydrogen atoms of the coordinated water molecules were located from difference electron density syntheses and refined using geometric restrictions. We failed to locate the hydrogen atoms of the water molecule of solvation. The atomic coordinates were deposited with the Cambridge Structural Database and can also be obtained from the authors.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 99-03-32788).

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Received October 16, 2000;
in revised form January 12, 2001