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Synthesis and crystal structure of supramolecular adduct of tetranuclear uranyl chloride aquacomplex with macrocyclic cavitand cucurbituril

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Crystals of supramolecular compound $\{[(UO_2)_4O_2Cl_4(H_2O)_6](H_2O\subset C_{36}H_{36}N_{24}O_{12})\}\cdot 4H_2O$ were obtained under conditions of hydrothermal synthesis from solutions of uranyl(VI) nitrate and cucurbituril in the presence of rubidium chloride. The crystal and molecular structure were determined by X-ray diffraction analysis.

Key words: uranyl ion, aquacomplex, cucurbituril, supramolecular compound, crystal structure, X-ray diffraction analysis.

Hydrolysis of uranyl (UO_2^{2+}) salts results in polynuclear aquacomplexes, the chemical composition and crystal structure of which have been the subject of numerous speculations. X-ray scattering studies of aqueous solutions of uranyl(VI) chloride revealed the presence of uranium in the form of binuclear and trinuclear complexes.[1] Experiments on titration of uranyl salts indicated the formation of binuclear, trinuclear, and tetranuclear complexes depending on the ionic medium.[2—4] Single crystals of a number of binuclear aquacomplexes

$[(UO_2)_2Cl_2(OH)_2(H_2O)_4]$,[5]
$[(UO_2)_2(OH)_2(NO_3)_2(H_2O)_3]$[6]

and tetranuclear uranium aquacomplexes

$[(UO_2)_4Cl_2O_2(OH)_2(H_2O)_6]\cdot 4H_2O$,[7]
$Rb_4[(UO_2)_4Cl_8O_2(H_2O)_2]\cdot 2H_2O$,[8]
$K_2[(UO_2)_4Cl_4O_2(OH)_2(H_2O)_6]$,[9]
$[(UO_2)_4O_2Cl_4(C_4H_8O)_2(H_2O)_4]$[10]

were obtained and structurally characterized.

In this work we report the synthesis and crystal structure of a supramolecular adduct of tetranuclear uranyl chloride aquacomplex with macrocyclic cavitand cucurbituril $\{[(UO_2)_4O_2Cl_4(H_2O)_6](H_2O\subset C_{36}H_{36}N_{24}O_{12})\}\cdot 4H_2O$ (**1**).

Results and Discussion

Cucurbituril is a trivial name for the compound which has the chemical composition $C_{36}H_{36}N_{24}O_{12}$ and a barrel-shaped molecule (the point symmetry group is D_{6h}, the van der Waals diameter of the inner cavity is 5.5 Å).[11,12] The O atoms of strongly polarized carbonyl groups bound to the rims of the barrel can form hydrogen bonds with the water molecules entering into the composition of some transition metal aquacomplexes. Recently,[13—15] we successfully used this supramolecular strategy for the synthesis of adducts of cucurbituril and cluster chalcogenide aquacomplexes of molybdenum and tungsten $[M_3Q_4(H_2O)_9]^{4+}$ (M = Mo, W; Q = S, Se). Crystallization of indium aquacomplexes with cucurbituril allowed us not only to obtain new supramolecular adducts, but also to isolate solid aquacomplexes that were previously studied only in solutions and structurally characterize them.[16]

Compound **1** was obtained as large yellow crystals under conditions of hydrothermal synthesis starting from solutions of uranyl(VI) nitrate and cucurbituril. To enhance the solubility of cucurbituril, rubidium chloride was added to the reaction mixture.[17] Crystals suitable for X-ray study were obtained by recrystallization of complex **1** under conditions of hydrothermal synthesis.

According to the results of X-ray study of compound **1**, the U atoms of the four uranyl groups (the U—O distances span the range from 1.735(6) to 1.774(5) Å) lie in the same plane and are linked by two types of bridges, namely, two μ_3-bridging O atoms (the U(1)—O(1) and U(2)—O(1) distances are 2.263(3) and 2.212(5) Å, respectively) and four μ_2-bridging Cl atoms (the U(1)—Cl(1) and U(2)—Cl(1) distances are 2.8331(14) and 2.7996(15) Å, respectively) (Fig. 1). All the bridging atoms and the O atoms of the water molecules coordinated to the U atoms can be considered lying in the plane pass-

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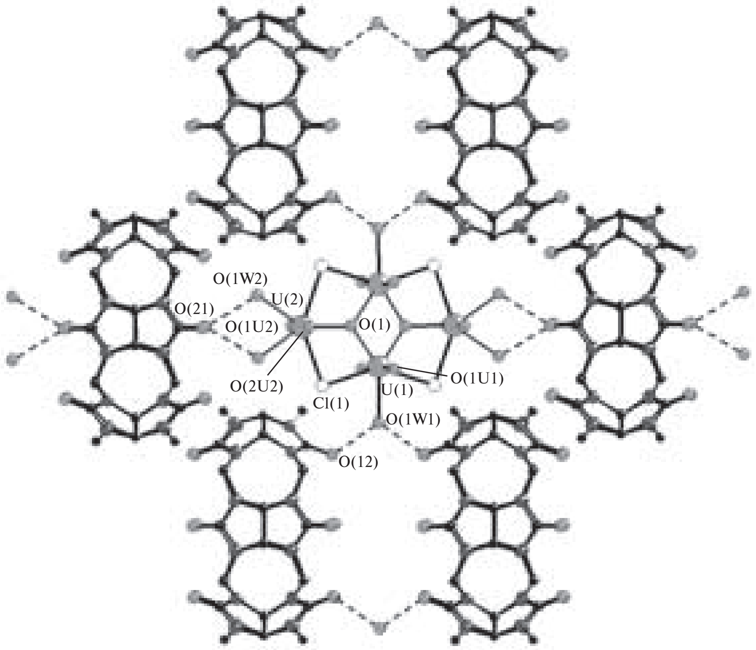

Fig. 1. Fragment of the crystal structure of **1**. Shown are the atomic numbering scheme for the uranyl complex and the hydrogen bonds with cucurbituril molecules (dashed lines).

ing through the U atoms (the mean deviation of the atoms from this plane is 0.143 Å). The principal geometric parameters of the tetranuclear uranyl chloride fragment are listed in Table 1. The coordination polyhedron of the uranium atom has a pentagonal bipyramid configuration, which is typical of uranium aquacomplexes.[18] The uranyl groups are characterized by slight distortion of linear geometry (the average value of the O—U—O angle is 174.6°). The vibrational bands at 924 and 897 cm^{-1} in the IR spectrum of complex **1** correspond[8,9] to the vibrations of uranyl group.

Mention may be made that tetranuclear anionic uranyl chloride aquacomplex $[(UO_2)_4O_2Cl_8(H_2O)_2]^{4-}$ (see Ref. 8); the complex with THF, $[(UO_2)_4O_2Cl_4(C_4H_8O)_2(H_2O)_4]$, comprised of individual molecules;[10] and tetranuclear aquacomplexes $[(UO_2)_4O_2Cl_2(OH)_2(H_2O)_6]\cdot 4H_2O$ [7] and $K_2[(UO_2)_4O_2Cl_4(OH)_2(H_2O)_6]$ [9] are structurally similar to complex **1**. However, the last two complexes have a lower symmetry due to the presence of different μ_2-bridging ligands (μ_2-OH and μ_2-Cl).

Hydrogen bonds between the water molecules coordinated to the U atoms and the O atoms of the carbonyl groups of cucurbituril molecule (see Fig. 1) (the O......O distances for O(1W1)......O(12) and O(1W2)......O(21) are 2.732(6) and 2.861(9) Å, respectively) are responsible for

Table 1. Principal bond lengths (*d*) and bond angles (ω) in the tetranuclear uranyl chloride fragment of compound **1**

Bond	*d*/Å	Angle	ω/deg
U(1)—U(1)#1	3.6686(5)	O(1U1)#2—U(1)—O(1U1)	174.4(3)
U(1)—O(1U1)	1.774(5)	O(1U1)—U(1)—O(1W1)	87.19(15)
U(1)—O(1W1)	2.464(6)	O(1W1)—U(1)—U(1)#1	180.0
U(1)—U(2)	3.9752(2)	U(2)—U(1)—U(2)#1	125.041(7)
U(1)—O(1)	2.263(3)	U(1)#1—U(2)—U(1)	54.959(7)
U(1)—Cl(1)	2.8331(14)	O(1U2)—U(2)—O(1W2)	86.7(3)
U(2)—O(1U2)	1.744(7)	O(1U2)—U(2)—O(2U2)	174.8(3)
U(2)—O(2U2)	1.735(6)	O(2U2)—U(2)—O(1W2)	89.1(2)
U(2)—O(1W2)	2.444(5)	O(1W2)#3—U(2)—O(1W2)	70.1(2)
U(2)—O(1)	2.212(5)	U(2)—Cl(1)—U(1)	89.78(4)
U(2)—Cl(1)	2.7996(15)		

Note. Equivalent atoms were generated by the following symmetry transformations: $-x, -y, -z + 2$ (#1); $-x, y, -z + 2$ (#2); and $x, -y, z$ (#3).

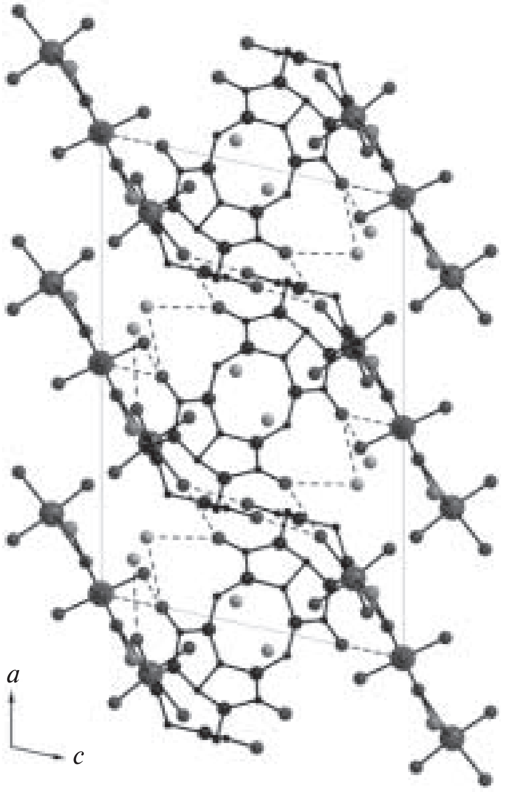

Fig. 2. Packing of supramolecular adducts in the crystal of compound **1** (view along the *b* axis; hydrogen bonds are shown as dashed lines).

the formation of the adduct of tetranuclear uranium aquacomplex with cucurbituril. The inner cavity of the cucurbituril molecule is filled with a guest water molecule disordered over four positions (O(1C)) and executing an intense thermal motion.

The packing of the supramolecular adducts in the crystal of **1** is shown in Fig. 2. The tetranuclear aquacomplexes and cucurbituril molecules form alternating layers stacked along the *c* axis and linked by a system of hydrogen bonds. The centers of the cucurbituril molecules and uranyl aquacomplexes occupy the crystallographic positions 2*d* (0, 1/2, 1/2) and 2*a* (0, 0, 0), respectively, with the $2/m$ (C_{2h}) point symmetry, thus forming two interpenetrating base-centered *C*-sublattices shifted by (0, 1/2, 1/2) with respect to each other. The space between the cucurbituril molecules and aquacomplexes is filled with the solvate water molecules disordered over two positions (O(1S1) and O(1S2)). A well-developed network of hydrogen bonds links all structural units into the supramolecular assembly.

Thus, we demonstrated the possibility of crystallization of polynuclear aquacomplexes using macrocyclic cavitand cucurbituril taking the mixed oxochloride complex of uranyl(VI) as an example.

Experimental

Starting compounds (uranyl nitrate, rubidium chloride of "extra pure" grade, and cucurbituril decahydrate (Merck)) were used as received. Elemental analysis was performed at the Novosibirsk Institute of Organic Chemistry of the Siberian Branch of the Russian Academy of Sciences. IR spectra were recorded on a Bruker IFS-85 Fourier spectrometer as KBr pellets.

Cucurbituril[hexaaquatetra(μ_2-chloro)di(μ_3-oxo)tetrauranyl]pentahydrate (1). Cucurbituril ($C_{36}H_{36}N_{24}O_{12}$, 15 mg, 0.013 mmol), uranyl nitrate (104 mg, 0.26 mmol), RbCl (104 mg, 0.86 mmol), and water (1 mL) were placed in a glass ampule. The sealed ampule was heated at 150 °C for 24 h and then slowly cooled down to ~20 °C. Yellow crystals obtained were filtered off and dried in air. The yield was 12 mg (32% with respect to cucurbituril). IR, ν/cm^{-1}: 3296 (s), 1750 (s), 1604 (m), 1476 (s), 1418 (s), 1374 (s), 1325 (s), 1295 (s), 1261 (s), 1240 (s), 1194 (s), 1149 (m), 966 (s), 924 (s), 897 (s), 819 (s), 803 (s), 761 (m), 678 (m), 634 (w), and 496 (w). Found (%): C, 17.62; H, 2.42; N, 13.39. $C_{36}H_{58}Cl_4N_{24}O_{33}U_4$. Calculated (%): C, 17.66; H, 2.39; N, 13.73.

X-ray study of a single crystal of **1** (the crystal dimensions were 0.36×0.033×0.20 mm) was carried out on a four-circle Nonius Kappa CCD automatic diffractometer equipped with an area detector at 291(2) K. The crystal system is monoclininc, the space group is $C2/m$ (No. 12), $a = 17.3302(3)$, $b = 17.6981(4)$, $c = 11.5526(3)$ Å, $\beta = 102.0789(9)°$, $V = 3464.87(13)$ Å^3, $M = 2446.97$, $d = 2.345$ g cm^{-3}, $\lambda\text{MoK}\alpha = 0.71073$ Å, $Z = 2$, and $\mu = 9.576$ mm^{-1}. Frame integration and processing of the data collected were carried out using the Denzo,[19] Scalepack,[19] and maXus[20] program packages. A total of 11205 reflections (7300 independent reflections) were measured in the angle range $2\theta \leq 69.90°$. All calculations were performed with the independent reflections obtained after averaging using the maXus program package. The structure was solved by direct method and refined by the full-matrix least squares method in the anisotropic approximation using the SHELX-97 program package;[21] the GOOF value was 1.078; the residual peak and hole electron density was 3.218 and −5.086 e/Å^3 (near the heavy atoms), respectively; $R_1 = 0.0460$ and $wR_2 = 0.1166$ for 6082 reflections with $F_0 > 4\sigma(F_0)$; and $R_1 = 0.0596$ and $wR_2 = 0.1279$ for all independent reflections used in the calculations. Hydrogen atoms of cucurbituril molecules were located geometrically. No H atoms were located for water molecules. The atomic coordinates were deposited in the Cambridge Structural Database and are available on request.

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