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Cobalt and Calcium Methacrylatouranylates: Synthesis and Structure

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Abstract—Two new uranyl complexes are synthesized: $[Co(H_2O)_6][UO_2(Mac)_3]_2\cdot 8H_2O$ (**I**) and $\{Ca(H_2O)_2[UO_2(Mac)_3]_2\}$ (**II**) (Mac is methacrylate ion $CH_2C(CH_3)COO^-$). The crystals of complexes **I** and **II** are studied by the X-ray diffraction method (CIF files CCDC nos. 2124087 (**I**) and 2124088 (**II**)) and IR spectroscopy. The uranyl-containing structural units of the crystals of compounds **I** and **II** are mononuclear complexes $[UO_2(Mac)_3]^-$ with the crystal chemical formula AB_3^{01} ($A = UO_2^{2+}$, B^{01} = Mac). In the crystals of complex **I**, the $[UO_2(Mac)_3]^-$ complexes coexist with octahedral aqua complexes $[Co(H_2O)_6]^{2+}$ and outer-sphere water molecules. In the crystals of complex **II**, each calcium ion binds two water molecules and two $[UO_2(Mac)_3]^-$ anions to form trinuclear electroneutral complexes $\{Ca(H_2O)_2(UO_2)_2(Mac)_6\}$ with the crystal chemical formula $A'M^1_2A_2B^{01}_2B^{11}_4$ ($A' = Ca^{2+}$, $A = UO_2^{2+}$, B^{01} and B^{11} = Mac, $M^1 = H_2O$). In compound **II**, the uranium-containing complexes are joined into a 3D framework through intermolecular contacts, which are characterized using the method of molecular Voronoi–Dirichlet polyhedra.

Keywords: uranyl complexes, methacrylate ions, crystal structure, Voronoi–Dirichlet polyhedra

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INTRODUCTION

About 20 methacrylate-containing uranyl compounds were characterized to the present time, and the data on their compositions and structures were obtained only in the recent years. In addition to uranyl methacrylate dihydrate $UO_2(Mac)_2\cdot 2H_2O$ [1], where Mac is the methacrylic acid anion $CH_2C(CH_3)COO^-$, only several adducts $UO_2(Mac)_2\cdot nL\cdot mH_2O$ (where L is carbamide or its derivatives) were studied [1, 2]. The crystal structures of methacrylatouranylates of some mono- (Li, Na, Rb, Cs, Tl [3]) and divalent (Mg, Zn, Sr, Ba, Pb [4–6]) metals were determined. In the compounds characterized, the ratio r_m = Mac : U is equal to 2, 3, or 4. The data available show that $r_m = 3$ is most frequently met at which hexagonal bipyramidal complexes $[UO_2(Mac)_3]^-$ with the crystal chemical formula (CCF) AB_3^{01} ($A = UO_2^{2+}$, B^{01} = Mac) are formed. The CCF parameters including coordination modes of the ligands were written according to [7]. In these complexes, the U(VI) atoms manifest a coordination number (CN) of 8 and each methacrylate ion acts as the bidentate chelating ligand B^{01}. At $r_m = 2$ methacrylate ions are usually coordinated via the B^{01} mode. However, the compositions and structures of the formed complexes depend on the nature of electroneutral coligands L that are present in the crystallized system. Centrosymmetric neutral complexes $[UO_2(Mac)_2(H_2O)_2]$ with CN(U) = 8 and CCF $AB_2^{01}M_2^1$ are formed in the simplest case (water is the coligand [1]). If amide molecules act as L in adduct formation, the structures of the formed complexes depend on the ratio r_L = L : U in the crystals. For instance, at $r_L = 1.5$ corresponding to the $(UO_2)_2(Mac)_4(L)_3$ composition, the substances disproportionate to the already considered anionic complex $[UO_2(Mac)_3]^-$ with CN(U) = 8 and cationic complex $[UO_2(Mac)(L)_3]^+$ with the CCF $AB^{01}M_3^1$ and CN(U) = 7. If $r_L = 1.0$, the adduct consists of dimers $[UO_2(Mac)_2(L)]_2$ with CN(U) = 7 and CCF $AB^2B^{01}M^1$ ($A = UO_2^{2+}$, B^2 and B^{01} = Mac, M^1 is tetramethylcarbamide [1]). As can be seen from the CCF, the Mac anions in this adduct exhibit different coordination modes: bidentate bridging B^2 and bidentate cyclic B^{01}. Another known example of compounds containing Mac ions with different crystal structural roles is $Pb[UO_2(Mac)_4]$ for which $r_m = 4$ and the CCF is $AB^{01}M_3^1$ [6].

The purpose of this work is to study the structures and some properties of the new methacrylate uranyl complexes: trimethacrylatouranylate hexaaquacobalt(II)octahydrate $[Co(H_2O)_6][UO_2(Mac)_3]_2\cdot 8H_2O$ (**I**) and trimethacrylatouranylate diaquacalcium

$\{Ca(H_2O)_2[UO_2(Mac)_3]_2\}$ (**II**) in which Ca and Co play the role of divalent cations.

EXPERIMENTAL

It is difficult to synthesize methacrylatouranylates because of a tendency of methacrylic acid to fast and irreversible polymerization that appears as a turbidity of an aqueous solution and is accompanied by the formation of a gel-like product and, therefore, the synthesis was carried out in black-colored vessels. Uranium(VI) oxide was obtained by the thermal (350°C) decomposition of uranyl nitrate hexahydrate.

Synthesis of crystals of complex I. A weighed sample of $CoCO_3$ (1.575 mmol, 0.1875 g) was dissolved in an aqueous solution of methacrylic acid (8.40 mmol, 0.723 g) on heating in a water bath to the complete termination of carbon dioxide release, and UO_3 (0.525 mmol, 0.150 g) was added to the resulting solution. The initial molar ratio of the reactants was $CoCO_3 : UO_3 : HMac = 3 : 1 : 16$. The isothermal evaporation of the obtained solution at room temperature for 4–5 days gave vinous prismatic crystals. The yield was 75%. Chemical analysis results: found, %: U, 34.3. For $Co(UO_2(CH_2C(CH_3)COO)_3)_2 \cdot 14H_2O$ anal. calcd., %: U, 34.97.

Synthesis of crystals of complex II. A weighed sample of $CaCO_3$ (1.05 mmol, 0.105 g) was added to an aqueous-alcohol solution of methacrylic acid (8.40 mmol, 0.723 g), and the mixture was heated to the complete termination of carbon dioxide release after which UO_3 (0.525 mmol, 0.150 g) was added. The obtained solution was subjected to isothermal evaporation at room temperature. The molar ratio of the starting reactants was $CaCO_3 : UO_3 : HMac = 2 : 1 : 16$. Yellow crystals were formed in approximately 5 days. The yield was about 60%. Chemical analysis results: found, %: U, 41.9. For $Ca(UO_2)_2(CH_2C(CH_3)COO)_6 \cdot 2H_2O$ anal. calcd., %: U, 42.27.

X-ray diffraction (XRD) was carried out on a Bruker KAPPA APEX II automated four-circle diffractometer with a 2D detector. Unit cell parameters were refined over the whole data set [8]. Absorption corrections were applied to the experimentally determined reflection intensities using the SADABS program [9]. The structures were solved by a direct method using SHELXS97 [10] and refined by full-matrix least squares using SHELXL-2014 [11] for F^2 for all data in the anisotropic approximation for all non-hydrogen atoms except for the O atoms of disordered water molecules in complex **I**. The H atoms of the methacrylate anions are localized in the geometrically calculated positions with $U_{iso} = 1.2U_{equiv}(C)$ for CH_2 groups and $U_{iso} = 1.5U_{equiv}(C)$ for CH_3 groups, and the orientation of the CH_3 groups in structure **II** was refined. In structure **I**, the positions of the CH_2 and CH_3 groups were disordered. The H atoms of the water molecules in structure **I** were not localized. The coordinates of the H atoms of the water molecules in structure **II** were found using the CALC_OH procedure [12] in the WinGX program package [13]. The coordinates of these atoms were fixed after one cycle of their refinement with $U_{iso} = 1.5U_{equiv}(O)$. The structure of complex **I** was refined as a pseudomerohedral twin with a contribution of the second domain of 0.4190(13). The Flack parameter x [14] (Table 1) shows the validity of absolute structure determination for complex **II**.

The experimental XRD parameters and final reliability factors for the crystals of complexes **I** and **II** are given in Table 1. The characteristics of selected bond lengths and bond angles of the UO_8 polyhedra and parameters of hydrogen bonds are listed in Tables 2 and 3, respectively. The coordination number of atoms in the structures were calculated using the method of intersecting spheres [15, 16].

The coordinates of atoms and temperature parameters were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 2124087 (**I**) and 2124088 (**II**); http://www.ccdc.cam.ac.uk/structures).

IR spectra were recorded on an FT-801 FTIR spectrometer at room temperature in a range of 500–4000 cm^{-1}. The samples were prepared by pressing KBr pellets. Absorption bands were assigned using published data [17–19].

IR of complex **I** (ν, cm^{-1}): 3418 br ν(H_2O); 2991 w, 2967 w, 2928 w ν(CH_3); 1644 m δ(H_2O), ν(C=C); 1503 vs ν_{as}(COO); 1461 vs, 1440 vs ν_s(COO); 1376 m δ(CH_3); 1238 m δ(CH); 1009 w ω(CH_2); 931 vs $\nu_{as}(UO_2)$; 867 s, 832 m ν(C–C); 620 s δ(OCO).

IR of complex **II** (ν, cm^{-1}): 3447 br ν(H_2O); 2928 w ν(CH_3); 1636 m δ(H_2O), ν(C=C); 1507 w ν_{as}(COO); 1458 m, 1438 m ν_s(COO); 1374 w δ(CH_3); 1238 w δ(CH); 930 m $\nu_{as}(UO_2)$; 866 w, 831 w ν(C–C); 620 s δ(OCO).

The results of IR spectroscopy for complexes **I** and **II** are consistent with the further presented XRD data. In both spectra, the most intense absorption bands correspond to vibrations of the uranyl ion and carboxylate groups.

RESULTS AND DISCUSSION

Structures **I** and **II** contain uranium atoms of one crystallographic sort. They occupy positions with the point symmetry C_1. The coordination polyhedron of U(VI) atoms in both structures is the hexagonal bipyramid UO_8, whose axial positions are occupied by the oxygen atoms of the nearly linear (OUO angle 179.26°–179.93°) and equal-shoulder uranyl groups, whereas the equatorial plane contains six oxygen atoms of three bidentate cyclic methacrylate ions (Fig. 1). The same $CCFAB_3^{01}$ ($A = UO_2^{2+}$, B^{01} = Mac)

Table 1. Crystallographic data and parameters of the XRD experiments for complexes **I** and **II**

Parameter	Value	
	I	**II**
Crystal system	Monoclinic	Orthorhombic
Space group, Z	$P2_1/n$, 2	$P2_12_12$, 2
a, Å	6.8455(2)	8.9635(3)
b, Å	24.0652(8)	23.8200(7)
c, Å	14.0593(6)	8.0466(2)
β, deg	90.078(2)	90
V, Å^3	2316.10(14)	1718.03(9)
ρ, g/cm^3	1.953	2.178
μ, mm^{-1}	7.417	9.636
T, K	100(2)	100(2)
Crystal sizes, mm	0.40 × 0.10 × 0.08	0.36 × 0.18 × 0.12
θ_{max}, deg	29.999	34.996
Range of h, k, l	$-9 \le h \le 9$, $-33 \le k \le 33$, $-19 \le l \le 19$	$-13 \le h \le 14$, $-38 \le k \le 38$, $-12 \le l \le 12$
Number of reflections measured/independent (N_1), (R_{int})	32498/6654 (0.0393)	46252/7533 (0.0392)
Number of reflections with $I > 1.96\sigma(I)$ (N_2)	5660	7153
Number of refined parameters	256	213
R_1 for N_2	0.0297	0.0170
wR_2 for N_1	0.0641	0.0344
S	1.082	1.002
Residual electron density (min/max), e/Å^3	−2.386/2.046	−1.392/1.013

corresponds to the uranium-containing complexes $[UO_2(Mac)_3]^-$ in structures **I** and **II**. The volume of the Voronoi–Dirichlet polyhedra (VDP) of the uranium atoms is 9.45 and 9.43 Å^3 for complexes **I** and **II**, respectively, which coincides (within inaccuracy) with an average value of 9.3(2) Å^3 found for the coordination polyhedron UO_n at n = 5–9 [20].

The studied structures of complexes **I** and **II** differ in the crystal structural role of divalent cations (Co in **I** and Ca in **II**) compensating the charge of the uranium-containing acido complexes. Complex **I** turned out to be isostructural with magnesium and zinc methacrylatouranylates described previously [3]. The Co atoms occupy the centrosymmetric positions, and the water molecules around them are disordered and form two orientations of an insignificantly distorted octahedral complex $[Co(H_2O)_6]^{2+}$. Therefore, the coordination formula for complex **I** can be written as $[Co(H_2O)_6][UO_2(Mac)_3]_2 \cdot 8H_2O$. The Co–O distances range from 2.066 to 2.122 Å. The revealed cationic $[Co(H_2O)_6]^{2+}$ and anionic $[UO_2(Mac)_3]^-$ complexes in structure **I** are bound to each other and to the outer-sphere water molecules arranged between them by a system of hydrogen bonds and a set of electrostatic interactions. The positions of the hydrogen atoms of the water molecules were not determined and all possible hydrogen bonds were not revealed because of an

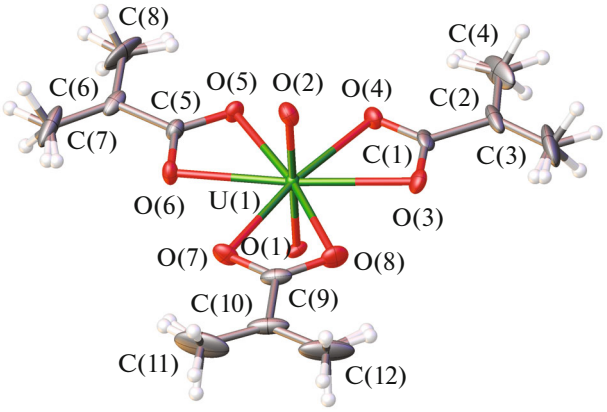

Fig. 1. Complex $[UO_2(Mac)_3]^-$ in the structure of crystals of compound **I**. Thermal shift ellipsoids are shown with 50% probability.

Table 2. Selected geometric parameters of the uranium(VI) polyhedron and hydrogen bond parameters in the structure of complex **I**

Bond	*d*, Å	Ω, % *	Angle	ω, deg
Hexagonal bipyramid UO_8				
U–O(1)	1.762(4)	21.95	O(1)UO(2)	179.94(17)
U–O(2)	1.770(4)	21.92	O(3)UO(4)	52.19(11)
U–O(3)	2.483(3)	9.26	O(4)UO(5)	68.37(10)
U–O(4)	2.465(3)	9.54	O(5)UO(6)	52.09(10)
U–O(5)	2.486(3)	9.27	O(6)UO(7)	67.68(10)
U–O(6)	2.470(3)	9.46	O(7)UO(8)	51.85(11)
U–O(7)	2.487(3)	9.22	O(8)UO(3)	67.81(11)
U–O(8)	2.476(3)	9.39		

Hydrogen bond parameters**

D–H...A	Distances, Å			Angle D–H...A, deg	Ω(D–H), %	Ω(H...A), %	Face rank
	D–H	H...A	D...A				
C(4)H(3)...O(12)	0.980	2.781	3.752	171.16	26.64	14.36	0
C(4)H(4)...O(6)	0.981	2.652	3.520	147.61	26.55	11.10	0
C(4)H(5)...O(6)	0.979	2.619	3.499	149.75	26.64	11.54	0
C(7)H(6)...O(14)	0.978	2.822	3.794	172.69	26.71	11.04	0
C(7)H(7)...O(4)	0.981	2.622	3.517	151.80	26.55	11.05	0
C(7)H(8)...O(4)	0.981	2.647	3.496	145.02	26.56	11.40	0
C(7)H(8)...O(2)	0.981	2.759	3.570	140.42	26.56	10.91	0
C(11)H(11)...O(14)	0.979	2.834	3.806	172.01	26.64	13.57	0
C(11)H(12)...O(8)	0.978	2.684	3.541	146.48	26.63	11.56	0
C(11)H(13)...O(8)	0.982	2.609	3.495	150.25	26.51	11.48	0
C(12)H(15)...O(13)	0.951	2.843	3.738	157.29	33.02	13.73	0

* Hereinafter, solid angle Ω (expressed in percent of 4π steradian) under which the common face of the VDP is seen from the core of any of them.
** Hereinafter, hydrogen bonds with H...A < 3 Å and angle D–H...A > 130 deg are presented.

insufficiently low quality of crystals of compound **I** and, hence, only selected hydrogen bonds are given in Table 2.

Unlike complex **I**, the study of the crystals of complex **II** made it possible to establish the coordinates of all atoms including H atoms. It is revealed that the Ca atoms localized on the C_2 axes exhibit CN = 6 similarly to the Co atoms in complex **I** and form distorted octahedra CaO_6 (Ca–O distances range from 2.324 to 2.349 Å). However, in these octahedra only two oxygen atoms (both O(9)) localized on one of the octahedron edges compose the water molecules. Other atoms (two pairs of O(6) and O(7)) are oxygen atoms of four different methacrylate ions in the composition of two adjacent complexes $[UO_2(Mac)_3]^-$. Therefore, trinuclear electroneutral complexes $\{Ca(H_2O)_2[UO_2(Mac)_3]_2\}$ with the CCF $A'M^1_2A_2B^{01}_2B^{11}_4$ ($A' = Ca^{2+}$, $A = UO_2^{2+}$, B^{01} and B^{11} = Mac, $M^1 = H_2O$) formed by one cationic and two anionic complexes $(Ca(H_2O)_2^{2+}$ and $UO_2(Mac)_3^-$, respectively; Fig. 2) can be considered to be the supramolecular structural unit of the crystals of compound **II**. The UCaU angle in these trimers, which are joined into chains propagated along [001] via hydrogen bonds, is ≈86°.

The absence of a random arrangement of any atoms in complex **II** makes it possible to characterize nonvalent interactions in this structure using the method of molecular Voronoi–Dirichlet polyhedra (MVDP). This method allows one to evaluate intermolecular contacts based on the MVDP characteristics calculated as the sum of parameters of the VDP atoms entered into one molecule [21–23]. From the viewpoint of the MVDP method, faces of the zero rank correspond to any intermolecular contacts. As known [21–23], the face rank (FR) determined by the calculation of the CN of atoms by the method of inter-

Table 3. Selected geometric parameters of the uranium(IV) polyhedron and hydrogen bond parameters in the structure of complex **II**

Bond	d, Å	Ω, %	Angle	ω, deg
Hexagonal bipyramid UO_8				
U–O(1)	1.767(2)	21.80	O(1)UO(2)	179.26(10)
U–O(2)	1.778(2)	21.82	O(3)UO(4)	53.24(7)
U–O(3)	2.450(2)	9.54	O(4)UO(5)	70.4 (7)
U–O(4)	2.427(2)	9.96	O(5)UO(6)	52.26(6)
U–O(5)	2.443(2)	9.97	O(6)UO(7)	64.12(6)
U–O(6)	2.535(2)	8.56	O(7)UO(8)	51.96(7)
U–O(7)	2.511(2)	8.86	O(8)UO(3)	68.19(7)
U–O(8)	2.467(2)	9.49		

Hydrogen bond parameters

D–H...A	Distances, Å			Angle D–H...A, deg	Ω(D–H), %	Ω(H...A), %	Face rank
	D–H	H...A	D...A				
O(9)–H(2)...O(3)	0.961	1.866	2.826	176.56	33.70	22.59	0
C(4)–H(6)...O(5)	0.950	2.731	3.585	150.02	32.67	11.18	0
C(7)–H(10)...O(4)	0.980	2.531	3.405	148.45	26.76	12.97	0
C(12)–H(17)...O(8)	0.980	2.571	3.345	135.88	26.80	14.12	0

Table 4. Characteristics of intermolecular interactions in the structure of complex **II** from the viewpoint of the MVDP method*

Contact A/Z	k_{AZ}	d, Å	S_{AZ}, Å^2	Δ_{AZ}, %
H/U	4	3.303	0.02	<0.01
O/O	8	2.873–4.273	0.69	0.09
C/O	36	3.280–4.349	3.57	0.49
H/O	168	1.866–4.843	310.22	42.32
C/C	40	3.390–4.286	19.82	2.70
H/C	100	2.925–4.138	46.72	6.37
H/H	204	2.425–5.375	351.96	48.02
Sum	560	1.866–5.375	733.00	100

* k_{AZ} is the total number of faces with FR = 0 of the MVDP $Ca[UO_2(Mac)_3]_2 \cdot 2H_2O$; d is the range of the corresponding interatomic distances A/Z; S_{AZ} is the total surface area of the faces of this type for the VDP of the atoms in one formula unit of the substance; Δ_{AZ} is the partial contribution (in percent) of the corresponding nonvalent contacts A/Z to the integral parameter ${}^0S = \Sigma S_{AZ}$ of the MVDP (indicated in the bottom row).

secting spheres indicates the minimum number of chemical bonds that link the atoms to the common VDP face. The crystals of compound **II** contains atoms of five chemical elements and, hence, 15 types of intermolecular contacts are theoretically possible. However, structure **II** really contains only seven types of intermolecular contacts with FR = 0 (Table 4). The $\{Ca(H_2O)_2[UO_2(Mac)_3]_2\}$ complexes are bound into a 3D framework mainly due to dispersion interactions H/H and hydrogen bonds H/O corresponding to the partial contributions $\Delta_{AZ} \approx 48$ and 42.3%, respectively (Table 4). Note that some data in Table 4 are given in more detail in Table 3. For example, the shortest intermolecular H/O contact in structure **II** with the H–O distance equal to 1.866 Å, which is indicated in the H/O row in Table 4, really corresponds to the O(9)–H(2)...O(3) interaction (4th row from the bottom in Table 3).

According to the data in Table 4, the crystals of compound **II** contain intermolecular C/C interactions for which the C–C distance varies from 3.39 to 4.29 Å. An additional analysis showed that the distances

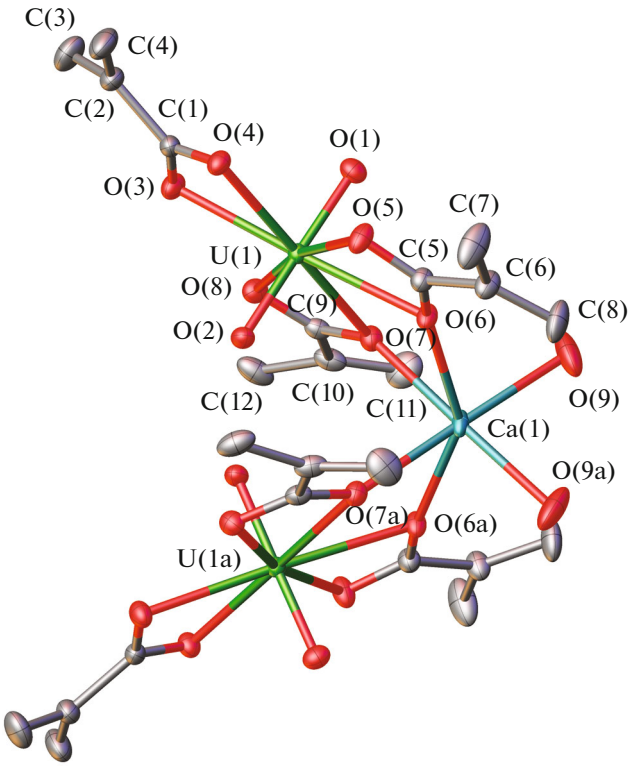

Fig. 2. Trinuclear complex $\{Ca(H_2O)_2[UO_2(Mac)_3]_2\}$ in the structure of compound **II**. Thermal shift ellipsoids are shown with 50% probability. Symmetry transform: (a) $1 - x, 1 - y, z$. Hydrogen atoms are omitted for simplicity.

between the centers of the nearest C=C bonds in the structure ranged from 3.84 to 3.95 Å and satisfied one of topochemical Schmidt's criteria [24] necessary for the solid phase [2+2] cycloaddition reaction to occur. However, the second necessary condition for photocyclodimerization, namely, the parallel arrangement of double bonds in the crystal lattice [24], does not obey. It is most likely that for this reason the obtained crystals of methacrylatouranylate **II** are stable on prolonged storage, including storage under solar irradiation.

To conclude, the data on structure **II** additionally confirm the opinion [25] about the dynamic equilibrium between the mono- and trinuclear complexes in the aqueous-salt systems containing carboxylate ions and uranyl cations. A set of interrelated interactions between heteronuclear complexes of different compositions and structures is observed in concentrated aqueous solutions in the presence of hydrated cations R^{2+} and complex anions $[UO_2(L)_3]^-$. In our opinion, the main steps of this equilibrium can schematically be described by Eq. (1):

$$\begin{aligned}[R(w)_n]^{2+} + A &\leftrightarrow \{R(w)_p[A]\}^+ \\ &\leftrightarrow \{R(w)_q[A]_2\} \leftrightarrow \{R(w)_r[A]_3\}^- \\ \leftrightarrow \{R(w)_s[A]_4\}^{2-} &\leftrightarrow \ldots \leftrightarrow \{R(w)_x[A]_y\}^z,\end{aligned} \quad (1)$$

where w is H_2O; A is $[UO_2(L)_3]^-$; $\{R(w)_x[A]_y\}^z$ is the complex with the charge z, which was formed in one of the steps (1, 2, 3, 4, ..., y); and n, p, q, r, s, and y are stoichiometric indices. According to the available data, the compositions and structures of the crystals formed upon the isothermal evaporation of the indicated solutions depend on the nature of both cations R^{2+} and carboxylate ions L^-. In particular, for ions R^{2+} and L = acetate, equilibrium (1) is usually shifted to the left and, hence, crystallization is observed most frequently for acetatouranylates in which only mononuclear complexes $[R(H_2O)_n]^{2+}$ and $[UO_2(L)_3]^-$ coexist in a ratio of 1 : 2. This is exemplified by acetatouranylates with R^{2+} = Be (n = 4) [26] and Mg, Co, Zn, and Ni (n = 6) [27, 28] or Ba (n = 0) [29]. At the same time, the trinuclear complexes $\{Sr(H_2O)_4[UO_2(L)_3]_2\}$ in a mixture (1 : 1) with the mononuclear $[Sr(H_2O)_6]^{2+}$ and $[UO_2(L)_3]^-$ complexes were observed in the crystals of strontium acetatouranylate [25]. Pentanuclear acetatouranylate ions $\{Sr[UO_2(L)_3]_4\}^{2-}$ [25] (analog of complex $\{R(w)_s[A]_4\}^{2-}$ in Eq. (1) at s = 0) were also revealed in a similar system in the presence of cesium ions. A similar situation is observed in the system containing strontium and uranyl *n*-butyratouranylates in which crystals of $\{Sr(H_2O)_4[UO_2(L)_3]_2\}\cdot 2H_2O$ containing the trinuclear complexes [25] are formed as well.

Complex $\{Ca(H_2O)_2[UO_2(Mac)_3]_2\}$ (**II**) characterized in this work is the first example of a trinuclear complex for L = Mac. Note that stoichiometrically identical $R[UO_2(Mac)_3]_2\cdot 13H_2O$ (monoclinic at R = Sr and triclinic at R = Ba) crystallize from aqueous-salt systems containing Sr^{2+} (or Ba^{2+}), UO_2^{2+}, and Mac ions [5]. These methacrylatouranylates contain four crystallographically different complexes $[UO_2(Mac)_3]^-$ each, and only one of them (containing U(4) atoms) is in the composition of the binuclear complexes $[R(H_2O)_6][UO_2(Mac)_3]\}^+$ (analog of complex $\{R(w)_p[A]\}^+$ in reaction (1) at p = 6). Taking into account the available results, it can be assumed that one of the factors favoring the shift of equilibrium (1) to the right is an increase in hydrophobicity of carboxylate ions L with an increase in the number of carbon atoms in the ions.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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