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ARTICLE

Structural diversity of uranyl acrylates

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A series of novel uranyl acrylate compounds with a general composition $UO_2(CH_2CHCOO)_2{\cdot}nH_2O$, where n = 0, 2, 2.22, or 3, was synthesized and characterized by powder and single crystal X-ray diffraction, and IR spectroscopy. A comprehensive crystal structure analysis was performed by classical methods along with the method of Voronoi-Dirichlet tessellation to reveal the reasons of an unusual structural diversity of uranyl acrylates. Topological relations in hydrated compounds with molecular $[UO_2(CH_2CHCOO)_2(H_2O)_2]$ complexes, which play a role of the main structural unit, were discussed. Single crystal X-ray diffraction performed at 150 and 250 K indicated a phase transition occurring in the structure of $UO_2(CH_2CHCOO)_2{\cdot}2H_2O$. High temperature powder X-ray diffraction evidences a transformation of a sample of $UO_2(CH_2CHCOO)_2{\cdot}2H_2O$ to the waterless compound in a temperature range of 323–373 K.

Introduction

The uranyl cation UO_2^{2+} is the main form of the hexavalent uranium in both natural and technological processes.[1] Being almost linear in crystal structures, uranyl cations have a strong tendency to complexation, especially, with O-donor ligands and exhibit rich and diverse coordination chemistry.[2–12] As well, uranyl cations cause luminescent properties of its compounds[13,14] and can initiate photochemical polymerization.[15–19] Particularly, uranyl salts serve for photosensitization in polymerization reactions of vinyl-containing monomers, such as methacrylic acid[17], acrylonitrile[18], methylmethacrylate[18,19], etc.

The interest to uranyl monocarboxylate complexes, both aliphatic and aromatic, has been rising last decade due to their use as models to mimic interaction of the uranyl cation with carboxylate groups of humic acids, which play important role in migration of actinides in natural systems.[20–24] To date, crystal structures of many uranyl salts of saturated monocarboxylic acids have been reported.[11,25–31] Among them are uranyl formate, acetate, propionate, *i*- and *n*-butyrates, and *n*-valerate. Recent report on these salts showed, that their crystal structure strongly depends on the length of the carboxylic chain. Crystal structures of uranyl formates $[UO_2(HCOO)_2(H_2O)]$[25] and $[UO_2(HCOO)_2(H_2O)]{\cdot}xH_2O$[26] are based upon 3D framework or nanotubules and contain bidentate bridging formate-anions. The structure of uranyl acetate dihydrate significantly differs from the formate ones and is based on $[UO_2(CH_3COO)_2(H_2O)]$ chains.[27] The acetate anions in this structure play role of either bidentate bridging or chelating ligand. Further increase of the chain length leads to a significant change of structures. The uranyl propionate, *i*- and *n*-butirates, and *n*-valeratedihydrate salts[28–31] have common main structural units. These are molecular $[UO_2L_2(H_2O)_2]$ complexes, which contain two bidentate chelating carboxylate anions and two terminal water molecules located in *trans*-positions. Each complex contains four acceptors and four donors of hydrogen bonds (H-bonds) and forms eight H-bonds with the neighboring complexes. The difference between structures of these salts is that in the *n*-butyrate salt the H-bonds bind the complexes into a 3D framework, while in the rest three salts the complexes are bound into layers.[31]

Though structures of uranyl salts of saturated carboxylic acids are well studied, crystal structures of their unsaturated analogs are far less investigated. The first representative of this family, uranyl crotonate dihydrate, was X-rayed in 1982,[32] and since that time there were no data reported until 2015, when the crystal structure of uranyl methacrylate dihydrate was published.[33] Both crystal structures are similar to those of the propionate, *i*-butyrate, and *n*-valerate analogs and consist of $[UO_2L_2(H_2O)_2]$ complexes connected into layers by H-bonds. Despite this, crystal structure of the simplest unsaturated uranyl carboxylate, uranyl acrylate, is still not studied. In this article we report synthesis and crystal structure analysis of a group of compounds with general formula $UO_2(CH_2CHCOO)_2{\cdot}nH_2O$.

Experimental

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[g] *Electronic Supplementary Information (ESI) available: SC X-ray diffraction frames illustrating the phase transition and table of selected bonds and angles. CCDC 1429293-1429297 contain crystallographic data for this paper. See DOI: 10.1039/x0xx00000x*

Materials and methods

Caution! ^{238}U is an alpha-emitting radionuclide and standard precautions for handing radioactive materials should be followed when working with the quantities used in the syntheses that follow.

Analytical reagent grade chemicals were used without further purification. UO_3 was obtained by decomposition of uranyl nitrate, $UO_2(NO_3)_2{\cdot}6H_2O$, in air at temperature of 350°C for 24 hours. As acrylate ions tend to polymerize in the presence of both uranyl cations and UV radiation the following preparations should be carried out in absence of daylight.

Synthetic procedures

$[UO_2(CH_2CHCOO)_2]$ (**1**) was crystallized by slow evaporation of a solution obtained by dissolving UO_3 in excess of acrylic acid and minimum amount of water. 0.100 g of UO_3 (0.35 mmol) was dissolved in a mixture of water (0.2 mL) and acrylic acid (2.28 g, 33.5 mmol). Due to presence of a precipitate the resultant solution was filtered and then let to evaporate at room temperature. After few days yellow block crystals have precipitated and filtered with a glass filter.

$[UO_2(CH_2CHCOO)_2(H_2O)_2]{\cdot}0.22H_2O$ (**2**). UO_3 (0.1 g, 0.35 mmol) was dissolved in a solution of acrylic acid (0.40 g, 5.6 mmol) in water (5 mL) in presence of nickel nitrate $Ni(NO_3)_2{\cdot}6H_2O$ (0.102 g, 0.35 mmol). The ratio of the initial reagents was 1:16:1, respectively. The solution was then let to evaporate at room temperature until yellow block crystals were obtained along with a green viscous mass. Due to presence of the viscous mass, which likely is polymerization products, the crystals were picked directly from the solution.

$[UO_2(CH_2CHCOO)_2(H_2O)_2]{\cdot}H_2O$ (**3**) and **$[UO_2(CH_2CHCOO)_2(H_2O)_2]$** (**4**). Uranyl acrylates **3** and **4** were obtained by slow evaporation of a solution prepared by pouring of acrylic acid (1.14 g, 16.8mmol) into a water suspension of UO_3 (0.300 g, 1.05 mmol of UO_3 in 15 ml of water). After few days rhombic yellow plate crystals precipitated, which were filtered from the mother liquor with a glass filter. Single crystal X-ray diffraction revealed presence of two phases, $[UO_2(CH_2CHCOO)_2(H_2O)_2]{\cdot}H_2O$ and $[UO_2(CH_2CHCOO)_2(H_2O)_2]$, in the obtained mixture. Since both compounds have similar crystal morphology, the phases cannot be separated manually.

IR (KBr, cm^{-1}): 3425 v.s. [$\nu(H_2O)$]; 1639 m. [ν(C=C)]; 1519 v.s. [ν_{as}(COO)]; 1457 v.s. [ν_s(COO)]; 1373 m. [$\delta(CH_2)$]; 1277 m. [δ(C-H)]; 1068 w. [$\delta(CH_2)$]; 982 m. [δ(C-H)]; 935 v.s. [$\nu_{as}(UO_2)$]; 830 w. [ν(C-C)]; 683 s. [δ(COO)].

Crystallography

Single crystal X-ray diffraction data were collected at 100 K on Agilent Technologies Super Nova (**1**–**3**) or Bruker KAPPA APEX II DUO (**4**) diffractometers using MoKα radiation (λ = 0.71073 Å). Single crystals were mounted on glass fibers with epoxy glue for structure determination. Empirical (**1**, **3**, **4**) or analytical (**2**) absorption corrections based on crystal faces were applied with CrysAlis^{Pro} (**1**–**3**) or SADABS (**4**) software. The structures were solved by direct methods using SHELXS-97 and then anisotropically refined by full-matrix least-squares refinement on F^2 with SHELX software and OLEX2 software package.[34,35] Positions of the hydrogen atoms of acrylate groups were calculated geometrically and refined in riding model with $U_{iso}(H) = 1.2U_{eq}(C_i)$, where $U_{eq}(C_i)$ are equivalent thermal parameters of carbon atoms. The hydrogen atoms of water molecules in **2**–**4** were located from difference Fourier synthesis and refined with the O–H bond lengths restrained to 0.95 Å ~~(**2** and **3**) or 0.85 Å~~.

We calculated diffraction pattern of **4** using SC X-ray diffraction pattern and revealed that it does not match with the experimental pattern. Due to this we have carried out an additional diffraction data collection of the same crystal of **4** at the temperature of 250 K and this allowed us to determine a high temperature (HT) modification (**4b**) of this compound.

Table 1. Crystallographic data for uranyl acrylates

Chemical formula	$UO_2(CH_2CHCOO)_2$	$UO_2(CH_2CHCOO)_2·2.22H_2O$	$UO_2(CH_2CHCOO)_2·3H_2O$	$UO_2(CH_2CHCOO)_2·2H_2O$ (**4**)	
	(**1**)	(**2**)	(**3**)	**4a**	**4b**
formula weight	412.14	452.17	466.19	448.17	448.17
crystal system	Orthorhombic	Trigonal	Monoclinic	Monoclinic	Monoclinic
sp. gr., *Z*	Pnnm	R $\bar{3}$	$P2_1/c$	$P2_1/n$	C2/m
a, Å	13.3140(11)	19.5621(8)	11.6745(18)	10.7059(10)	10.724(6)
b, Å	9.7055(8)		12.4709(4)	7.7322(7)	7.721(4)
c, Å	7.0691(9)	8.7321(9)	16.003(2)	13.5945(12)	6.897(4)
β, deg			148.27(4)	107.093(2)	107.246(9)
V, $Å^3$	913.47(15)	2893.9(3)	1225.4(3)	1075.65(17)	545.3(5)
ρ_{calcd}, g/cm^3	2.997	2.335	2.527	2.767	2.729
μ, $мм^{-1}$	17.764	12.640	13.275	15.111	14.903
T, K	300(2)	295(2)	298(2)	150(2)	250(2)
Crystal dim., mm^3	0.12 × 0.06 × 0.04	0.28 ×0.18 ×0.14	0.19 ×0.08 ×0.02	0.26×0.19×0.03	0.26×0.19×0.03
reflections/unique	3030/894	2991/1369	5953/2193	13552/1086	3533/852
goodness of fit	1.047	1.065	1.055	0.997	1.072
R_1 (I>2σ(I))	0.032	0.042	0.035	0.023	0.022
wR_2 (all data)	0.079	0.100	0.077	0.086	0.050

For comparison's sake, crystal structure of the low temperature (LT) modification (**4a**) was resolved in $P2_1/n$ space group. Relevant crystallographic data and details of the experimental conditions for all crystals are summarized in Table 1 and selected bonds are listed in Table S1.

Powder X-ray diffraction

Room temperature powder diffraction of the mixture of **3** and **4** was carried out using Bruker D8 Advance diffractometer and the resulting pattern was analyzed with TOPAS software [36]. It was shown, that **3** and **4** are present in the mixture in a ratio of 0.25:0.75.

High temperature powder diffraction measurements of **4** in a temperature range of 298–623 K was performed using a Shimadzu XRD-600 diffractometer (Cu Kα radiation, θ-2θ geometry) equipped with a Sample Heating Attachment HA-1001. Scan increment and measuring range for each temperature step equal 0.02 and 10–50°, respectively.

Infrared spectroscopy

Infrared spectrum of a mixture of **3** and **4** was recorded as KBr pellet on a Perkin Elmer Spectrum 100 FT-IR spectrometer in the range 400-4000 cm^{-1}. Absorption bands were assigned using literature.[37]

Results and discussion

Synthesis and thermal behaviour

Four new uranyl acrylate compounds with general formula $UO_2(CH_2CHCOO)_2·nH_2O$ were obtained by slow evaporation of their solutions at room temperature. The water content and structure of the resulting compound depend mainly on acrylic acid and water proportion in the reaction mixtures. A waterless modification with formula $UO_2(CH_2CHCOO)_2$ is formed in a strong excess of acrylic acid. The hydrates, $UO_2(CH_2CHCOO)_2·2H_2O$ and $UO_2(CH_2CHCOO)_2·3H_2O$, can be obtained from a sole reaction mixture containing an excess of water with molar ratio of acrylic acid and water equal to 1:50, respectively. The fourth obtained compound, $UO_2(CH_2CHCOO)_2·2.22H_2O$, has been synthesized during an attempt of synthesis of Ni-containing uranyl acrylate. The reaction mixture contained acrylic acid and water in a 1:50 molar ratio, respectively, along with nickel nitrate. All attempts to obtain this compound without nickel nitrate failed as well as attempts to obtain pure phase of this compound. Analyzing these experiments, it seems that nickel nitrate plays an important role in the single crystal formation of $UO_2(CH_2CHCOO)_2·2.22H_2O$. Therefore, the water content in a resulting compound depends on the acrylic acid and water ratio. The high ratio increases likelihood of the waterless compound obtaining, while decrease of the ratio leads to various hydrated uranyl acrylates formation.

A high temperature powder diffraction experiment showed that crystals of $UO_2(CH_2CHCOO)_2·2H_2O$ loose water at the temperature range of 323–373 K and turn into $UO_2(CH_2CHCOO)_2$ (Fig. 1). It is likely that the other two hydrates, $UO_2(CH_2CHCOO)_2·2.22H_2O$ and $UO_2(CH_2CHCOO)_2·3H_2O$, would behave similarly, though these compounds were not studied by high temperature powder diffraction due to lack of their pure phase samples. Further heating up to 623 K decomposes the sample.

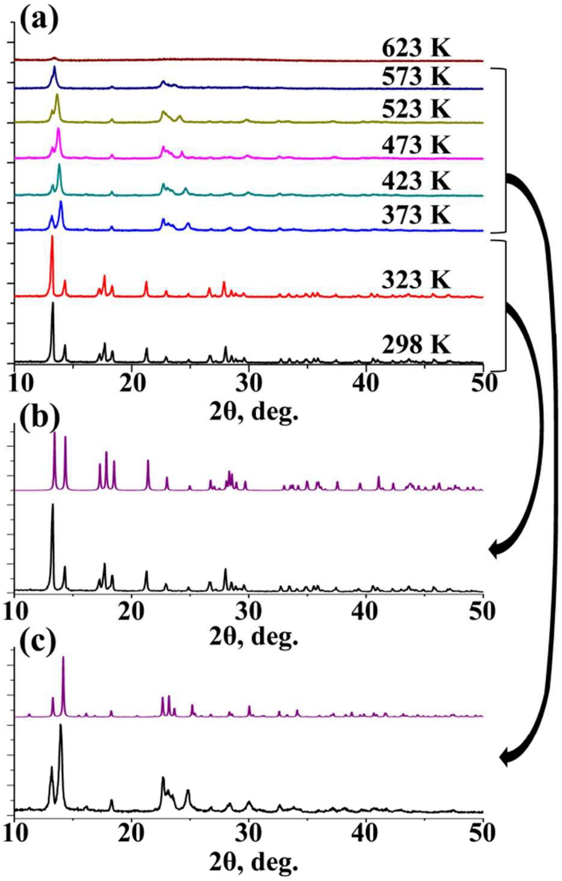


Figure 1. (a) High-temperature X-ray diffraction patterns of $[UO_2(CH_2CHCOO)_2(H_2O)_2]$ (**4**). (b) Only $[UO_2(CH_2CHCOO)_2(H_2O)_2]$ exists at the temperature range of 298–323 K. (c) Heating up to 373 K leads to dehydration of the sample and formation of $[UO_2(CH_2CHCOO)_2]$. Decomposition of the latter compound occurs at the temperature range of 573–623 K, the product of decomposition is amorphous. In (b) and (c), calculated and experimental patterns are shown in purple and black, respectively.

Structure description

$[UO_2(CH_2CHCOO)_2]$(**1**) crystallizes in Pnnm space group and consists of uranyl acrylate chains (Fig. 2) extending along the **b** axis. There is a single crystallographic sort of uranium atoms, which forms UO_2O_5 coordination polyhedra in the shape of pentagonal bipyramid. Both U=O bonds are equal to 1.755(7) Å and the equatorial U–O bonds are in a range of 2.302(8)–2.602(8) Å. There are two types of acrylate anions in **1** with B^2 and B^{11} coordination types. Coordination types are given according to a designation described in refs.[38,39] and show an amount of donor atoms in a ligand with the uppercase letter (M – mono-, B – bi-, T – tridentate, etc.). The superscript numbers show an amount of metal atoms connected through one, two, three, etc. donor atoms with the given ligand, respectively. In the case of **1**, there are two sorts of acrylate anions. One of them is a bidentate bridging B^2 ligand, while another is coordinated through a single donor atom to the first uranium atom (the first superscript number in the B^{11} symbol) and chelating the second one with two donor atoms (Fig. 2). The $[UO_2(CH_2CHCOO)_2]$ chains are packed in a way shown on Fig. 2. The acrylate anions of one chain lie on a mirror plane perpendicular to the **c** axis. Thus, a distance between the acrylate groups of neighboring chains is a half of the **c** axis and is equal to 3.53 Å.

$[UO_2(CH_2CHCOO)_2(H_2O)_2]\cdot 0.22H_2O$ (**2**), **$[UO_2(CH_2CHCOO)_2(H_2O)_2]\cdot H_2O$** (**3**), and LT (low-temperature) and HT (high-temperature) modifications of **$[UO_2(CH_2CHCOO)_2(H_2O)_2]$** (**4a** and **4b**, respectively). In **2**–**4**, the main structural unit is an electroneutral molecular

Table 2. Hydrogen bond parameters in the structures of uranyl acrylates

O-H···O	d(O-H), Å	d(H···O) , Å	d(D···O) , Å	ω(D-H-A), °	Symmetry operator
		$[UO_2(CH_2CHCOO)_2(H_2O)_2]\cdot 0.22H_2O$ (**2**)			
O(4)-H(1)···O(3)	0.949(9)	1.750(10)	2.689(5)	169.6(15)	-y+5/3, x-y+4/3, z+1/3
O(4)-H(2)···O(2)	0.950(10)	1.896(16)	2.773(5)	152(3)	x-y+4/3, x+2/3, -z-1/3
		$[UO_2(CH_2CHCOO)_2(H_2O)_2]\cdot H_2O$ (**3**)			
O(5)-H(4)···O(3)	0.94(2)	1.78(3)	2.689(7)	162(7)	x-1, -y+1/2, z-1/2
O(5)-H(3)···O(9)	0.95(2)	1.86(4)	2.719(8)	149(7)	-x, y-1/2, -z+1/2
O(8)-H(5)···O(6)	0.92(2)	1.90(3)	2.754(8)	153(5)	x+1, -y+1/2, z+1/2
O(8)-H(6)···O(9)	0.93(2)	1.94(4)	2.829(8)	159(8)	x,y,z
O(9)-H(1)···O(4)	0.93(2)	2.01(5)	2.784(7)	140(7)	x, -y+1/2, z-1/2
O(9)-H(2)···O(7)	0.94(2)	2.00(6)	2.802(8)	142(8)	x,y,z
		$[UO_2(CH_2CHCOO)_2(H_2O)_2]$ (**4a**)			
O(5)-H(5A)···O(4)	0.95	1.91	2.86(2)	172	-x-1/2,y+1/2,-z+1/2
O(5)-H(5B)···O(6)	0.95	1.85	2.80(2)	172	-x-1/2,y-1/2,-z+1/2
O(8)-H(8A)···O(3)	0.95	1.86	2.81(2)	173	-x+1/2,y+1/2,-z+1/2
O(8)-H(8B)···O(7)	0.95	1.87	2.82(2)	174	-x+1/2,y-1/2,-z+1/2

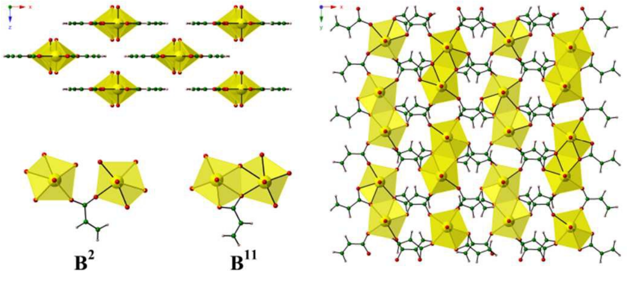
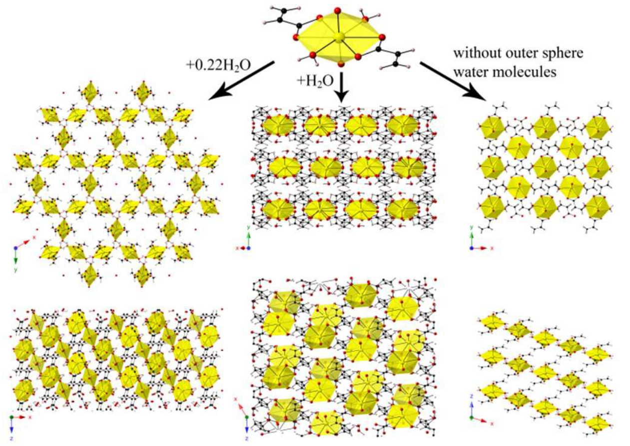


Figure 2. Packing mode and coordination types of acrylate anions in the structure of $[UO_2(CH_2CHCOO)_2]$ (**1**). Uranium, oxygen, carbon, and hydrogen are shown in yellow, red, green, and light orange, respectively.

$[UO_2(CH_2CHCOO)_2(H_2O)_2]$ complex (Fig. 3) with $AB^{01}{}_2M^1{}_2$ crystallochemical formula,[33] which is widespread among neutral uranyl monocarboxylates.[28–30,32,33] Uranyl groups are hexa-coordinated by O atoms, four of which belong to two acrylate anions and two are from water molecules. The U=O and U–O bond lengths in the complexes are in ranges of 1.750(5)–1.777(12) and 2.447(6)–2.549(16) Å, respectively. In the complexes, acrylate anions and water molecules are bidentate chelating and terminal ligands with B^{01} and M^1 coordination types, respectively. As in the previously reported $[UO_2L_2(H_2O)_2]$ complexes, L = crotonate or methacrylate, water molecules are located in *trans*-positions to each other. The acrylate anions in the structures of **2**–**4** are almost planar. In **3**, one of two crystallographic sorts of acrylate anions is disordered over two positions.

In **2**–**4**, each H and O atom, excepting uranyl O atoms, which are known for their inactivity, participate in hydrogen bonding (parameters are listed in Table 2). The complexes connected to each other and outer sphere water molecules by H-bonds to form 3D frameworks in **2** and **3** or layers in **4** (Fig. 3). In the structure of **2**, $[UO_2(CH_2CHCOO)_2(H_2O)_2]$ complexes stacked to form hexagonal channels extending along the **c** axis. Outer sphere water molecules occupy the channels and are disordered along them. Due to this water molecules cannot be located unambiguously by single crystal X-ray diffraction and the water amount in **2** is only approximately equal to 0.22 per $[UO_2(CH_2CHCOO)_2(H_2O)_2]$ unit. It is noteworthy, that “inner walls” of the channels are formed by H atoms of acrylate anions or O atoms of uranyl groups. Both these groups of atoms rarely participate in H-bonding or, at least, responsible only for weak intermolecular interactions. This fact could be one of the reasons of outer sphere water molecules disorder.



$[UO_2(CH_2CHCOO)_2(H_2O)_2]\cdot 0.22H_2O$ $[UO_2(CH_2CHCOO)_2(H_2O)_2]\cdot H_2O$ $[UO_2(CH_2CHCOO)_2(H_2O)_2]$

Figure 3. A view on $[UO_2(CH_2CHCOO)_2(H_2O)_2]$ complex (up) and views on crystal structure of $[UO_2(CH_2CHCOO)_2(H_2O)_2]\cdot 0.22H_2O$ (**2**, left), $[UO_2(CH_2CHCOO)_2(H_2O)_2]\cdot H_2O$ (**3**, middle) and low temperature modification of $[UO_2(CH_2CHCOO)_2(H_2O)_2]$ (**4a**, right). Uranium, oxygen, carbon, and hydrogen are shown in yellow, red, black, and light orange, respectively.

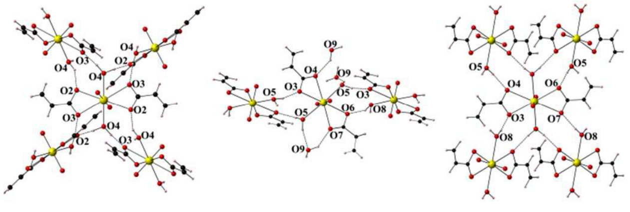


Figure 4. Hydrogen bonds formed by a $[UO_2(CH_2CHCOO)_2(H_2O)_2]$ complex in the structures of **2** (left), **3**(middle), and **4a** (right). The coloring scheme is the same as in Fig. 2.

Relationship between structures of 2, 3, and 4a

In the structures of **2** and **4**, each $[UO_2(CH_2CHCOO)_2(H_2O)_2]$ complex forms H-bonds with four neighboring complexes (Fig. 4). It is noteworthy, that U atoms of the central and the neighboring complexes lie exactly in the same plane. Taking into account the fact that outer sphere water molecules do not participate in strong or moderate H-bonding, a question arises: how structural units with the same environment can form two different structures, one of which is three-periodic (3D) and the other is two-periodic (2D)? To answer this question we have simplified the structures keeping the connectivity of the complexes (Fig. 5a,b) to obtain four-connected square nodes of H-bonded nets. Based on the square nodes only one 3D regular net with NbO topology (**nbo** in terms of RSCR[40] notation) and one 2D regular net, square planar net (**sql**), can be constructed. Taking into account that the **sql** is also the leader among 2D H-bonded networks,[41] it is not surprising that **2** and **4a** realize **nbo** and **sql** H-bonded motifs, respectively. The 2D structure is obtained provided that the H-bonded $[UO_2(CH_2CHCOO)_2(H_2O)_2]$ units are coplanar (Fig. 5d), as in the case of **4a**. To expand the dimensionality of the resulting structure, the structural units should be rotated around a pair of the parallel bonds making other two bonds inclined to the plane of the neighboring unit (Fig. 5e). The rotational angle between a pair of the neighboring units is equal to 76.9° in the structure of **2**. Therefore, different dimensionality of **2** and **4a**, which are built of the same structural units, is due to the rotation of the building units and these compounds are the topological isomers.

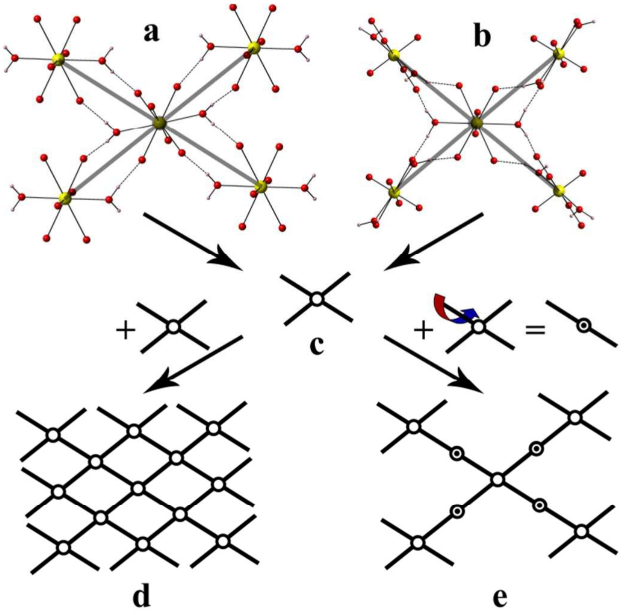


Figure 5. A view of $[UO_2(CH_2CHCOO)_2(H_2O)_2]$ complexes in **4a** (a) and **2** (b) with C and H atoms of the carboxylate chains being omitted, and their schematic building block (c). Interaction of the building blocks without rotation (d) and with rotation (e) results in a 2D or 3D framework, respectively. Hydrogen bonds are shown as dotted lines. The coloring scheme is the same as in Fig. 2.

It is noteworthy, that uranyl crotonate, propionate, *i*-butyrate, and *n*-valerate also adopt the **sql** structural type observed in **4a**, while uranyl *n*-butyrate is a 3D **nbo** framework analogous to **2**.[31] Symmetry of monoclinic uranyl *n*-butyrate crystals is lower than the symmetry of trigonal uranyl acrylate. Despite this, structures of these compounds are very similar, though hexagonal channels in the structure of the *n*-butyrate compounds are occupied by carboxylate chains and contain no outer sphere water molecules. Size of the channels in **2** is equal to ~11.3 Å and is higher than that in the uranyl n-butyrate structure (~10.9 Å), though the alkyl chain in the *n*-butyrate anion is significantly longer than in the acrylate analogue. This contradiction is caused by the presence of the water molecules in the channels of **2**.

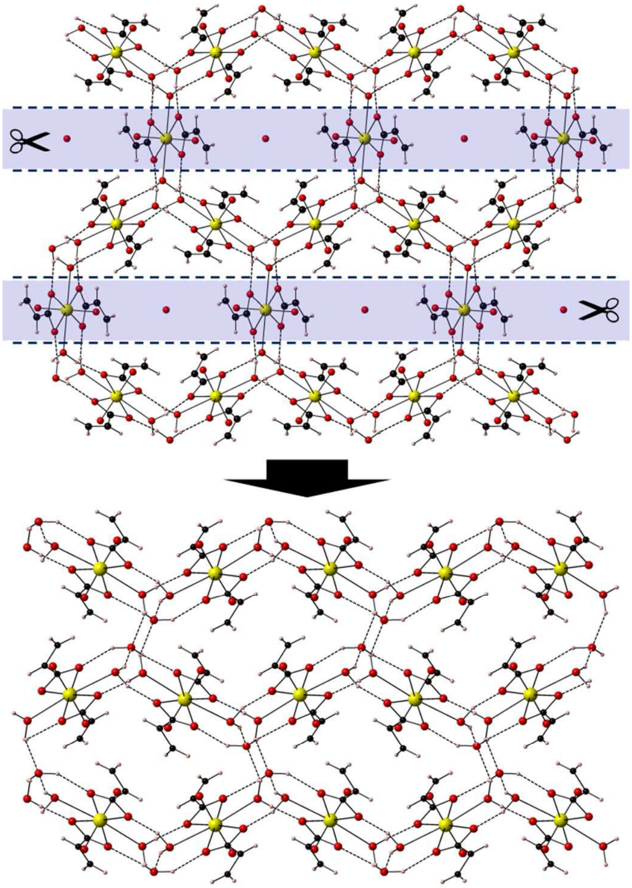


Figure 6. A relation between the structures of **2** (up) and **3** (down). The highlighted area containing outer sphere water molecules and $UO_2(CH_2CHCOO)_2$ fragments is to be removed from the structure of **2** to obtain the structure of **3**. The coloring scheme is the same as on Fig. 2.

In the structure of **3**, each $[UO_2(CH_2CHCOO)_2(H_2O)_2]$ complex forms hydrogen bonds with two neighboring complexes and three outer sphere water molecules (Fig. 4). Thus, each outer sphere water molecule interacts with three complexes. Participation of the outer sphere water molecules in the complexes connectivity changes the H-bonded structure significantly, and its becomes a binodal 3,5-c net. Nevertheless, a view on the structure simplified with the procedure described above allows one to see the relations between **3** and **2** (Fig. 6). Along with the structure of **2**, the simplified structure of **3** contains channels occupied by carboxylate chains. Due to small size of the acrylate anions chain and the absence of outer sphere water molecules in the channels, the latter are four-membered instead of six-membered as in the cases of uranyl *n*-butyrate and **2**. Therefore, the structure of **3** can be “tailored” from the structure of **4** by removal of some $UO_2(CH_2CHCOO)_2$ fragments as it shown on Fig. 6 to decrease the channels size. The removal of one third of the $UO_2(CH_2CHCOO)_2$ fragments leaves additional outer sphere water molecule per $[UO_2(CH_2CHCOO)_2(H_2O)_2]$ complex serving as a linker, resulting in $[UO_2(CH_2CHCOO)_2(H_2O)_2]\cdot H_2O$ formula of **3**.

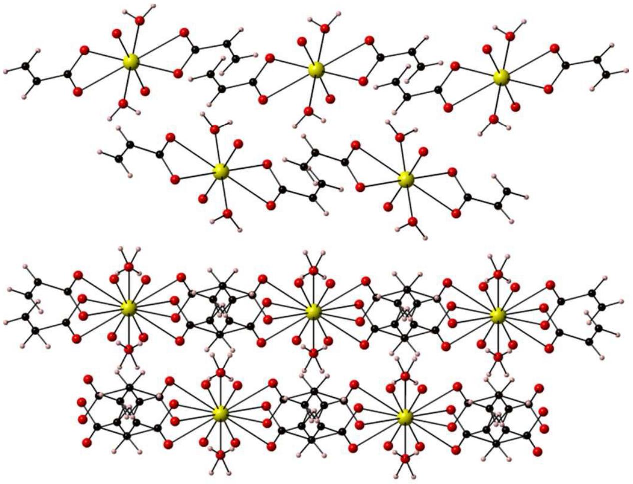


Figure 7. A view on ordered low- (up) and disordered high-temperature (down) modifications of **4**, **4a** and **4b**, respectively. The disordered structure of **4b** is a superposition of both orientations of complexes present in the ordered structure of **4a** (up) with a 50 to 50 probability. The coloring scheme is the same as on Fig. 2.

Temperature-induced phase transition in 4

$[UO_2(CH_2CHCOO)_2(H_2O)_2]$ (**4**) undergoes a temperature-induced phase transition during cooling from 250 to 150 K (see Fig. S1). The phase transition leads to a decrease of the symmetry from C2/m to $P2_1/n$ along with a slight alteration of the β angle from 107.246(9) to 107.093(2)° and doubling of the c unit cell parameter and its volume. In crystal structure of the low temperature modification **4a** there are two crystallographically independent $[UO_2(CH_2CHCOO)_2(H_2O)_2]$ complexes with different orientations in respect to (001) crystallographic plane, while crystal structure of the high-temperature modification **4b** is disordered and contains superposition of both orientations (Fig. 7). The disorder does not affect the closest intralayer U–U distances, which vary by 0.006 Å, but decrease interlayer distance by 0.1 Å. Along with the variation of interlayer distance, geometric parameters of the complexes change during the phase transition. This can be illustrated by values of O(w)UO(a) angles, where O(w) and O(a) are the closest O atoms of a water molecule and an acrylate anion in a given $[UO_2(CH_2CHCOO)_2(H_2O)_2]$ complex, respectively. In **4a**, the angles lie in a narrow range between 64.1 and 64.3°, while in the disordered **4b** the angles are equal to 57.8 and 70.7°.

Intermolecular interactions in 1, 3, and 4a

For analysis of the intermolecular interactions in the structures of $[UO_2(CH_2CHCOO)_2]$ (**1**), $[UO_2(CH_2CHCOO)_2(H_2O)_2]\cdot H_2O$ (**3**), and $[UO_2(CH_2CHCOO)_2(H_2O)_2]$ (**4a**) the method of molecular Voronoi-Dirichlet polyhedra has been applied (MMVDP).[42–46] Due to limitations of MMVDP it cannot be applied to the structures of **2** and **4b** because these contain disordered atoms and positions of some H atoms are lacking. The structure of **3** was divided into two parts containing different possible orientations of the disordered acrylate anions and both parts were calculated and found to have the same set of intermolecular contacts. In terms of MMVDP, the following set of descriptors is used: S_{ij} and Δ_{AZ} show the contribution of an A/Z contact to a molecular area in the absolute ($Å^2$) and partial (percents of the total intermolecular surface) units, where A and Z are the chemical sorts of atoms of different molecules sharing a common VDP face; k_{ij} – overall amount of molecular VDP faces corresponding to the A/Z contact type per formula unit; d_{min} and d_{max} – minimal and maximal distances between the A and Z atoms that share a common face of VDP. The calculated values are listed in Table 3.

According to the obtained data overall areas of the intermolecular contacts in **1**, **3**, and **4a** are 177.0, 367.9, and 131.7 $Å^2$, respectively, and agree well with the amount of structural units and their dimensionality. In all studied structures, the largest contribution into overall area is made by H/O, H/H, and H/C contacts corresponding to H-bonds and dispersion interactions. Note that the largest partial contribution of hydrogen bonds is observed in **1**, though its structure does not contain typical hydrogen bond donors. This is caused by a large contribution of weak C–H···O interactions and can be indicated by elongated minimal distances d_{min} compared to the other two structures containing moderate H-bonds.

Another feature of these compounds is the presence of C/C and C/O contacts which are almost absent in the structure of uranyl propionate.[31] For example, the total area of C/C and C/O contacts in **4a** is equal to 12.4 $Å^2$, while in the structure of uranyl propionate $[UO_2(C_2H_5COO)_2(H_2O)_2]$ their area is less than 0.4 $Å^2$.[31] This difference is caused by the presence of double bonds in the acrylate anions as well as their parallel arrangement, which likely contributes to stability of the studied structures. As well, parallel orientation of the acrylate anions and the presence of short C···C contacts between sp^2 hybridized carbon atoms satisfy topochemical criteria,[47,48] thus, making possible solid-state UV-initiated polymerization in these compounds.

Novikov et al. introduced the $\Delta_{\pi\pi}$ criterion that serves to indicate π-stacking in crystal structures of heteroaromatic compounds.[49] The $\Delta_{\pi\pi}$ value is the sum of all intermolecular contacts between sp^2 hybridized atoms, i.e. $\Delta_{\pi\pi} = \Delta_{C/C} + \Delta_{C/N}$ in case of heteroaromatic compounds containing pyridine rings. Along with the $\Delta_{\pi\pi}$ value, which contribution to the overall intermolecular area should exceed 2%, additional d_{Cg} value showing a distance between geometric centers of neighboring rings is employed and should not exceed 4.2 Å to indicate the

Table 3. Characteristics of molecular Voronoi-Dirichlet polyhedra in **1**, **3**, and **4a**

Contact type	$[UO_2(CH_2CHCOO)_2]$ (**1**)					$[UO_2(CH_2CHCOO)_2(H_2O)_2]\cdot H_2O$ (**3**)					$[UO_2(CH_2CHCOO)_2(H_2O)_2]$ (**4a**)				
	k_{ij}	d_{min}, Å	d_{max}, Å	S_{ij}, Å^2	$\Delta_{A/Z}$,%	k_{ij}	d_{min}, Å	d_{max}, Å	S_{ij}, Å^2	$\Delta_{A/Z}$,%	k_{ij}	d_{min}, Å	d_{max}, Å	S_{ij}, Å^2	$\Delta_{A/Z}$,%
H/O	72	2.69	4.68	117.8	66.6	101	1.78	4.66	206.9	56.2	84	1.85	3.94	171.7	54.7
H/H	8	2.70	3.64	25.5	14.4	92	2.10	4.61	120.0	32.6	48	2.42	4.21	83.7	26.7
H/C	24	3.59	4.07	8.4	4.7	38	2.80	4.42	19.1	5.2	68	2.61	4.03	39.1	12.5
O/O	6	3.56	4.31	2.5	1.4	7	3.16	4.34	5.1	1.4	10	3.19	4.35	6.8	2.2
C/C	24	3.58	3.79	15.4	8.7	16	3.47	4.31	10.5	2.9	6	3.47	3.58	2.6	0.8
C/O	20	3.58	4.17	7.4	4.2	12	3.28	4.56	6.3	1.7	26	3.30	4.50	9.8	3.1
Sum	154	2.69	4.68	177.0	100	266	1.78	4.66	367.9	100	242	1.85	4.50	313.7	100

*k_{ij} is the total number of the nonvalent contacts per formula unit; S_{ij} is the total area of the VDP faces corresponding to A/Z contacts; Δ_{AZ} is the partial contribution of the nonvalent A/Z contacts to the total area of a formula unit molecular VDP (S_{ij} in the Sum strings).

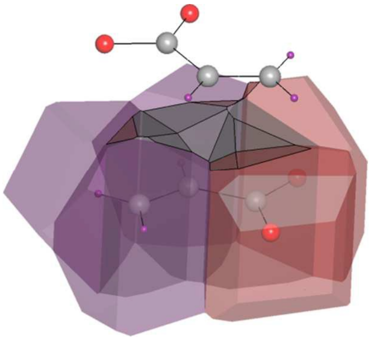


Figure 8. Molecular Voronoi-Dirichlet polyhedron of an acrylate anion within the structure of **1**. Faces of VDP responsible for the intermolecular C/C and C/O contacts are marked with black lines. Carbon, oxygen, and hydrogen atoms are shown in grey, red, and purple, respectively.

presence of π-stacking and its significant role in supramolecular organization of a structure. In our opinion, this method can be extended to the case of non-aromatic molecules containing double bonds such as acrylate anion. In **1**, **3**, and **4a** there are two types of contacts, C/C and C/O, responsible for intermolecular interactions between neighboring acrylate anions (Fig. 8). Both contacts give a contribution of 12.9, 4.6, and 3.9% for **1**, **3**, and **4a**, respectively, into the overall area of intermolecular contacts. The contribution of these values is significantly high, especially in **1**, due to interactions of the acrylate anions of neighboring chains. Extending the d_{Cg} value to non-aromatic systems, we define it as the distance between geometric centers of interacting acrylate groups. In **1**, **3**, and **4a**, the d_{Cg} value vary from 3.55 to 4.04 Å, while the shortest distance between two acrylate anions, which do not share common MVDP edges, is equal to 4.26 Å. These facts justify use of the same border values of 2% and 4.2 Å for $\Delta_{\pi\pi}$ and d_{Cg}, respectively, as in the case of the heteroaromatic compounds for the acrylate compounds to reveal presence of π-π interactions between acrylate anions.

Conclusions

We have synthesized four novel uranyl acrylates with general formula $UO_2(CH_2CHCOO)_2\cdot nH_2O$, where n = 0, 2, 2.22, or 3. The waterless compound $[UO_2(CH_2CHCOO)_2]$ (**1**) is based on chains containing UO_2^{2+} cations bridged by acrylate anions, while crystal structures of the other three compounds, $[UO_2(CH_2CHCOO)_2(H_2O)_2]\cdot 0.22H_2O$ (**2**), $[UO_2(CH_2CHCOO)_2(H_2O)_2]\cdot H_2O$ (**3**), $[UO_2(CH_2CHCOO)_2(H_2O)_2]$ (**4**), consist of discrete molecular $[UO_2(CH_2CHCOO)_2(H_2O)_2]$ complexes. In the structures of **2**–**4**, hydrogen bonds connect the complexes into layers in **4** and 3D framework in **2** and **3**. The H-bonded network of **2** contains large channels occupied by water molecules. The complexes in the structures of **2** and **4** have the same environment, but these compounds are topological isomers. The structure of **3** relates to **2** by removal of $UO_2(CH_2CHCOO)_2$ fragments from the latter one. The removal of one third on the fragments results into $UO_2(CH_2CHCOO)_2\cdot 3H_2O$ formula of **3**.

Analysis of intermolecular interactions by the method of molecular Voronoi-Dirichlet polyhedra showed an important role of the hydrogen bonds in interactions of the structural units in **1**–**4**. In **1** lacking of donors of hydrogen bonds, large area of H/O contacts is caused by numerous weak C–H···O interactions between neighboring chains.

Single crystal X-ray diffraction experiments carried out at 150 and 250 K have revealed a phase transition in a crystal of **4**. The low and high temperature (LT and HT) modifications have $P2_1/n$ and $C2/m$ symmetry, respectively. The difference between the modifications is related to the disorder of $[UO_2(CH_2CHCOO)_2(H_2O)_2]$ complexes present in the high-temperature modification, while the structure of the low-temperature phase is fully ordered. High temperature powder X-ray diffraction showed loss of water molecules by powdered sample of **4** after heating of **1** up to 373 K. Further heating up to 623 K leads to decomposition of the sample.

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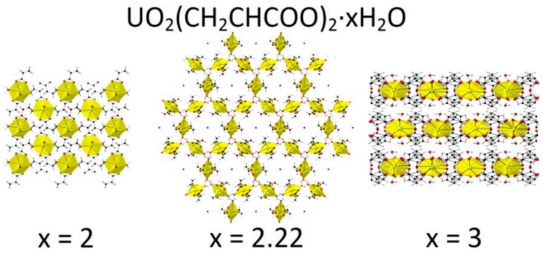

Uranyl acrylate can contain different number of water molecules and exhibits significant structural diversity caused by flexibility of hydrogen bonds.