

Tris(acrylato)uranylates as a scaffold for NLO materials



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ABSTRACT

Novel uranyl acrylate complexes with general formula $R[UO_2(CH_2CHCOO)_3]$ ($R=K^+$, NH_4^+ , Rb^+ , or Cs^+) were synthesized and characterized by X-ray diffraction, IR spectroscopy and second harmonic generation (SHG) measurements. All four compounds are isostructural and crystallize in the non-centrosymmetric $P2_13$ space group. Acrylate anions act as bidentate chelating ligands forming $[UO_2(CH_2CHCOO)_3]^-$ complexes which are connected through electrostatic interactions with counter ions. SHG measurements revealed the inverted correlation between the $Q = I_{2\omega}/I_{\omega}$ SiO_2 values and the radii of counter ions.

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Uranium(VI) tends to form linear uranyl cation UO_2^{2+} , which is often used in technological processes and possesses important properties such as luminescence [1–5], and participation in photochemical reactions [5–9]. As well, some uranyl-containing compounds possess nonlinear optical (NLO) properties [10–12], although data concerning trends in the structure – NLO properties of these compounds are absent. The CSD [13] contains data about isostructural series of tris(carboxylato)uranylates of the $R[UO_2(An)_3]$ composition ($R=Na$, $An=CH_3COO^-$ [14–16]; $R=K^+$, NH_4^+ , Rb^+ , Tl^+ or Cs^+ , $An=C_2H_5COO^-$ [4,17]) that crystallize in the chiral $P2_13$ space group. Because of the hexagonal-bipyramidal geometry of the uranium(VI) coordination polyhedron and nearly C_{3h} point group of the above $[UO_2(An)_3]^-$ anions, the vectorial part of hyperpolarizability (β_{vect}) should nearly vanish, however the ceptor part (β_{cept}) is expected to be non-zero. We assumed that the ceptor part can be enlarged by the elongation of the π -system in the equatorial plane of the anion. Indeed, the calculations of hyperpolarizability of the $[UO_2(An)_3]^-$ anions with $An =$ acetate, acrylate and crotonate within the finite field approach as implemented in the GAUSSIAN09 program [18] confirmed, that for these compounds $\beta_{vect} = 0$ a.u., and $\beta_{cept} = 507$, 789, and 1081 a.u., respectively. The M052X/6-31 + G^* level of theory was adopted for the calculation based on its successful application to the estimation of the molecular and cluster nonlinearities [19–22]. For the U atom, the Stuttgart RSC 1997 ECP basis set was utilized. Taking into account the close molecular volumes of acrylate and propionate we expected tris(acrylato)uranylates to

crystallize at the $P2_13$ space group. Although uranyl carboxylate complexes are well studied [23], the only crystal structure of uranyl- and acrylate-containing compound determined to date is $[UO_2(CH_2CClCOO)_2(O=P(C_6H_5)_3)_2]$ [24]. Herein we present synthesis, X-ray diffraction, IR spectroscopy and second harmonic generation measurements on some novel uranyl acrylate complexes.

As acrylate ions tend to polymerize in solution in the presence of both uranyl cations and UV radiation all preparations should be carried out in the absence of daylight. The target products were obtained by slow evaporation at room temperature of yellow transparent solution obtained by the dissolution of water suspension of UO_3 (0.200 g, 0.63 mmol) in acrylic acid (0.363 g, 5.04 mmol) and subsequent addition of crystalline KOH (0.071 g, 1.26 mmol), $(NH_4)_2CO_3$ (0.060 g, 0.63 mmol), RbOH (0.129 g, 1.26 mmol) or Cs_2CO_3 (0.205 g, 0.63 mmol). The yields are 54, 56, 52, and 46% for **I**, **II**, **III**, and **IV**, respectively. Single-crystal X-ray diffraction confirmed that compounds crystallize in the chiral $P2_13$ space group (Table 1). The powder X-ray diffraction patterns of **I–IV** revealed that the samples contained only the target products (see Supplementary materials).

The crystal structures of **I–IV** consist of molecular $[UO_2(CH_2CHCOO)_3]^-$ complexes connected into a framework through electrostatic interactions with counter ions. Each uranium atom lies on a three-fold axis and adopts hexagonal bipyramidal geometry (Fig. 1). Two uranyl oxygen atoms are in the axial positions ($d(U=O) = 1.71(2)$ – $1.77(1)$ Å, Table 2) and six oxygen atoms of acrylate groups are in the equatorial plane ($d(U-O) = 2.445(5)$ – $2.481(9)$ Å). The acrylate groups act as bidentate-chelate ligands of the B^{01} coordination mode [25,26]. The volumes of Voronoi–Dirichlet

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Table 1
Crystal data, parameters of data collection and characteristics of the refinement of structures I–IV.

Compound	I	Ia	II	III	IV
Formula	K[$\text{UO}_2(\text{Acr})_3$]	K[$\text{UO}_2(\text{Acr})_3$]	$\text{NH}_4[\text{UO}_2(\text{Acr})_3]$	Rb[$\text{UO}_2(\text{Acr})_3$]	Cs[$\text{UO}_2(\text{Acr})_3$]
Molecular weight (g mol ⁻¹)	522.29	522.29	501.23	568.66	616.10
Temperature (K)	100(2)	300(2)		100(2)	
Radiation (λ , Å)	$\text{MoK}\alpha$ (0.71073)				
Crystal system	Cubic				
Space group	$P 2_1 3$				
a (Å)	11.479(1)	11.5573(2)	11.5509(6)	11.6225(5)	11.8238(12)
V (Å ³)	1512.6(2)	1543.74(6)	1541.16(14)	1570.00(12)	1653.0(3)
Z	4				
D _{calc} (g cm ⁻³)	2.294	2.247	2.160	2.406	2.476
μ (mm ⁻¹)	11.032	10.810	10.561	13.444	12.014
F(000)	952	952	920	1024	1096
Crystal size (mm)	0.34 × 0.29 × 0.08	0.20 × 0.18 × 0.14	0.29 × 0.27 × 0.12	0.36 × 0.32 × 0.24	0.32 × 0.28 × 0.21
θ Range (°)	3.07–29.95	3.05–27.47	2.49–27.94	3.04–26.90	2.44–27.94
Limiting indices	$-12 \leq h \leq 16$, $-13 \leq k \leq 13$, $-16 \leq l \leq 11$	$-15 \leq h \leq 12$, $-11 \leq k \leq 13$, $-12 \leq l \leq 12$	$-15 \leq h \leq 15$, $-15 \leq k \leq 15$, $-15 \leq l \leq 14$	$-14 \leq h \leq 14$, $-14 \leq k \leq 14$, $-14 \leq l \leq 14$	$-15 \leq h \leq 15$, $-15 \leq k \leq 15$, $-15 \leq l \leq 15$
Reflections collected	6573	2600	11,226	15,284	18,549
Independent reflections/R _{int}	1469/0.066	1174/0.031	1236/0.069	1132/0.089	1328/0.077
Unique reflections [$I \geq 2\sigma(I)$]	1280	996	1093	1072	1221
Refinement method	Full-matrix least-squares on F ²				
Data/restraints/parameters	1469/0/58	1174/2/57	1236/6/58	1132/0/58	1328/16/66
Goodness-of-fit on F ²	1.008	1.067	0.996	1.000	1.006
R ₁ [$I > 2\sigma(I)$] (all data)	0.034 (0.046)	0.049 (0.061)	0.031 (0.043)	0.030 (0.033)	0.044 (0.049)
wR ₂ [$I > 2\sigma(I)$] (all data)	0.073 (0.077)	0.110 (0.119)	0.079 (0.096)	0.076 (0.078)	0.097 (0.098)
Max peak/hole (e Å ⁻³)	1.97/−0.74	1.98/−0.67	1.77/−1.10	2.59/−0.74	1.92/−0.89
Flack	−0.002(19)	−0.01(3)	0.01(3)	0.01(3)	0.06(3)

polyhedra (VDP) of uranium atoms in I–IV vary from 9.17 to 9.34 Å³ and coincide with the average of 9.3(4) Å³ reported for UO_n VDPs [27]. The alkali cations in I, III, and IV have a distorted octahedron coordination, and each ammonium cation in II is involved in H-bonds with three oxygen atoms of different [UO₂(CH₂CHCOO)₃][−] complexes ($d(\text{N} \cdots \text{O}) = 2.82(1)$ Å, $\text{NHO} = 168^\circ$). Increase in radii of cations in I–IV is accompanied by the enlargement of unit cell volumes (from 1512.6(2) to 1653.0(3) Å³) and thermal displacements of carbon atoms. In IV, which has the largest unit cell, the carbon atoms of the vinyl group are disordered about the direction perpendicular to equatorial plane of uranyl cation.

The $d(\text{C} - \text{C})$ and $d(\text{C} = \text{C})$ bond distances are in agreement with data in [28,29] and lie in the range of 1.47(1)–1.50(1) Å and 1.29(1)–

1.32(1) Å, respectively (Table 2). The calculation of distances between carbon atoms that could be treated as reaction centers of solid-state polymerization (sp^2 -carbon atoms with interatomic distances < 4.1 Å [30]) indicates C2···C3 interactions as the only reaction centers. For I–III the corresponding C···C distances are equal to 3.89–4.05 Å, and the angles between the planes of neighboring acrylate anions are equal to 66–69°. The Hirshfeld surface analysis [31,32] of C···C interactions for acrylate anions indicates, that these contacts are also the shortest among all C···C ones (Fig. 2). Thus, it could be considered that solid-state polymerization is unlikely in these compounds unless their structure changes. X-ray experiment for I at room temperature revealed the disorder of vinyl groups so that the C2···C3 distances become significantly shorter (3.49 Å). Hence, the increase in temperature is accompanied by a shortening of the Csp²···Csp² distances that might facilitate polymerization reaction.

Infrared spectra of uranyl acrylates were recorded as KBr pellet on a Perkin Elmer Spectrum 100 FT-IR spectrometer in the range of 450–4000 cm⁻¹ and were assigned using [33]. (Fig. 3). Each spectrum contains strong absorption bands assigned to asymmetric uranyl group stretching in the region 916–932 cm⁻¹. Other strong absorption bands correspond to vinyl group stretching (1642–1644 cm⁻¹), asymmetric (1520–1531 cm⁻¹) and symmetric (1456–1459 cm⁻¹) carboxylate group bending.

SHG measurements of powder samples compared with the intensity of radiation generated by α -quartz give $Q = I_{2\omega}/I_{\omega}^2$ SiO₂ values of 16.0, 1.2, 4.5, and 4.1 for I–IV, respectively, showing an inverted correlation with counter cation radii. This correlation is as expected for the optical nonlinearity χ as defined by $Q = A\chi^2$, where A is constant for defined structure type. Taking into account that $\chi \sim d^n$ (where d is the distance between cation and the nearest electron cloud of partially covalent cation-anion bond, and $n > 1$ [34]) it seems that optical nonlinearity drops in K–Rb–Cs series due to the decrease of atomic electronegativity and increase of cation radii, which both lead to less covalent and elongated R–O bonds. In the case of NH₄⁺, significant decrease of optical nonlinearity seems to be caused by the formation of H-bonds.

In conclusion, we have found that uranyl complexes with carboxylic acids provide a route to chiral materials with NLO properties. The elongation of a π -system of the alkyl chain, or its modification with donor

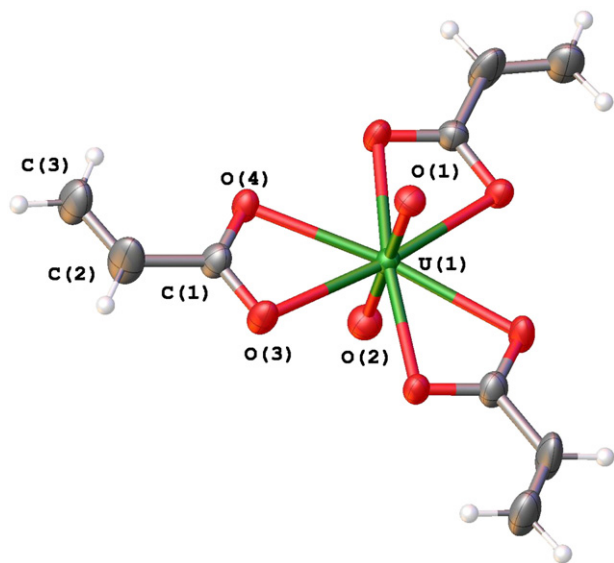


Fig. 1. ORTEP view (50% probability) of the [UO₂(CH₂CHCOO)₃][−] complex in the crystal structure of I. Numeration scheme of independent atoms is given.

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