



## Structural features of two polymorphs of ammonium uranyl crotonate

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## HIGHLIGHTS

- Structures of two polymorphs of the first uranyl tricrotonate complex were solved.
- The main structural units of both polymorphs are anionic complexes  $[\text{UO}_2(\text{C}_3\text{H}_5\text{COO})_3]^-$ .
- Triclinic crystals of  $\alpha$ -polymorph have layer structure.
- Cubic crystals of  $\beta$ -polymorph have three dimensional structure.
- BCC lattice is the most abundant among U atoms in U-sublattices of  $R[\text{UO}_2\text{L}_3]$  compounds.

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## ABSTRACT

X-ray crystallography, FTIR spectroscopy and thermal analysis were conducted for crystals of two polymorphs of  $\text{NH}_4\text{UO}_2(\text{C}_3\text{H}_5\text{COO})_3$ , which are the first examples of uranyl tricarboxylate complexes with ions of unsaturated aliphatic monocarboxylic acid. The main structural units of both polymorphs are anionic complexes  $[\text{UO}_2(\text{C}_3\text{H}_5\text{COO})_3]^-$ . Uranium atoms adopt hexagonal bipyramidal coordination polyhedron, and crotonate ions realize bidentate cyclic type of coordination. Due to different packing of ammonium ions and  $[\text{UO}_2(\text{C}_3\text{H}_5\text{COO})_3]^-$  complexes triclinic crystals of  $\alpha$ -polymorph have layer structure and cubic crystals of  $\beta$ -polymorph have three dimensional structure. Features of three dimensional packing of  $R^+$  ions and  $[\text{UO}_2\text{L}_3]^-$  complexes in structures of 25 known  $R[\text{UO}_2\text{L}_3]$  compounds are discussed.

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## Introduction

Up to date there are a lot of examples of coordination compounds of uranium with main structural units of uranyl tricarboxylate complexes  $[\text{UO}_2\text{L}_3]^-$ , where  $L^-$  is an anion of a saturated monocarboxylic acid  $\text{C}_n\text{H}_{2n+1}\text{COO}^-$  (acetate, propionate, butyrate etc.) [1–3]. Yet data on such complexes with ions of unsaturated monocarboxylic acid  $\text{C}_n\text{H}_{2n-1}\text{COO}^-$  (acrylate, crotonate etc.) were not reported. In particular, there is only one compound of U(VI) in CCDC [4] containing crotonate ions, in which uranyl ion is coordinated by two carboxylate ligands and two water molecules:  $[\text{UO}_2(\text{C}_3\text{H}_5\text{COO})_2(\text{H}_2\text{O})_2]$  [5]. During investigation of phase equilibrium in saline systems with uranyl crotonate we obtained crystals of two polymorphs of  $\text{NH}_4\text{UO}_2(\text{C}_3\text{H}_5\text{COO})_3$ . The scope of this work was to define structural features of  $\text{NH}_4\text{UO}_2(\text{C}_3\text{H}_5\text{COO})_3$ , which is the first uranyl tricarboxylate complex with ions of unsaturated aliphatic monocarboxylic acid (see Scheme 1).

## Experimental

## Synthesis

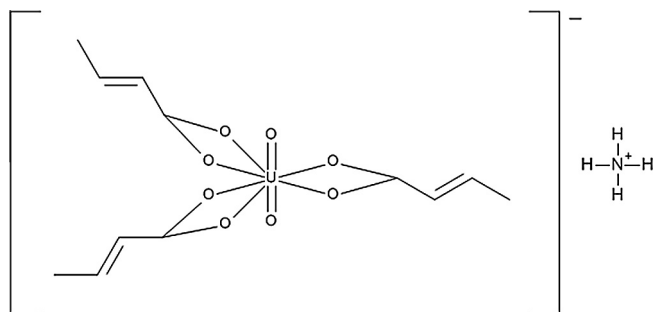
The title compound  $\text{NH}_4\text{UO}_2(\text{C}_3\text{H}_5\text{COO})_3$  was obtained from water solution, containing  $\text{UO}_2(\text{C}_3\text{H}_5\text{COO})_2 \cdot 2\text{H}_2\text{O}$  (prepared according to [5]) and commercially available crotonic acid and ammonia solution at molar ratio 1:2:2. Isothermic evaporation (25 °C) of the solution afforded yellow prismatic and light-yellow plate crystals, which according to X-ray analysis differ in symmetry. Plate crystals have triclinic symmetry ( $\alpha$ -polymorph) and prismatic crystals have cubic symmetry ( $\beta$ -polymorph). Both polymorphs are stable in ambient conditions. For the composition  $\text{UC}_{12}\text{O}_8\text{NH}_{19}$  Anal. Calc. U, 43.8. Found: U, 43.3%.

## X-ray crystallography

X-ray diffraction data were collected at  $T = 123$  K with the automatic four-circle diffractometer SuperNova (Agilent Technologies) with two-coordinate CCD detector Atlas and micro-focus

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**Scheme 1.** Structural formula of  $\text{NH}_4\text{UO}_2(\text{C}_3\text{H}_5\text{COO})_3$ .

SuperNova (Cu) X-ray source ( $\lambda = 1.54178 \text{ \AA}$ ). Intensities were measured by  $\omega$ -scanning of  $1^\circ$  frames to  $2\theta = 135^\circ$ . Absorption correction was made using a multifaceted crystal and a program package CrysAlisPro [6]. Both structures were refined by full-matrix least-squares method with anisotropic displacement parameters for all non-hydrogen atoms using SHELXTL software [7]. All hydrogen atoms were refined in calculated positions by the riding model. Hydrogen atoms of ammonium were not localized in the presence of heavy atoms. Residual electron density peaks are located at uranium atoms, their relatively high intensities are due to high absorption of uranium containing compounds. Details of data collection and structure refinement parameters are given in [Supplementary materials](#), selected bond lengths and angles are given in [Table 1](#). Atomic coordinates and displacement parameters are deposited in CCDC [4] (Nos. 980917 and 980916 for  $\alpha$  and  $\beta$  respectively). Calculated XRPD patterns of both polymorphs are also provided in [Supplementary materials](#).

#### FTIR spectroscopy and thermal analysis

FTIR spectra were measured using FT-801 spectrometer in the region  $500\text{--}4500 \text{ cm}^{-1}$ . Samples were prepared as KBr pellets.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed with OD-103 derivatograph (MOM, Hungary). Samples of approximately 0.1 g were heated to

**Table 1**

Geometric parameters of coordination polyhedra of U atoms in  $\alpha$ - and  $\beta$ - $\text{NH}_4\text{UO}_2(\text{C}_3\text{H}_5\text{COO})_3$ .

Bond	<i>d</i> (Å)	$\Omega$ (%) <sup>a</sup>	Angle	$\omega$ (deg.)
<i><math>\alpha</math>-NH<sub>4</sub>UO<sub>2</sub>(C<sub>3</sub>H<sub>5</sub>COO)<sub>3</sub> Hexagonal bipyramid U1O<sub>8</sub></i>				
U1–O1	1.765(7)	21.98	O1–U1–O2	178.0(3)
U1–O2	1.767(7)	21.53	O3–U1–O4	52.4(2)
U1–O3	2.450(7)	9.35	O4–U1–O5	69.4(2)
U1–O4	2.495(7)	9.07	O5–U1–O6	52.6(2)
U1–O5	2.845(10)	9.62	O6–U1–O7	66.4(2)
U1–O6	2.442(7)	9.59	O7–U1–O8	52.5(2)
U1–O7	2.453(7)	9.39	O8–U1–O3	67.2(2)
U1–O8	2.444(7)	9.47		
<i>Hexagonal bipyramid U2O<sub>8</sub></i>				
U2–O9	1.777(7)	21.69	O9–U2–O10	177.9(3)
U2–O10	1.770(7)	21.65	O11–U2–O12	52.6(2)
U2–O11	2.448(6)	9.55	O12–U2–O13	68.0(2)
U2–O12	2.462(7)	9.41	O13–U2–O14	52.8(2)
U2–O13	2.458(7)	9.40	O14–U2–O15	68.3(2)
U2–O14	2.482(7)	9.17	O15–U2–O16	52.7(2)
U2–O15	2.453(7)	9.57	O16–U2–O11	66.4(2)
U2–O16	2.443(7)	9.56		
<i><math>\beta</math>-NH<sub>4</sub>UO<sub>2</sub>(C<sub>3</sub>H<sub>5</sub>COO)<sub>3</sub> Hexagonal bipyramid UO<sub>8</sub></i>				
U–O1	1.724(14)	22.63	O1–U–O2	180
U–O2	1.744(15)	21.69	O3–U–O4 (×3)	67.8(2)
U–O3 (×3)	2.470(8)	9.16	O4–U–O3 (×3)	52.2(2)
U–O4 (×3)	2.454(8)	9.40		

<sup>a</sup>  $\Omega$  is the solid angle (in percent of  $4\pi$  steradian), at which the shared face of the Voronoi–Dirichlet polyhedra of adjacent atoms is seen from the nucleus of any of them.

$850^\circ\text{C}$  at a  $5^\circ/\text{min}$  rate in platinum crucibles using Pt–Pt/Rh thermocouple and preheated aluminum oxide as a reference.

#### Crystallochemical analysis

Crystallochemical analysis was performed in terms of stereoatomic model of crystal structures [8]. Coordination numbers of all atoms were calculated using the method of intersecting spheres [9]. All calculations, including searching of possible hydrogen bonds in the absence of hydrogen atoms, were based on characteristics of atomic and molecular Voronoi–Dirichlet polyhedra (VD) using TOPOS program package [10].

## Results and discussion

#### FTIR spectroscopy

FTIR spectra of both polymorphs (provided in [Supplementary materials](#)) are similar and present absorption bands due to vibrations of  $\text{NH}_4^+$ ,  $\text{UO}_2^{2+}$  and  $\text{C}_3\text{H}_5\text{COO}^-$  ions. Assignment of bands (provided for  $\alpha$ -polymorph in [Table 2](#), assignment of bands for  $\beta$ -polymorph is similar) was carried out according to [11,12]. Peculiarities in spectra of compounds with unsaturated hydrocarbon ligands show up as bands due to stretching and deformation vibrations of groups of atoms next to double bonds. Thus, the most intense bands in spectra of alkenes correspond to deformation out-of-plane vibrations of  $=\text{CH}$  ( $650\text{--}1000 \text{ cm}^{-1}$ ) [12]. Stretching vibrations of double  $\text{C}=\text{C}$  bonds arise at  $1659 \text{ cm}^{-1}$ . Conjugation of double bond with carbonyl group in crotonate ion leads to additional shoulder band due to  $\nu(\text{C}=\text{C})$  vibration at wave number lower by  $\approx 30 \text{ cm}^{-1}$  ( $1633 \text{ cm}^{-1}$ ) and to higher intensity of the main band. Stretching vibrations of  $=\text{CH}$  groups arise at  $3041 \text{ cm}^{-1}$  with low intensity.

#### Thermal analysis

According to experimental data both polymorphs of  $\text{NH}_4\text{UO}_2(\text{C}_3\text{H}_5\text{COO})_3$  undergo similar two-stage thermal decomposition

**Table 2**

Assignment of adsorption bands in FTIR spectra of  $\alpha$ - $\text{NH}_4\text{UO}_2(\text{C}_3\text{H}_5\text{COO})_3$ .

Wave number ( $\text{cm}^{-1}$ )	Assignment
3193 m., br.	$\nu(\text{NH}_4)$
3041 w.	$\nu(=\text{CH})$
2983 w.	$\nu_{\text{as}}(\text{CH}_3)$
2947 w.	$\nu_{\text{s}}(\text{CH}_3)$
2916 w.	$\nu_{\text{as}}(\text{CH}_2)$
2847 w.	$\nu_{\text{s}}(\text{CH}_3)$
1659 s.	$\nu(\text{C}=\text{C}), \delta(\text{NH}_4)$
1633 w.	
1535 Shoulder	$\nu_{\text{as}}(\text{COO})$
1510 v.s.	
1453 v.s.	$\delta_{\text{as}}(\text{CH}_3)$
1402 Shoulder	$\nu_{\text{s}}(\text{COO})$
1376 Shoulder	$\delta_{\text{s}}(\text{CH}_3)$
1295 m.	$\omega(\text{CH})$
1255 m.	$\text{tw}(\text{CH})$
1105 w.	$\nu(\text{C}=\text{C})$
1044 w.	$\gamma(\text{CH}_3)$
966 s.	$\omega(=\text{CH}), \text{tw}(=\text{CH})$
934 v.s.	$\nu_{\text{as}}(\text{UO}_2)$
917 s.	
851 m.	$\gamma(\text{CH})$
746 s.	$\omega(=\text{CH}), \text{tw}(=\text{CH})$
698 w.	$\delta(\text{COO})$
528 m.	$\omega(\text{COO})$

<sup>a</sup> v.s. – very strong, s. – strong, m. – medium, w. – weak, br. – broad.

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