

## Actinide Structural Studies. 18.\* Structure of Oxonium Dioxotris(salicylato)uranate(VI) Pentahydrate

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**Abstract.**  $[\text{H}_3\text{O}][\text{UO}_2(\text{C}_6\text{H}_4\text{OHCO}_2)_3]\cdot 5\text{H}_2\text{O}$ ,  $M_r = 790.2$ , hexagonal,  $P6_2c$ ,  $a = 16.802(3)$ ,  $c = 6.903(3)$  Å,  $V = 1687.7$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.56$  g cm<sup>-3</sup>,  $\lambda(\text{Mo K}\alpha) = 0.71069$  Å,  $\mu(\text{Mo K}\alpha) = 46.2$  cm<sup>-1</sup>,  $F(000) = 764$ ,  $T = 293$  K,  $R = 0.062$  for 932 unique observed [ $I/\sigma(I) > 2.0$ ] reflections. The title compound contains a  $\text{UO}_2$  group [ $\text{U}-\text{O} 1.777(16)$  Å] coordinated by six O atoms [ $\text{U}-\text{O} 2.46(2)$  Å] belonging to bidentate carboxylate groups of three salicylate molecules. The salicylate groups are located in a plane normal to the hexagonal axis. The  $\text{UO}_2$  group is strictly linear, and perpendicular to the plane of the salicylate molecules.

**Introduction.** The uranyl ion is known to form several complex compounds with salicylic acid (for early references see Gmelin, 1936). Compounds with two and three molecules of salicylic acid attached to the uranyl ion were identified but only two of them have been examined by powder X-ray diffraction:  $\text{UO}_2\cdot(\text{C}_6\text{H}_4\text{OHCOO})_2\cdot 2\text{H}_2\text{O}$  (Manojlovic, 1958) and  $\text{UO}_2\cdot(\text{C}_6\text{H}_4\text{OHCOO})_2\cdot 3\text{H}_2\text{O}$  (Amirthalingan & Padmanabhan, 1959). These were found to be triclinic and hexagonal, respectively, and their lattice constants determined. In the course of our studies on the coordination chemistry of carboxylate complexes of dioxouranium(VI) we have obtained red single crystals of  $[\text{HUO}_2(\text{C}_6\text{H}_4\text{OHCO}_2)_3]\cdot 6\text{H}_2\text{O}$  suitable for X-ray examination.

**Experimental.** The material can be prepared by a variety of routes. A qualitative preparation of uranyl disalicylate from uranyl acetate and sodium salicylate (hot solutions in  $\text{H}_2\text{O}$  with excess of sodium salicylate) gave a red-brown non-crystalline precipitate. This was redissolved in ethanol and slow evaporation yielded a mixture of orange-brown hexagonal prisms (believed to be the disalicylate described by Amirthalingan & Padmanabhan, 1959) and red hexagonal prisms; one of the latter was used for the structure determination. The

same red material can be prepared from uranyl acetate and salicylic acid (1:2 ratio in hot  $\text{H}_2\text{O}$ ) (identification from unit-cell parameters). These crystals are very soft and easily distorted. They also tend to change colour on standing, becoming a deeper red; this suggests that the degree of hydration is variable, with  $\text{H}_2\text{O}$  being lost without changing the crystal packing.

A red hexagonal prismatic single crystal of the title compound was used for analysis. Data were collected with a Syntex  $P2_1$  four-circle diffractometer. Maximum  $2\theta$  was  $50^\circ$  with scan range  $\pm 1.15^\circ$  ( $2\theta$ ) around the  $K\alpha_1-K\alpha_2$  angles, scan speed  $2-29^\circ$  min<sup>-1</sup> depending upon the intensity of a 2 s prescan; backgrounds were measured at each end of the scan for 0.25 of the scan time. Index ranges were:  $h$  0 to 20;  $k$  -20 to 17;  $l$  0 to 8. Three standard reflections were monitored every 200 reflections and showed slight changes during data collection. The data were rescaled to correct for this. Density determinations by flotation were undertaken but gave variable results depending on the age and preparative route used, probably because of variations in the degree of hydration. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 reflections ( $20 < 2\theta < 22^\circ$ ). In total 3372 reflections were processed using profile analysis to give 1099 unique reflections ( $R_{\text{int}} = 0.046$ ); 932 were considered observed [ $I \geq 2\sigma(I)$ ] and used in refinement; they were corrected for Lorentz, polarization and absorption effects, the last by the Gaussian method; maximum and minimum transmission factors were 0.63 and 0.41. Crystal dimensions were  $0.12 \times 0.18 \times 0.21$  mm. Systematic absences:  $00l$ ,  $l \neq 2n$ ;  $hhl$ ,  $l \neq 2n$ .

The Laue group was identified as  $6/mmm$  by comparison of individual  $F$  values and confirmed from the low merging  $R$  value. The possible space groups  $P6_3mc$ ,  $P6_3/mmc$  and  $P6_2c$ , differ in the site symmetry at uranium for  $Z = 2$ ;  $3m$ ,  $\bar{6}m2$  and  $\bar{6}$  respectively. Only the last space group *i.e.*  $P6_2c$  is consistent with coordinated salicylate groups; it was therefore selected initially and confirmed by the successful refinement. This symmetry requires the equatorial ligands to be strictly planar and the  $\text{UO}_2$  group to be linear.

The U atom was located by the Patterson interpretation section of *SHELXTL* (Sheldrick, 1983) in

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Table 1. *Atom coordinates* ( $\times 10^4$ ) *and temperature factors* ( $\text{\AA}^2 \times 10^3$ )

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
U(1)	3333	6667	2500	47 (1)*
O(11)	3333	6667	5075 (23)	50 (5)*
O(1)	4889 (13)	6893 (13)	2500	41 (8)*
O(2)	3784 (16)	5472 (14)	2500	39 (9)*
O(3)	6581 (15)	7250 (26)	2500	98 (17)*
O(4)	6105 (7)	8609 (7)	2500	7 (2)
O(5)	7308 (26)	1153 (27)	5155 (65)	103 (11)
C(11)	4673 (24)	6055 (25)	2500	35 (7)
C(1)	5299 (12)	5686 (10)	2500	45 (6)
C(2)	4997 (12)	4748 (11)	2500	34 (5)
C(3)	5617 (18)	4429 (22)	2500	57 (6)
C(4)	6548 (22)	5086 (17)	2500	69 (9)
C(5)	6905 (20)	6033 (19)	2500	70 (9)
C(6)	6242 (11)	6299 (16)	2500	44 (5)

\* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

Table 2. *Bond lengths* ( $\text{\AA}$ )

U(1)—O(11)	1.777 (16)	U(1)—O(1)	2.447 (23)
U(1)—O(2)	2.476 (30)		
O(1)—C(11)	1.267 (48)	O(2)—C(11)	1.315 (38)
O(3)—C(6)	1.403 (49)	C(11)—C(1)	1.464 (55)

position 2(c) and the light atoms then found on successive Fourier syntheses. Two  $\text{H}_2\text{O}$  molecules were located in position 6(h) and a third in the general position 12(i), with 0.5 occupancy, giving a total of  $6\text{H}_2\text{O}$  per uranyl group.

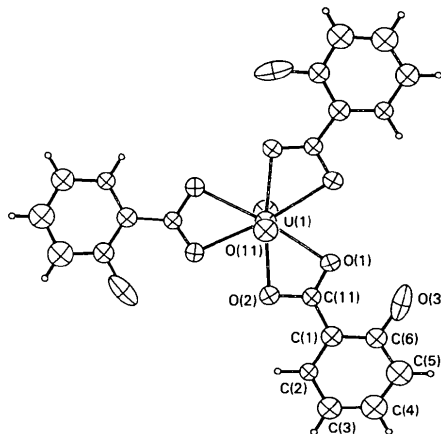
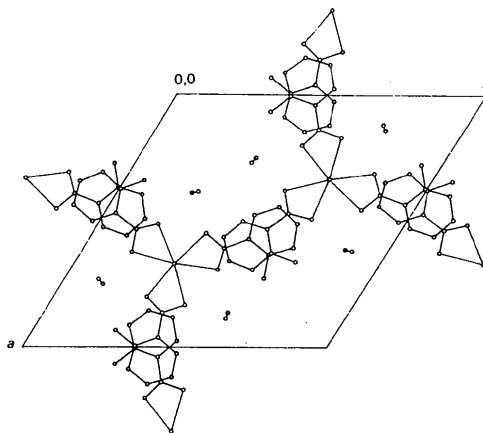
Anisotropic temperature factors were used only for U and O atoms bound to the uranyl group. The anisotropic refinement of the C-atom positions led to large  $U_{33}$  values suggesting possible disordered displacements of these atoms from the equatorial plane. No satisfactory model could be found to account for this and in the final refinement these atoms were given isotropic temperature factors. C—C distances in the benzene ring were constrained to 1.392 (1)  $\text{\AA}$ . Aromatic H atoms were given isotropic temperature factors  $U = 0.07 \text{\AA}^2$  and were inserted at calculated positions and not refined. Other H atoms were not located.

Final refinement was on  $F$  by cascaded least-squares methods refining 52 parameters. Largest positive and negative peaks on a final difference Fourier synthesis were of height +5 and  $-2 \text{\AA}^{-3}$ , respectively, with all substantial peaks close to U, though some smaller peaks lay near the aromatic ring. A weighting scheme of the form  $w = I/[\sigma^2(F) + gF^2]$  with  $g = 0.0043$  was used and shown to be satisfactory by an analysis of variance. Final  $R = 0.062$ ,  $wR = 0.063$ . Maximum shift/e.s.d. in final cycle 0.1. Computing was with *SHELXTL* (Sheldrick, 1983) on a Data General DG30. Scattering factors in the analytical form and anomalous-dispersion factors taken from *International Tables for X-ray Crystallography* (1974). Final atomic

coordinates are listed in Table 1 and selected bond lengths and angles in Table 2.\*

**Discussion.** The crystal structure of the title compound is unusual among uranyl complexes with organic molecules because of its high  $\bar{6}$  symmetry. The uranyl group is strictly linear and the salicylate ions are planar and located on the same plane as the U atoms. These planes are stacked up in the direction of the hexagonal axis; the 3.45  $\text{\AA}$  distance between adjacent layers suggests weak van der Waals interactions between them, probably *via* the water molecules. There are 12 water molecules in the unit cell, six of them in the same plane as the  $\text{U}(\text{C}_6\text{H}_4\text{OHCO}_2)_3$  group (see Fig. 2).

\* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and bond angles have been deposited with the British Library Document Supply centre as Supplementary Publication No. SUP 51574 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Fig. 1. View of the  $[\text{UO}_2(\text{C}_6\text{H}_4\text{OHCO}_2)_3]^-$  anion, showing the atomic numbering.Fig. 2. Packing diagram, viewed down *c*.

The coordination of O atoms to the U atom is hexagonal bipyramidal. The U—O distance in the  $\text{UO}_2$  group is 1.777 (16) Å, typical for  $\text{UO}_2$  groups in many uranyl complexes. The six equatorial O atoms belonging to the salicylic ions are at a mean distance U—O 2.46 (2) Å. The hydroxyl groups are unbonded (see Fig. 1). The U—O<sub>6</sub> array is a slightly deformed planar hexagon with O—U—O angles of 52.4 (7)° (O atoms of the same salicylate) and O—U—O of 67.6 (8)° (O atoms of adjacent salicylates). The observed bond lengths listed in Table 1 are in fair agreement with those found in other uranyl complexes containing organic-acid molecules.

Although the title compound was prepared from sodium salicylate, we found no evidence for  $\text{Na}^+$  ions during the structure determination; the same material can also be prepared with the exclusion of any sodium-containing compounds. We therefore conclude that the single cation per uranyl group necessary for charge balance must be a proton. The compound therefore does not correspond to potassium trisalicylate (reported by Weinland & Hager, 1927). We were unable to locate this proton. However, the

symmetrical bonding of the salicylate groups makes it unlikely that the proton is attached to one of these anions. The unit cell therefore probably contains two protonated water molecules, distributed at random, in positions 6(h) and 12(i).

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## Structures of Tetracarbonyl(2-3- $\eta$ -maleic acid)iron, *cis*- $[\text{Fe}(\text{C}_4\text{H}_4\text{O}_4)(\text{CO})_4]$ (1) and Tetracarbonyl(2-3- $\eta$ -fumaric acid)iron, *trans*- $[\text{Fe}(\text{C}_4\text{H}_4\text{O}_4)(\text{CO})_4]$ (2)

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**Abstract.** (1) *cis*- $[\text{Fe}(\text{C}_4\text{H}_4\text{O}_4)(\text{CO})_4]$ ,  $M_r = 284$ , monoclinic,  $P2_1/c$ ,  $a = 12.897$  (2),  $b = 10.799$  (2),  $c = 15.416$  (2) Å,  $\beta = 104.78$  (1)°,  $V = 2076$  (6) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.817$ ,  $D_m = 1.80$  (5) g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 1.48$  cm<sup>-1</sup>,  $F(000) = 1136$ ,  $T = 298$  K, final  $R = 0.031$  for 1941 observed reflections. (2) *trans*- $[\text{Fe}(\text{C}_4\text{H}_4\text{O}_4)(\text{CO})_4]$ ,  $M_r = 284$ , orthorhombic,  $Pccn$ ,  $a = 6.048$  (2),  $b = 13.443$  (3),  $c = 12.703$  (3) Å,  $V = 1032.7$  (5) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.826$ ,  $D_m = 1.80$  (5) g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 1.49$  cm<sup>-1</sup>,  $F(000) = 568$ ,  $T = 298$  K, final  $R = 0.039$  for 908 observed reflections. Compound (1) contains two

molecules in the asymmetric unit. Compound (2) contains only half a molecule in the asymmetric unit, with the molecular symmetry,  $C_2$ , relating to the crystallographic twofold rotation axis. The corresponding bond lengths and angles in the two isomers agree well. The coordination polyhedron around the iron atom in both structures is a trigonal bipyramid with the ethylenic double bond of the maleic and fumaric acid groups in the equatorial plane. Both compounds have rows of hydrogen bonds, directed along the  $a$  and the  $b$  axes, respectively. The planes containing the Fe atom and the ethylenic double bonds of the acids are rotated from the equatorial plane  $[\text{Fe}(\text{CO})_2]$  by 3.9 (3) and 5.8 (4)° in compound (1), and 11.2 (3)° in compound (2).

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