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Structural Studies on the Actinide Carboxylates. VIII [1]. Preparation, Properties and Crystal Structure of Fumarate Dioxouranium(VI) Dihydrate, $UO_2(C_4H_2O_4)(H_2O)_2$

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The synthesesis, thermal behaviour and crystal structure of fumarate dioxouranium(VI) dihydrate are described. The compound crystallizes in the monoclinic system, space group $P2_1/n$ *with* $a = 9.952(3)$, $b = 7.502(2)$, $c = 5.571(2)$ Å, $\beta = 98.6(3)^\circ$ *and* $Z = 2$. *555 observed reflections* ($I > 3\sigma(I)$) *were refined to a final* $R = 0.0235$. *The fumarate ligands bridge the uranyl groups in chains. The geometry around the uranium is approximately hexagonal-bipyramidal, with the two water molecules coordinated to the uranyl group.*

Introduction

In previous papers we have reported structural studies on uranyl derivatives with malonic [2, 3], succinic [4], maleic [1] and glutaric [5] acids, finding different coordination modes for the carboxylic groups to the uranium atoms. The aim of these studies was to correlate the influence of the different lengths of the carbon chains (and also the presence of a double bond in the chain), on the coordination mode of the carboxylic groups that can be monodentate or bidentate on the same uranyl group or can bridge different uranyl units. We report here on fumarate dioxouranium dihydrate, in which the dicarboxylic acid has the same chain length as succinic acid but its geometry is modified by the presence of a double bond in the carbon chain, as in its *cis* isomer, maleic acid.

Experimental

Synthesis

This complex can be isolated as well-formed crystals from the aqueous solution obtained by adding uranyl nitrate hexahydrate to a warm solution of fumaric acid and lithium hydroxide in molar ratio UO_2^{2+}/fumaric acid/lithium hydroxide = 1:2:2.

Anal. Calc. for $UO_2(C_4H_2O_4)(H_2O)_2$ (%): C, 11.43; H, 1.43; U, 56.55. Found: C, 11.47; H, 1.44; U, 56.68.

Thermal Studies

Thermal analysis were carried out as reported previously [5]. DTA curves were obtained by using both high (1600 °C) and intermediate temperature (850 °C) cells. A heating rate of 10 °C min^{-1}, a static air atmosphere and pre-calcined alumina as reference material were used.

Crystal Data

$C_4H_6O_8U$, FW 420.11, monoclinic, $a = 9.952(3)$, $b = 7.502(2)$, $c = 5.571(2)$ Å, $\beta = 98.6(3)^\circ$, $U = 411.3$ Å^3, $D_c = 3.39$ g cm^{-3} for $Z = 2$. μMoKα = 0.7107 Å, μ(MoKα) = 188.8 cm^{-1}, space group $P2_1/n$.

The X-ray intensity data were collected on a four-circle Philips PW 1100 automated diffractometer with graphite monochromated MoKα radiation. The unit cell was determined on the basis of 20 strong reflections found by mounting the crystal at random, varying the orientation angles ϕ and χ in the range of 120° each with the detector position varying between $\theta = 6^\circ$ and $\theta = 10^\circ$. For the determination of precise lattice parameters 20 strong reflections with $8^\circ \leqslant \theta \leqslant 14^\circ$ were considered. Integrated intensities for hkl

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TABLE I. Atomic Coordinates ($\times 10^4$)^a and Anisotropic Temperature Factors^b ($\times 10^3$) with e.s.d.s in Parentheses.

	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U	0	0	0	15.6(3)	13.2(3)	15.1(3)	−4.3(3)	−0.2(2)	1.2(3)
O(1)	1105(8)	860(11)	−1913(14)	38(4)	24(4)	32(4)	2(4)	18(3)	−1(4)
O(2)	−1157(7)	2995(10)	582(13)	29(4)	22(4)	28(4)	−11(4)	−9(3)	8(3)
O(3)	798(7)	2394(10)	2810(13)	22(4)	22(4)	31(4)	−13(4)	−10(3)	11(3)
O(4)	1922(9)	−765(12)	3156(16)	33(5)	34(5)	33(5)	−12(4)	−17(4)	17(4)
C(1)	−273(11)	3371(13)	2373(19)	27(6)	8(5)	27(5)	−6(5)	1(5)	−8(4)
C(2)	−442(11)	4903(18)	3983(18)	27(5)	19(6)	25(5)	−1(5)	0(4)	6(5)
H(1)	258(17)	−121(22)	259(30)						
H(2)	209(15)	−92(21)	490(28)						
H(3)	−124(14)	590(20)	358(24)						

^{a}For hydrogen atoms ($\times 10^3$). ^{b}In the form $\exp[-2\pi^2 \Sigma U_{ij} a_i^* a_j^* h_i h_j]$.

reflections with k, l $\geqslant 0$ and $3° \leqslant \theta \leqslant 25°$ were measured using the $\theta/2\theta$ scan method with a scan speed of 1.8° min^{-1}, scan width of 1° and two background counts of 10 sec at each of the scans. Of the 862 reflections thus considered, the 555 having a net intensity greater than 3 σ (σ = standard error based on count statistics) were used in the structure determination and refinement. Every two hours, two standard reflections were monitored to check the crystal stability and only random fluctuations were noticed.

The values of I and $\sigma(I)$ were corrected for Lorentz and polarization effects and for absorption following the North *et al.* method [6].

Solution and Refinement of the Structure

There are two formula units per cell and the molecules lie on crystallographic inversion centres with the uranium atoms positions at 0, 0, 0 and ½, ½, ½ as result of the interpretation of the Patterson map. All other non-hydrogen atoms were located on difference Fourier maps. Refinement was then carried out by full matrix least-squares methods for positional and anisotropic parameters for all the non-hydrogen atoms. The scattering factor of the uranium was from ref. 7, whereas those of the other non-hydrogen atoms from ref. 8. The anomalous terms for uranium were taken from ref. 9. At this point (R = 0.025) a Fourier difference map showed no unusual features except some peaks which could be attributed to hydrogen atoms. These were introduced in a final least-squares refinement with fixed isotropic B values (5 Å^2) reducing the R value to 0.0235. (Unit weights were used through the refinement). The hydrogen scattering factors were from ref. 10.

The calculations were carried out on the CYBER 76 computer of the 'Centro di Calcolo Interuniversitario, Italia Nord Oreintale' with the SHELX 76 programs [11]. The positional and thermal parameters with their estimated standard deviations derived from the last cycle of least-squares are given in Table I. Observed and calculated structure factors are available from the authors.

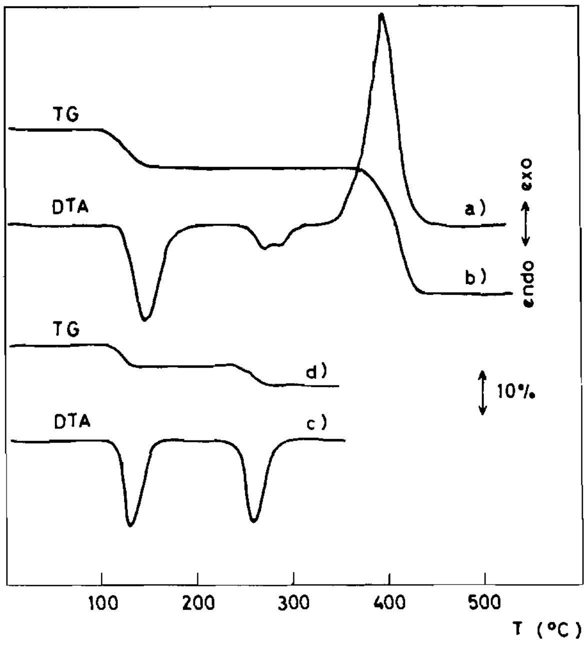

Fig. 1. DTA and TC curves (a) high temperature cell, (b) open crucible, (c) intermediate cell, (d) sealed crucible.

Results and Discussion

Thermal Analysis

The DTA curve (a) of diaquouranyl fumarate obtained in the high temperature cell is shown in Fig. 1. The thermogravimetric curve (b) shows two inflections, the first one being caused by the evolution of the two coordinated water molecules (calc. 8.5%, exp. 8.56%), and which corresponds to the

TABLE II. Bond Lengths (Å) and Angles (°) with e.s.d.s in Parentheses.

U–O(1)	1.764(7)	U–O(3)	2.436(7)
U–O(2)	2.567(7)	U–O(4)	2.466(8)
C(1)–O(2)	1.26(1)	C(1)–O(3)	1.29(1)
C(1)–C(2)	1.48(2)	C(2)–C(2)″	1.34(2)
C(2)–H(3)	1.09(14)	O(4)–H(1)	0.83(17)
		O(4)–H(2)	0.96(15)
O(1)–U–O(1)′	180.0	O(1)–U–O(2)	95.1(3)
O(1)–U–O(3)	86.9(3)	O(1)–U–O(4)	91.6(4)
O(2)–U–O(3)	51.9(2)	O(3)–U–O(4)	64.5(3)
O(4)–U–O(2)′	64.6(3)	H(2)–O(4)–H(1)	108(14)
U–O(2)–C(1)	91.3(6)	U–O(3)–C(1)	96.7(6)
O(2)–C(1)–C(2)	122(1)	O(3)–C(1)–C(2)	120(1)
O(2)–C(1)–O(3)	119(1)	C(1)–C(2)–C(2)″	119(1)
C(1)–C(2)–H(3)	124(7)		

Contacts

O(3)···H(1)‴	1.97(17)	O(3)···O(4)‴	2.78(1)
O(2)–O(3)	2.193(9)	O(3)···O(4)	2.62(1)
O(4)···O(2)′	2.69(1)		

Key for symmetry

none	x	y	z
primed	–x	– y	– z
double primed	1 – x	1 – y	1 – z
triple primed	½ – x	½ + y	½ – z

endothermic effect observed between 110–200 °C in the DTA curve. The decomposition of anhydrous fumarate produced the second mass loss observed in the TG curve (calc. 26.9%, exp. 26.89%). The second endothermic effect which appears between 225–300 °C does not correspond to any mass loss of the initial sample.

When differential thermal analysis was made with the intermediate (850 °C) Dupont cell (curve c), the area of this second endothermic peak increases considerably, and if a sealed crucible is used as sample holder two inflections can be observed in the TG curve in the temperature range 100–300 °C (curve d). The experimental mass-losses agree very well with those calculated, considering that the evolution of the two coordinated water molecules takes place in successive steps. (calc. 1st step: 4.28%, exp. 4.33%, calc. 2nd step: 4.47%, exp. 4.41%).

The X-ray powder pattern of uranyl fumarate dihydrate heated to 200 °C corresponds with that of uranyl fumarate monohydrate obtained as described by Müller [12].

It can be concluded that when a 'self-generated' water atmosphere exists, uranyl fumarate monohydrate is formed as an intermediate product, and dehydrates between 225–300 °C.

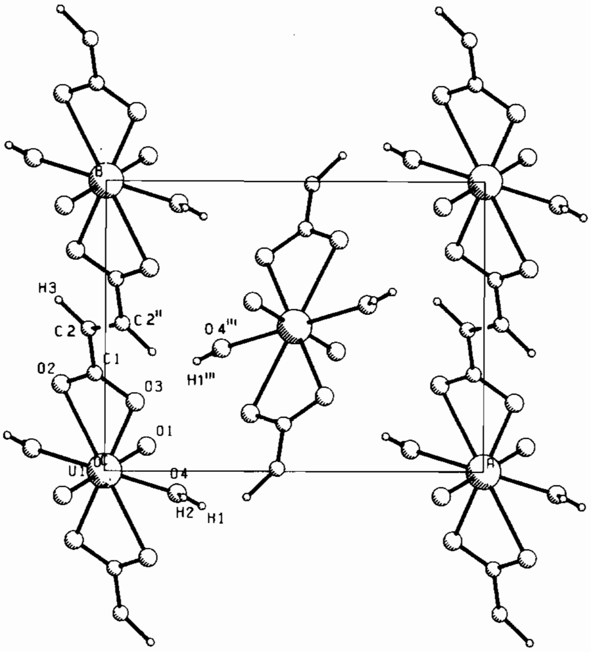

Fig. 2. Unit cell content viewed down *c*.

Crystal Structure

The structure is shown projected down c in Fig. 2. Bond distances and angles are listed in Table II. The uranium is eight-coordinate with the ligands in *trans* positions as required by space-group conditions, the uranium lying in a crystallographic inversion centre. In particular the linear uranyl ions are equatorially surrounded by two water oxygen and four carboxylate oxygen atoms forming an irregular hexagonal bipyramid. The deviations of the atoms coordinated to the uranium from their best mean plane are significant and are characteristic of a puckered structure (see Table III).

The fumarate ligand is chelated through O(2) and O(3) of one carboxylic group to one uranyl unit (having U at 0, 0, 0) and with the second carboxylic group centrosymmetrically related to the first one, to an adjacent uranyl unit (with U at 0, 1, 1).

The uranyl distance 1.764(7) is comparable to the value of 1.77(1) found in the heptacoordinate maleic acid derivative [1].

The U–O distances in the equatorial plane range between 2.436(7) and 2.567(7) Å, with a significant difference between the two extreme values (in this case represented by the two U–O distances in the carboxylic group). A similar situation has been found in the polymeric structure of the bis iminodiacetato dioxouranium(VI) [13] with values for the analogous distances of 2.53(1) and 2.58(1) Å, and it has been attributed to possible strain in the ligand shared between different uranium atoms (as in the present

TABLE III. Least-Squares Planes with Deviations (Å) of the Relevant Atoms. The Equation of the Planes in the Direct Space are in the Form: PX + QY + RZ = S.

	P	Q	R	S
Plane (1) O(2) –0.147, O(3) 0.155, O(4) –0.133	6.8987	2.9357	–3.9099	–
Plane (2) C(1) 0.001, C(2) –0.000, O(2) –0.000, O(3) –0.000	5.5433	4.4523	–3.6630	0.4793
Angle (°) between the two planes 14.1				

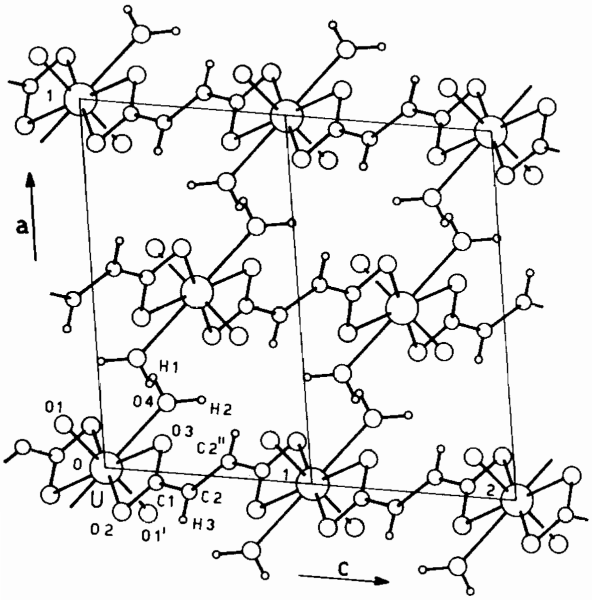

Fig. 3. Orientation of the uranyl fumarate chains viewed down *b*.

case). The equatorial coordination plane is far from planar (Table III), and the carboxylic group forms an angle of 14.1° with it.

The structure is polymeric-like, the U-ligand-U chains are shown in Fig. 3. There is a short intermolecular contact of 2.78 Å between O(3) and the O(4)''' of the water molecule at a distance of 1.97 Å with the water hydrogen H(1)'''. This suggests hydrogen bonding between the polymeric-chains.

A comparison of the structures of the compounds formed between the uranyl group and the dicarboxylic acids examined until now, *i.e.*, ammonium uranyl dimalonate monohydrate [2], strontium uranyldimalonate trihydrate [3], barium uranyldimalonate trihydrate [3], uranyl succinate monohydrate [4], potassium maleate hydrogen maleate dioxouranate(VI) [1], fumarate dioxouranium(VI) dihydrate and lithium glutarate hydrogenglutarate dioxouranate(VI) tetrahydrate [5], shows that all the structures are of polymeric type, which in turn suggests the following considerations.

The ligands form rings involving the carbon atoms in the chain only with malonic acid (3 carbon atoms in the chain) and maleic acid derivatives (*cis* structure of the free ligand 4 carbon atoms and a double bond in the chain). In these complexes the conformation of the free ligands favours the formation respectively of six- and seven-membered rings (including the uranium atom).

In the malonic acid derivatives [2, 3] polymeric chains are produced through a malonato group which is bidentate on one uranium atom and unidentate on an adjacent uranium atom, while in the maleic acid derivative [1] the polymeric chains are realized with the maleato ligand shared between three different uranium atoms. With succinic acid (4 carbon atoms in the chain) the *trans* configuration of the free ligand and the chain length allow the formation of polymeric chains, the ligand maintains its configuration and is shared by four different uranium atoms without any ring formation. In the compound with fumaric acid (present work) which has the same chain length as the previous one and the same *trans* configuration, the presence of the double C–C bond diminishes flexibility and the polymeric structure is simply given by the chelation of the two carboxylic groups on two opposite uranium atoms. With an aliphatic chain length of five carbon atoms (glutaric acid) [5] the polymeric structure is reached through the bridging of different uranium atoms by the carboxylic groups.

The presence of water molecules in the structures (whether or not coordinated to the uranyl groups) and the presence of ammonium cations generally determine the hydrogen bonding between the ligand–uranyl–ligand chains. Whether five or six oxygen atoms are coordinated in the uranyl equatorial plane is dictated by steric reasons: six coordination is found when the less hindered four membered rings are formed with the uranium (the carboxylic group acting as a chelate); as the size of the rings increases, only pentacoordination is possible.

TABLE IV. Comparison between some significant parameters in uranyl dicarboxylates compounds.

Compound	$U{-}O_{uranyl}$ (Å)	$U{-}O_{carboxylic}$ (Å)		$U{-}O_{water}$ (Å)	eq. geometry	size of the rings
$Sr(UO_2(C_3H_2O_4)_2 \cdot 3H_2O$ [3]	1.75(1) 1.78(1)	2.37(1) 2.37(1) 2.32(1) 2.36(1) 2.42(1)	av. 2.37		pentagonal	6-membered
$Ba(UO_2)(C_3H_2O_4)_2 \cdot 3H_2O$ [3]	1.73(2) 1.73(2)	2.33(2) 2.36(2) 2.31(2) 2.36(2) 2.38(2)	av. 2.35		pentagonal	6-membered
$NH_4(UO_2)(C_3H_2O_4)_2 \cdot H_2O$ [2]	1.77(1) 1.75(1)	2.41(1) 2.33(1) 2.32(1) 2.36(1) 2.39(1)	av. 2.36		pentagonal	6-membered
$UO_2(C_4H_4O_4) \cdot H_2O$ [4]	1.74(2)	2.37(2) 2.40(2)	av. 2.38	2.47(3)	pentagonal	no ring
$UO_2(C_4H_2O_4)K(C_4H_3O_4)$ [1]	1.77(1) 1.77(1)	2.43(2) 2.39(2) 2.39(2) 2.40(2) 2.37(2)	av. 2.40		pentagonal	7-membered
$UO_2(C_4H_2O_4) \cdot 2H_2O^a$	1.764(7)	2.567(7) 2.436(7)	av. 2.50	2.466(8)	hexagonal	4-membered
$UO_2(C_5H_6O_4)Li(C_5H_7O_4) \cdot 4H_2O$ [5]	1.68(2) 1.65(2)	2.46(2) 2.48(2) 2.51(2) 2.42(2) 2.45(2) 2.47(2)	av. 2.46		hexagonal	4-membered

[a] Present work.

Some significant parameters of the above mentioned compounds are summarized in Table IV. As expected the average equatorial U–O distances in the hexagonal equatorial geometries are significantly greater than those in the pentagonal ones, while no significant trend is noticed in the uranyl distances in relation to equatorial geometries and bonds.

Acknowledgements

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