Inorganica Chimica Acta, 184 (1991) 203–207

Mixed bidentate and bridging coordination by furoic acid in the X-ray structure of tris(furoato)bis(aquo)hydroxodioxouranium(VI) dihydrate

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(Received January 4, 1991)

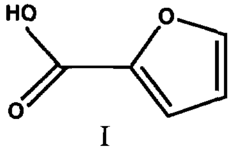
Abstract

X-ray diffraction study of the complex $[(UO_2)_2OH(C_5H_3O_3)_3(H_2O)_2]\cdot 2H_2O$ reveals a unique feature: the uranium(VI) atoms are present as hydroxo-bridged dimers which are linked through carboxylate ligands, to form infinite chains. One UO_2 group in the dimer is coordinated by two water molecules, two carboxylate oxygen atoms (bridging it to two adjacent UO_2 groups) and the hydroxo O atom. The second UO_2 group is coordinated by the hydroxo O atom, two bridging carboxylate oxygen atoms and a chelating bidentate furoate ion.

Introduction

The crystal structures of uranyl complexes with aliphatic monocarboxylic acids RCO_2H reveal an interesting general feature: small RCO_2H molecules tend to form infinite chains bridged by carboxylate oxygens coordinated to adjacent UO_2 groups. Such structures are found, for example, in uranyl formate monohydrate [1] and uranyl acetate [2]; however, the crotonate complex shows a monomeric structure with two bidentate crotonate molecules and two waters attached to UO_2, thus giving it hexagonal coordination [3].

All uranyl complexes with mono-basic aromatic acids studied hitherto also show monomeric structures [4]. It was therefore of interest to examine compounds with smaller rings, in which the tendency to chain formation might be enhanced. The uranyl complex with furoic acid (I) seemed to us to be a good candidate for such a study. Although the crystal structure of α-furoic acid itself is known [5], as are those of its complexes with Pr^{3+}, Y^{3+} [6] and Er^{3+} [7], its complexes with uranyl ion have not been examined in detail.



I

Experimental

The title compound was obtained by mixing warm aqueous solutions of uranyl acetate and α-furoic acid taken in the molar ratio 1:2. Upon evaporation of the solution at room temperature single crystals (brownish pillars) formed over a day. Their density determined by flotation was 2.66(5) g cm^{-3}. Our normal crystallographic techniques for data collection were employed [8], with structure solution by Patterson methods.

Results and discussion

The crystallographic data are: $[(UO_2)_2OH(C_5H_3O_3)_3(H_2O)_2]2H_2O$, $M_r = 962$, orthorhombic, $Pna2_1$, $a = 20.380(5)$, $b = 16.302(4)$, $c = 7.104(2)$ Å, $V = 2360.2(5)$ Å^3, $Z = 4$, $D_m = 2.707$, $D_x = 2.66(5)$ g cm^{-3}, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu = 131.4$ cm^{-1}, $T = 290$ K, $R = 0.0352$ for 1851 unique observed $(I/I(\sigma) \geq 2.0)$ reflections.

Reflections were processed using profile analysis to give 2256 unique reflections; 1851 were considered observed $(I/I(\sigma) \geq 2.0)$ 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 0.33 and 0.24.

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Final $R=0.035$ (0.047 for all data), $R_w=0.036$. Final atomic coordinates are given in Table 1, bond lengths and angles in Tables 2 and 3. Figure 1 shows a view of the molecule and Fig. 2 a projection of the unit cell down the b axis. Anisotropic temperature factors are given in Table 4; hydrogen atom coordinates and temperature factors appear in Table 5.

The structure of the title compound is polymeric with pentagonal bipyramidal coordination about the U atom. The bipyramids are linked into pairs by a common oxygen (O55) atom to form a dimer. However, these are bridged by furoic carboxylate groups to give infinite chains. The dimer exhibits a peculiar molecular network: one UO_2 group (U1) is coordinated by two water molecules, two carboxylate oxygens (bridging it to two adjacent UO_2 groups) and the hydroxo atom (O55). The second UO_2 (U2) group is coordinated by O55 and the two bridging carboxylate oxygens, and in addition by one bidentate furoic acid molecule. The mean pentagonal equatorial planes within the dimer make an angle of 37.1° to each other. The maximum and minimum deviations from the equatorial plane about U1 are +0.07 and −0.07 Å, respectively, with the O–O line of the UO_2 group making an angle of 179.4° to this plane. The corresponding data for the UO_2 (U2) plane are: +0.03 and −0.02 Å and 179.0°.

TABLE 1. Atom coordinates ($\times 10^4$) and temperature factors ($Å^2 \times 10^3$)

Atom	x	y	z	U^a
U(1)	−855.4(3)	7762.5(4)	7500.0	34(1)*
U(2)	1210.5(3)	7622.3(3)	7327.0(20)	28(1)*
O(101)	−604(8)	7959(8)	5179(22)	50(5)*
O(102)	−1075(8)	7605(9)	9862(25)	53(6)*
O(201)	1501(8)	7591(7)	9627(20)	43(5)*
O(202)	931(6)	7668(8)	5003(24)	44(5)*
O(11)	−351(5)	6456(7)	7441(40)	49(5)*
O(12)	−1570(7)	6641(9)	6323(29)	77(8)*
O(13)	−1879(6)	8368(8)	6911(27)	57(7)*
O(14)	−759(6)	9273(8)	8023(38)	68(9)*
O(21)	726(5)	6319(7)	7765(37)	46(5)*
O(22)	−2949(6)	8221(8)	6351(21)	41(5)*
O(23)	2127(7)	8554(7)	6440(23)	46(5)*
O(24)	1228(6)	9144(7)	7362(43)	46(4)*
O(55)	207(5)	8027(7)	8418(19)	29(4)*
O(111)	−545(7)	4806(9)	7589(58)	91(7)*
C(111)	149(8)	6048(10)	7592(62)	45(7)*
C(112)	61(8)	5145(11)	7776(34)	32(7)*
C(113)	541(8)	4596(10)	7805(51)	49(9)*
C(114)	261(14)	3834(16)	7884(49)	85(14)*
C(115)	−396(14)	3943(11)	7584(66)	94(13)*
O(211)	2753(7)	10040(9)	6068(24)	50(6)*
C(211)	1814(8)	9199(10)	6842(25)	27(6)*
C(212)	2116(10)	10024(12)	6653(32)	40(7)*
C(213)	1892(10)	10775(11)	6968(32)	43(8)*
C(214)	2419(11)	11318(12)	6529(35)	52(8)*
C(215)	2890(13)	10827(14)	6002(36)	60(9)*
O(311)	−1967(6)	10005(8)	6869(20)	44(5)*
C(311)	−2438(8)	8642(12)	6570(34)	42(7)*
C(312)	−2504(9)	9527(11)	6454(32)	38(6)*
C(313)	−2991(9)	10023(13)	5925(30)	39(7)*
C(314)	−2789(12)	10851(13)	6009(39)	60(9)*
C(315)	−2179(13)	10798(11)	6565(39)	64(10)*
O(001)	289(7)	10139(10)	8994(29)	65(7)*
O(002)	398(8)	8602(11)	11963(21)	72(7)*

[a] Starred items: equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 2. Bond lengths (Å)

U(1)–O(101)	1.756(16)	U(1)–O(102)	1.756(17)
U(1)–O(11)	2.365(11)	U(1)–O(12)	2.482(15)
U(1)–O(13)	2.345(13)	U(1)–O(14)	2.498(14)
U(1)–O(55)	2.302(10)	U(2)–O(201)	1.739(15)
U(2)–O(202)	1.748(17)	U(2)–O(21)	2.364(11)
U(2)–O(23)	2.489(13)	U(2)–O(24)	2.482(11)
U(2)–O(55)	2.285(11)	U(2)–C(211)	2.870(17)
U(2)–O(22a)	2.304(12)	O(11)–C(111)	1.221(20)
O(13)–C(311)	1.248(22)	O(21)–C(111)	1.264(20)
O(22)–C(311)	1.256(22)	O(22)–U(2a)	2.304(12)
O(23)–C(211)	1.263(21)	O(24)–C(211)	1.252(22)
O(111)–C(112)	1.359(23)	O(111)–C(115)	1.439(24)
C(111)–C(112)	1.489(24)	C(112)–C(113)	1.327(24)
C(113)–C(114)	1.369(31)	C(114)–C(115)	1.366(41)
O(211)–C(212)	1.363(25)	O(211)–C(215)	1.314(27)
C(211)–C(212)	1.486(26)	C(212)–C(213)	1.326(27)
C(213)–C(214)	1.425(29)	C(214)–C(215)	1.304(33)
O(311)–C(312)	1.377(23)	O(311)–C(315)	1.381(24)
C(311)–C(312)	1.451(27)	C(312)–C(313)	1.334(28)
C(313)–C(314)	1.411(31)	C(314)–C(315)	1.308(37)

Metal centres bridged by furoic acid groups are also found in the lanthanide complexes [6, 7] but in these structures the structural units are identical monomers, in contrast to the paired U atoms with different coordination found in the present structure.

The uranyl bond parameters fall in the normal range: U–O, mean 1.750(6) Å; and the O–U–O angle has a mean of 177.9(3)°. The U–O distances to the bridging carboxylate oxygens of furoic acid groups also show normal values — mean 2.345(20) Å, while the mean distance from the μ-hydroxo atom to the two adjacent uranium atoms is 2.293(9) Å, the U1–O55–U2 angle being 133.8(6)°. The two oxygen atoms of the water molecules are at 2.490(15) Å from U1; the mean U2–O bond distance to the bidentate carboxylate oxygens is 2.485(12) Å. The three furoic acid molecules show the usual geometry and dimensions, in fair agreement with the data reported earlier [5].

Each crystal water molecule is involved in a network of hydrogen bonds, as indicated by the interatomic distances listed below:

O001–O14 2.651 Å
–O24 2.765 Å

TABLE 3. Bond angles (°)

O(101)–U(1)–O(102)	176.9(7)	O(101)–U(1)–O(11)	91.2(8)
O(102)–U(1)–O(11)	89.8(8)	O(101)–U(1)–O(12)	89.4(7)
O(102)–U(1)–O(12)	93.7(7)	O(11)–U(1)–O(12)	65.5(5)
O(101)–U(1)–O(13)	90.9(7)	O(102)–U(1)–O(13)	90.3(7)
O(11)–U(1)–O(13)	139.7(5)	O(12)–U(1)–O(13)	74.2(5)
O(101)–U(1)–O(14)	86.4(7)	O(102)–U(1)–O(14)	91.3(8)
O(11)–U(1)–O(14)	148.9(4)	O(12)–U(1)–O(14)	145.3(5)
O(13)–U(1)–O(14)	71.4(4)	O(101)–U(1)–O(55)	87.6(6)
O(102)–U(1)–O(55)	89.8(6)	O(11)–U(1)–O(55)	76.4(4)
O(12)–U(1)–O(55)	141.7(4)	O(13)–U(1)–O(55)	143.9(4)
O(14)–U(1)–O(55)	72.5(4)	O(201)–U(2)–O(202)	178.9(6)
O(201)–U(2)–O(21)	89.5(7)	O(202)–U(2)–O(21)	91.5(7)
O(201)–U(2)–O(23)	90.0(6)	O(202)–U(2)–O(23)	88.9(6)
O(21)–U(2)–O(23)	153.5(4)	O(201)–U(2)–O(24)	90.9(8)
O(202)–U(2)–O(24)	88.4(8)	O(21)–U(2)–O(24)	154.7(5)
O(23)–U(2)–O(24)	51.8(4)	O(201)–U(2)–O(55)	89.7(6)
O(202)–U(2)–O(55)	90.9(5)	O(21)–U(2)–O(55)	80.9(4)
O(23)–U(2)–O(55)	125.6(4)	O(24)–U(2)–O(55)	73.8(5)
O(201)–U(2)–C(211)	89.6(6)	O(202)–U(2)–C(211)	89.3(5)
O(21)–U(2)–C(211)	179.1(4)	O(23)–U(2)–C(211)	26.0(4)
O(24)–U(2)–C(211)	25.8(5)	O(55)–U(2)–C(211)	99.5(4)
O(201)–U(2)–O(22a)	90.7(6)	O(202)–U(2)–O(22a)	89.1(6)
O(21)–U(2)–O(22a)	79.2(4)	O(23)–U(2)–O(22a)	74.3(4)
O(24)–U(2)–O(22a)	126.1(5)	O(55)–U(2)–O(22a)	160.1(4)
C(211)–U(2)–O(22a)	100.4(5)	U(1)–O(11)–C(111)	148.4(12)
U(1)–O(13)–C(311)	176.1(13)	U(2)–O(21)–C(111)	133.6(12)
C(311)–O(22)–U(2a)	154.8(15)	U(2)–O(23)–C(211)	94.1(10)
U(2)–O(24)–C(211)	94.7(10)	U(1)–O(55)–U(2)	133.8(6)
C(112)–O(111)–C(115)	101.8(17)	O(11)–C(111)–O(21)	126.6(16)
O(11)–C(111)–C(112)	116.5(15)	O(21)–C(111)–C(112)	116.6(16)
O(111)–C(112)–C(111)	120.1(15)	O(111)–C(112)–C(113)	113.5(16)
C(111)–C(112)–C(113)	125.5(15)	C(112)–C(113)–C(114)	107.7(18)
C(113)–C(114)–C(115)	106.5(21)	O(111)–C(115)–C(114)	109.5(21)
C(212)–O(211)–C(215)	103.3(17)	U(2)–C(211)–O(23)	59.9(9)
U(2)–C(211)–O(24)	59.5(8)	O(23)–C(211)–O(24)	119.3(15)
U(2)–C(211)–C(212)	178.0(13)	O(23)–C(211)–C(212)	121.6(16)
O(24)–C(211)–C(212)	119.1(15)	O(211)–C(212)–C(211)	116.1(16)
O(211)–C(212)–C(213)	111.2(17)	C(211)–C(212)–C(213)	132.7(19)
C(212)–C(213)–C(214)	106.1(18)	C(213)–C(214)–C(215)	103.7(18)
O(211)–C(215)–C(214)	115.7(22)	C(312)–O(311)–C(315)	104.3(16)
O(13)–C(311)–O(22)	125.8(18)	O(13)–C(311)–C(312)	116.9(17)
O(22)–C(311)–C(312)	117.3(16)	O(311)–C(312)–C(311)	118.4(16)
O(311)–C(312)–C(313)	108.0(16)	C(311)–C(312)–C(313)	133.5(18)
C(312)–C(313)–C(314)	110.6(18)	C(313)–C(314)–C(315)	103.1(19)
O(311)–C(315)–C(314)	114.0(19)		

O002–O55 2.716 Å
–O202 2.857 Å
–O001 2.872 Å

The O12 (coordinated water molecule) to O23 (carboxylate) distance (2.676 Å) indicates the presence of another hydrogen bond here.

To maintain the charge balance one proton per dimer is necessary. Since it was not possible to locate it by experiment it is suggested that it is attached to the bridging oxygen atom (O55). It is noteworthy that the structure of $UO_2(NO_2)_2(proline)_2$, a compound which also contains a five-membered cyclic ligand with a carboxylic group attached to it in the α-position, exhibits a different molecular pattern [9]. It is monomeric with hexagonal coordination about the UO_2 group. Oxygens are donated by two bidentate nitrate groups and by two monodentate carboxylate

TABLE 4. Anisotropic temperature factors ($\AA^2 \times 10^3$)

Atom	*U*(11)	*U*(22)	*U*(33)	*U*(23)	*U*(13)	*U*(12)
U(1)	21.7(3)	27.9(3)	53.0(5)	5.0(7)	4.1(6)	1.5(2)
U(2)	20.2(3)	22.6(3)	41.2(4)	1.5(6)	−3.1(5)	0.6(2)
O(101)	54(8)	42(8)	54(10)	3(8)	−6(8)	−13(7)
O(102)	44(8)	55(9)	60(11)	15(9)	17(8)	16(7)
O(201)	67(10)	39(7)	23(8)	6(6)	−12(7)	9(7)
O(202)	28(7)	47(9)	56(11)	−1(8)	5(8)	6(6)
O(11)	32(6)	39(7)	77(10)	30(14)	16(14)	8(5)
O(12)	33(8)	41(8)	158(20)	−28(10)	−13(10)	0(7)
O(13)	38(7)	31(7)	101(19)	−15(9)	−10(8)	3(6)
O(14)	33(7)	38(7)	133(24)	−20(11)	−8(10)	8(5)
O(21)	27(6)	29(6)	81(13)	6(10)	−3(10)	−8(4)
O(22)	26(7)	35(7)	62(10)	−4(7)	6(7)	1(6)
O(23)	34(7)	24(7)	79(11)	7(7)	13(8)	−7(6)
O(24)	38(6)	28(6)	72(9)	4(14)	4(13)	1(5)
O(55)	28(6)	21(6)	39(7)	2(6)	1(6)	6(5)
O(111)	74(9)	71(10)	127(17)	29(23)	−15(21)	−27(9)
C(111)	44(10)	34(9)	57(15)	29(18)	−6(15)	1(8)
C(112)	32(8)	42(10)	22(15)	3(9)	4(10)	−9(7)
C(113)	31(8)	30(8)	87(24)	−14(15)	−20(15)	10(7)
C(114)	140(26)	55(14)	60(29)	4(15)	9(21)	27(16)
C(115)	144(25)	24(9)	112(26)	−1(21)	−87(33)	−24(13)
O(211)	47(9)	45(9)	57(11)	11(8)	10(8)	−16(7)
C(211)	24(10)	25(9)	31(12)	6(7)	−8(7)	−14(8)
C(212)	33(11)	37(11)	50(14)	7(10)	−3(10)	−17(10)
C(213)	54(12)	26(9)	50(19)	13(10)	2(10)	7(8)
C(214)	72(17)	17(9)	66(16)	12(10)	−17(14)	−24(11)
C(215)	76(17)	46(14)	60(17)	28(13)	−19(15)	−26(14)
O(311)	45(8)	32(7)	54(12)	9(7)	6(7)	−11(6)
C(311)	10(9)	42(11)	75(16)	−2(11)	11(10)	−6(8)
C(312)	32(10)	28(9)	53(13)	−1(10)	3(11)	0(9)
C(313)	25(10)	55(13)	36(13)	−5(10)	−8(9)	0(9)
C(314)	61(15)	39(13)	78(20)	7(13)	−3(14)	8(12)
C(315)	88(18)	10(9)	95(21)	0(11)	10(16)	6(11)
O(001)	55(9)	55(10)	87(15)	−12(10)	10(9)	4(8)
O(002)	101(13)	78(12)	36(14)	−5(8)	9(8)	32(10)

The anisotropic temperature factor exponent takes the form: $-2\pi^2(h^2a^{*2}U(11)+k^2b^{*2}U(22)+\ldots+2hka^*b^*U(12))$.

TABLE 5. H atom coordinates ($\times 10^4$) and temperature factors ($\AA^2 \times 10^3$)

Atom	*x*	*y*	*z*	*U*
H(11a)	1003	4712	7774	70
H(11b)	483	3324	8111	70
H(11c)	−708	3508	7421	70
H(21a)	1463	10924	7408	70
H(21b)	2427	11906	6603	70
H(21c)	3308	11028	5584	70
H(31a)	−3420	9841	5556	70
H(31b)	−3038	11333	5707	70
H(31c)	−1906	11270	6764	70

groups. Such a coordination scheme indicates the very strong affinity of nitrate anions towards the UO_2^{2+} ion, which inhibits formation of polymeric networks.

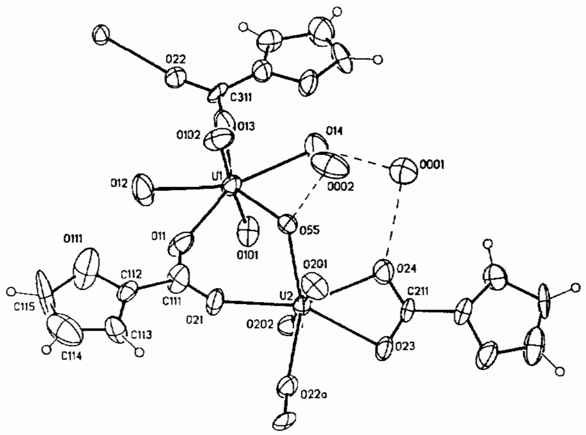

Fig. 1. View of the two distinct units of the uranyl furoate complex, showing the numbering of the principal atoms.

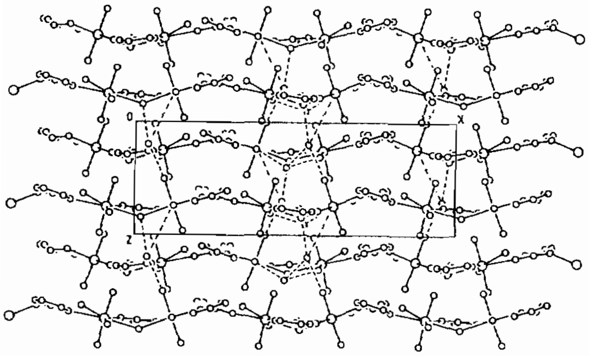

Fig. 2. Packing diagram, viewed down *b*, showing the H-bonding network.

Acknowledgements

One of us (J. L.) wishes to thank the British Council for a fellowship.

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