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The Crystal and Molecular Structure of Uranyl Oxalate Trihydrate

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Uranyl oxalate trihydrate, $UO_2C_2O_4.3H_2O$, crystals are monoclinic with lattice parameters $a=5\cdot623$ (5), $b=17\cdot065$ (2), $c=9\cdot451$ (3) Å and $\beta=98\cdot74$ (1)°. The space group is $P2_1/C$ with $Z=4$. 513 visually estimated reflexions were corrected for absorption and the structure refined by Fourier and least-squares methods to $R=0\cdot079$. Each uranium atom exists as a linear $(O-U-O)^{2+}$ ion with five secondary oxygen atoms coordinated to it in a perpendicular plane. The average distances are $U-O_I=1\cdot63$ (4) and $U-O_{II}=2\cdot49$ (4) Å. The oxalate groups are planar and tetradentate, each bridging two uranyl ions. Only one water molecule is coordinated to the uranium atom. The structure is consistent with the thermal behaviour of the compound.

Introduction

Several oxalato complexes of dioxouranium(VI) with varying uranium to oxalate ratios are known, but no detailed structural work has been reported. The fact that an anhydrous ammonium salt of $[UO_2(C_2O_4)_3]^{4-}$ was isolated was interpreted to show that in oxalato complexes the uranyl ion requires six ligands in a plane for coordination saturation (Chernyaev, 1966). In the bisoxalatodioxouranate(VI) complexes two water molecules are assumed to complete the hexagonal arrangement. But substitution reactions on bisoxalato complexes (Shchelokov & Belomestnykh, 1969) have indicated a pentagonal coordination for the uranyl ion, which is sterically and geometrically stable in a plane (Evans, 1963). We have initiated detailed structural investigation of solid oxalate complexes by the method of single-crystal X-ray diffraction. The crystal and molecular structures of uranyl oxalate trihydrate are discussed here.

Preparation

A hot saturated solution of oxalic acid was added to a concentrated solution of pure uranyl nitrate in $1\cdot0M$ nitric acid at 80°C. The crystals separated on standing and were washed with water, alcohol and ether. Chemical and thermal analysis confirmed the composition $UO_2C_2O_4.3H_2O$.

Crystallography

The crystal data are shown in Table 1. The cell dimensions are the same as those reported by Jenkins, Moore & Waterman (1965). However, two reflexions, 003 and 201, in their data are wrongly indexed. These could be re-indexed as 122 and $\overline{1}52$ respectively without affecting the cell constants derived by them. In the single-crystal Weissenberg photographs, the $h+k$ odd reflexions are generally weak, but the only extinctions are $h0l$: l odd, and $0k0$: k odd, the space group thus being uniquely determined as $P2_1/C$ in agreement with early goniometric measurements of Staritzky & Cromer (1956).

Table 1. Crystal data

Standard deviations given in parentheses refer to the last figure.

$a=$ 5·623 (5) Å	D_m = 3·07 (1) g.cm^{-3}
$b=$ 17·065 (2)	D_c = 3·05
$c=$ 9·451 (3)	V = 896 Å^3
$\beta=$ 98·74 (1)°	Z = 4

Space group $P2_1/c$. Systematic absences: $0k0$, k odd and $h0l$, l odd.

The diffraction data were photographed on three films using the equi-inclination multiple-film method using copper $K\alpha$ radiation. Crystal A of approximate dimensions $0.03 \times 0.008 \times 0.008$ cm was used to photograph layer lines hkn ($n=0,1,2$) while crystal B of approximate dimensions $0.012 \times 0.005 \times 0.005$ cm was used for nkl ($n=0,1,2$) layer-line data.

The intensities were estimated visually. Standard errors σ were assigned to each intensity and weights $w=1/\sigma^2$, were used in the final stages of the refinement. Greater weights were given to reflexions which could be measured on all three films than to those which could be measured on only one or two films. Thus $\sigma=0.05F_{obs}$ if $100 < F_{ob_1} < 250$; $\sigma=0.08F_{obs}$ if $50 < F_{obs} < 100$ or $250 < F_{obs} < 300$ and $\sigma=0.10F_{obs}$ if $300 < F_{obs}$ or $F_{obs} < 50$. Unobserved reflexions were given an intensity equal to half the local minimum observed intensity with $\sigma=0.50F_{obs}$ and were included in the least-squares analysis only if $F_{calc} \geq 0.5F_{obs}$.

Structure solution and refinement

The measured intensities were reduced to structure factors after applying the necessary Lorentz and polarization corrections. All the data obtained with crystal A were also corrected for absorption assuming the crystal was a cylinder of radius 0·004 cm ($\mu R=2.52$). Crystal B data were not corrected for absorption.

Separate Patterson functions of the two zero-layer intensities showed that the uranium atom was at (0·27, 0·067, 0·260). Structure factors calculated with the uranium atom at this position and an isotropic temperature factor of 0·5 gave an overall R_1 value $[\sum(F_{obs} - |F_{calc}|)/\sum F_{obs}]$ of 0·24 for the scaled reflexions. Further, the uranium atom position was such that its contribution for $h+k$ odd reflexions was negligible, in agreement with the observed intensity distribution. A three-dimensional difference Fourier synthesis using the heavy-atom phases showed five oxygen atom positions. Repeated structure-factor calculations with an increasing number of atoms located from Fourier maps led to the remaining oxygen and carbon atom positions.

The atomic positions and the isotropic temperature factors of all atoms were refined by the least-squares method using the program $ORFLS$ (Busing, Martin & Levy, 1962) on a CDC-3600 computer until a minimum R_2* of 0·12 was reached. The scattering factors for U^{2+} were derived from U^0 and U^{3+} data of Cromer & Waber (1965), while those for oxygen and carbon were from International Tables for X-ray Crystallography (1962). The uranium temperature factor was converted to anisotropic factors and refinement continued until the minimum of $R_1 = 0.079$ and $R_2 = 0.085$ was reached. The atomic coordinates are listed in Table 2 and the corresponding structure factors compared with the observed values in Table 3. In the final cycle of refinements all parameter changes were less than 0·2 of its standard deviation. A difference synthesis based on the data in Table 3 had no peaks that could be ascribed to any atom.

* $R_2=[\sum w(F_{obs}^2 - |F_{calc}|^2)/\sum w\ F_{obs}^2]^{1/2}$

Table 2. Atomic parameters

	x	y	z	B
U	0·27136 (22)	0·06735 (9)	0·25796 (13)	*
O(1)	0·4905 (71)	0·0516 (22)	0·3864 (48)	2·3
O(2)	0·0505 (71)	0·0871 (21)	0·1309 (47)	2·0
O(3)	0·3630 (52)	−0·0429 (18)	0·1261 (35)	1·5
O(4)	0·5550 (54)	0·0781 (20)	0·0780 (40)	2·0
C(1)	0·4512 (75)	−0·0417 (26)	0·0105 (50)	3·1
O(5)	0·0531 (50)	−0·0430 (18)	0·3509 (34)	2·0
O(6)	−0·0213 (55)	0·0918 (21)	0·4391 (41)	2·4
C(2)	0·0198 (70)	−0·0396 (22)	0·4686 (39)	3·2
O(7)	0·3226 (44)	0·2087 (15)	0·2912 (30)	1·3
O(8)	0·6769 (60)	0·2761 (20)	0·4818 (42)	2·7
O(9)	0·9674 (42)	0·3018 (16)	0·2373 (30)	2·6

* Anisotropic temperature factors

β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
0·0038 (5)	0·0017 (1)	0·0058 (3)	0·0006 (2)	−0·0014 (6)	0·0001 (1)

Table 3. *Observed and calculated structure factors* (× 10)

Unobserved reflexions are marked with an asterisk.

H K L = 0

H	K		FOBS	FCALC
1	0		448	-327
2	0		2176	-1904
3	0		1693	1793
4	0		2333	2289
5	0		1180	-1262
6	0		1093	-1065
0	2		3046	3077
0	6		3180	-3226
0	8		3120	-3355
0	10		1007	-1007
0	12	*	272	278
0	14		1514	1473
0	16		1050	971
1	1		1823	-1215
1	2		404	-308
1	3		3249	-2882
1	4	*	298	-188
1	5		2109	-2199
1	6	*	349	344
1	7		489	-344
1	8	*	346	273
1	9		1690	1698
1	10	*	354	361
1	11		2036	2063
1	13		1263	1272
1	14	*	459	-305
1	17		1121	-1086
2	1		458	304
2	2		1333	-1154
2	3		526	471
2	4	*	317	174
2	5		551	420
2	6		2002	1819
2	7	*	344	237
2	8		1934	1881
2	9	*	388	-469
2	10		865	923
2	11	*	421	-398
2	12		787	-685
2	13	*	459	-399
2	14		1649	-1631
2	16		1033	-1197
3	1		1262	1244
3	2	*	361	491
3	3		2702	2544
3	5		2263	2235
3	6		833	-882
3	7		683	645
3	8		956	-986
3	9		1033	-1143
3	11		1492	-1568
3	13		1204	-1096
4	1		421	-473
4	2		1422	1450
4	3		995	-1189
4	5		803	-890
4	6		1478	-1560
4	8		1797	-1738
4	9		666	771
4	10		803	-672
5	1		701	-530
5	2		748	-717
5	3		1562	-1476
5	5		1138	-1228
5	6		962	976
6	1		617	609
6	2		978	-876
6	3		1076	1190
6	5		1040	1088
6	6		939	897

H K L = 1

H	K		FOBS	FCALC
0	4		3123	-3336
0	6		1210	-1328
0	8		1306	1140
0	9	*	374	251
0	10		2065	2196
0	12		1847	1884
0	14	*	461	373
0	16		847	-792
1	1		4267	-4095
1	2		923	655
1	3		1059	-1107
1	4	*	313	306
1	5		1332	1268
1	6		937	1076
1	7		2939	2103
1	9		1832	1867
1	11	*	405	366
1	12	*	413	-389
1	13		1030	-1011
1	14	*	475	-286
1	15		1461	-1329
2	1		433	603
2	2		1848	1636
2	4		2105	1960
2	5	*	356	-435
2	6		1460	1378
2	7		681	-732
2	8	*	380	-419
2	9		557	-431
2	10		1739	-1755
2	12		1609	-1552
2	13	*	464	488
2	14		662	-730
2	15	*	476	545
2	16		722	709
2	19		1042	1061
3	1		1827	1925
3	2		982	-837
3	3		561	611
3	4		1016	-935
3	5		1244	-1145
3	6	*	398	-382
3	7		2033	-1993
3	8		693	537
3	9		1229	-1357
2	10		682	674
4	1		1432	-1651
4	2		1512	-1695
4	4		2429	-2394
4	5		634	515
4	6		1162	-1013
4	7		1304	1439
4	9		706	831
4	10		1289	1396
5	1		1483	-1501
5	2		1186	1022
5	3		549	-459
5	4		1103	1205
5	5		803	720
5	6		703	704
5	7		1392	1370
6	1		1175	1063
6	2		835	752
6	3	*	424	342
6	4		988	1065
-1	1		692	654
-1	5		1175	-1229
-1	6	*	343	334
-1	7		2615	-2716
-1	9		1867	-1819
-1	10	*	398	-232
-1	13		1307	1288
-1	15		1823	1712
-2	1		637	-792
-2	2		2735	2626
-2	4		2735	2639
-2	6		2154	2165
-2	7		663	652
-2	8		644	-579
-2	9	*	403	393
-2	10		1549	-1581
-2	12		1581	-1624
-2	14		914	-696
-3	1		2286	-2175
-3	2		612	-570
-3	3		726	-676
-3	4		688	-719
-3	5		1308	1380
-3	7		2033	1973
-3	8	*	436	388
-3	9		1308	1411
-3	10	*	479	615
-4	1		1015	986
-4	2		1342	-1360
-4	4		1825	-1829
-4	5	*	464	-401
-4	6		846	-981
-4	7		945	-1049
-4	8	*	494	399
-4	9		632	-515
-4	10		1247	1272
-5	1		1504	1500
-5	2		1106	1002
-5	3		553	495
-5	4		967	1056
-5	5		798	-747
-5	6		781	812
-5	7		1364	-1376
-6	1		1117	-987
-6	2		984	997
-6	3	*	404	-313
-6	4		1361	1288

H K L = 2

H	K		FOBS	FCALC
0	2		1745	-1567
0	4	*	315	336
0	5	*	399	396
0	6		1804	1912
0	7	*	356	236
0	8		2543	2585
0	10		739	773
0	12	*	452	-844
0	13	*	483	-284
0	14		1705	-1639
0	16		1275	-1321
1	0		551	391
1	1		1478	1439
1	2		586	477
1	3		2270	2379
1	4	*	346	-252
1	5		2015	2036
1	6		605	-540
1	8	*	437	-434
1	9		1505	-1682
1	11		1876	-1931
1	13		1023	-1097
1	14	*	464	415
1	17		1074	1009
2	0		2786	3013
2	1		1054	-1019
2	2		2388	2386
2	3		728	-805
2	5		1080	-1131
2	6		2021	-1976
2	8		2232	-2196
2	9		776	684
2	10		1163	-1239
2	11		655	518
2	12	*	475	404
2	13	*	515	509
2	14		1181	1163
2	15		1048	880
3	0		1393	-1379
3	1		1094	-943
3	2		739	-709
3	3		2245	-2051
3	5		1974	-1842
3	6		853	899
3	7		625	-524
3	8		1005	1145
3	9		1082	1069
3	11		1659	1590
4	0		1792	-1884
4	1		723	623
4	2		925	-1149
4	3		1115	1179
4	4	*	448	334
4	5		1213	1060
4	6		1512	1487
4	8		1512	1505
5	0		1484	1630
5	2		1168	1147
5	3		1510	1599
5	5		1265	1198
5	6		1122	-1110
6	0		1225	1070
6	1		675	-620
6	2		854	798
6	3		1301	-1246
-1	3		2878	-3052
-1	5		3008	-3240
-1	7		848	-926
-1	9		1331	1275
-1	11		1912	1862
-1	13		1418	1458
-2	0		3158	3031
-2	1		497	396
-2	2		2124	2076
-2	4		684	-696
-2	5	*	380	374
-2	6		2179	-2365
-2	8		1999	-2139
-2	9	*	418	-264
-2	10		838	-696
-2	11	*	458	-240
-2	12		800	626
-2	14		1404	1455
-3	0		856	-874
-3	1		1331	1151
-3	2	*	394	-394
-3	3		2241	1930
-3	5		1959	1801
-3	6	*	425	400
-3	7	*	425	320
-3	8		712	757
-3	9		1104	-1258
-3	11		1623	-1510
-4	0		2139	-1894
-4	1	*	433	-402
-4	2		1191	-1106
-4	3		743	-726
-4	5		763	-874
-4	6		1471	1248
-4	8		1791	1625
-4	9	*	525	410
-4	10		672	705
-5	0		999	909
-5	1	*	478	-576
-5	2		694	574
-5	3		1411	-1619
-5	5		1216	-1317
-5	6		837	-785
-6	0		1293	1265
-6	1		562	580
-6	2		959	887
-6	3		909	940

K L H = 0

K	L		FOBS	FCALC
0	2		2802	-2908
0	4		2877	2591
0	6		1878	-2063
0	8		1516	1662
0	10		990	-1012
2	3		1720	1755
4	3		2411	2555
5	3	*	296	260
6	3		1584	1720
7	3		664	-639
9	3	*	328	-209
10	3		1416	-1477
11	3	*	339	-256
12	3		1913	-1905
14	3		592	-621
15	3	*	426	285
16	3	*	465	468
1	4	*	282	-222
2	4		1157	993
3	4	*	302	-323
5	4	*	372	-374
6	4		1751	-1701
8	4		1878	-1981
9	4	*	349	349
10	4		862	-811
11	4	*	377	[illegible]
12	4	*	386	-372
13	4	*	402	[illegible]
14	4		1456	1435
1	4		678	-620
2	5		1716	-1799
4	5		2275	-2514
5	5	*	342	291
6	5		1086	-1113
7	5		704	573
8	5	*	351	374
9	5	*	372	315
10	5		1467	1469
12	5		1474	1385
1	6		530	464
2	6		1273	-1230
3	6		542	543
4	6	*	343	435
5	6	*	351	499
6	6		1553	1535
[illegible]	6		1584	1652
1	7		878	721
2	7		1183	1312
4	7		1913	1828
6	7		1015	916
1	8	*	367	-200
2	8		1055	1035
3	8		675	-718
5	8		679	-643
6	8		1121	-1041
1	9	*	338	-471
2	9		806	-694
4	9		1159	-1085
1	10	*	336	262
2	10		715	-712

K L H = 1

K	L		FOBS	FCALC
1	3		2441	2255
2	3		820	-799
3	3		719	650
4	3		527	-463
5	3		1118	-1166
6	3	*	379	-498
7	3		2181	-2199
8	3	*	431	400
9	3		1556	-1450
10	3	*	466	578
12	3	*	505	316
13	3		1153	1065
15	3		1429	1461
16	3	*	525	-366
0	4		1115	-1069
1	4		817	-733
2	4		417	-413
3	4		2488	-2286
5	4		2027	-2010
6	4		722	908
7	4		591	-676
8	4		626	828
9	4		1007	868
11	4		1836	1709
13	4		1072	1135
14	4	*	533	-566
1	5		2389	-2017
2	5		809	863
3	5		683	-591
4	5		579	565
5	5		1047	837
6	5		876	638
7	5		2035	1940
8	5		506	-506
9	5		1169	1341
10	5		635	-595
13	5		902	-908
15	5		1169	-1169
0	6		1204	1127
1	6		885	839
2	6		796	858
3	6		2310	2126
5	6		1756	1757
6	6		655	-787
7	6	*	431	291
8	6		820	-844
9	6		892	-863
10	6	*	479	-367
11	6		1304	-1442
1	7		1421	1514
2	7		654	-763
3	7	*	368	372
4	7		644	-722
5	7		941	-1035
6	7	*	390	-474
7	7		1258	-1419
8	7	*	431	413
9	7		820	-975
10	7	*	494	595
0	8		990	-951
1	8		506	-473
2	8		[illegible]	-567
3	8		1354	-1501
5	8		1179	-1160
6	8		750	711
8	8		725	694
9	8	*	446	590
10	8	*	503	420
11	8		1079	1063
1	9		863	-1040
[illegible]	9		[illegible]	648
[illegible]	9	*	[illegible]	-351
[illegible]	[illegible]		[illegible]	751
5	9		446	463
5	9	*	331	475
7	9		1016	964
0	10		574	451
2	10	*	437	379
3	10		877	758
5	10		702	574

K L H = 2

K	L		FOBS	FCALC
1	3		1115	-1010
2	3		1867	-2208
4	3		1865	-2099
5	3		575	734
6	3		1178	-1288
7	3		1178	1120
8	3		760	907
9	3	*	420	375
10	3		1517	1698
12	3		1360	1456
13	3		664	-706
14	3	*	494	397
15	3	*	512	-571
16	3		645	-644
0	4		2301	-2493
1	4		889	017
2	4		1938	-1799
3	4		1433	1287
4	4	*	361	411
5	4		930	996
6	4		1832	1949
8			181	1 066
9	4		962	-816
10	4		863	846
11	4		695	-704
12	4	*	494	-658
13	4	*	505	-512
14	4		1150	-1168
1	5		1726	1153
2	5		1626	1545
3	5	*	400	390
4	5		1991	2048
5	5		732	-578
6	5		982	1041
7	5		1073	-1058
8	5	*	481	-265
9	5		695	-731
10	5		1592	-1417
12	5		1039	-116
13	5		684	555
14	5		541	-484
0	6		1691	1521
1	6		771	-658
2	6		1419	1252
3	6		941	-823
4	6	*	325	-191
5	6		1086	-963
6	6		1354	-1238
7	6	*	418	-263
8	6		1373	-1317
9	6		607	625
10	6		766	-772
11	6		732	718
12	6	*	475	439
1	7		981	-1077
2	7		1149	-1072
3	7	*	462	-464
4	7		1369	-1363
5	7	*	476	508
6	7		759	-784
7	7		799	940
8	7	*	484	264
9	7		770	788
10	7		971	966
0	8		951	-981
1	8		381	416
2	8		762	-817
3	8		724	848
4	8	*	424	271
5	8		673	628
6	8		847	930
8	8		855	885
1	9		956	922
2	9		783	774
3	9	*	439	337
4	9		1075	1098
0	10		723	783
1	10		497	-450
2	10		634	626

Results and discussion

The (010) projection of the unit cell is shown in Fig. 1, where the numbering of the atoms corresponds to that used in Table 2. Table 4 gives all chemically relevant bond distances and bond angles, while Table 5 lists all intermolecular interatomic non-bonded distances less than 3·0 Å.

The uranium atoms exist in the crystal as linear uranyl groups. The average U–O distance of 1·63 (4) Å and the O–U–O angle of 178 (2)° are within the range
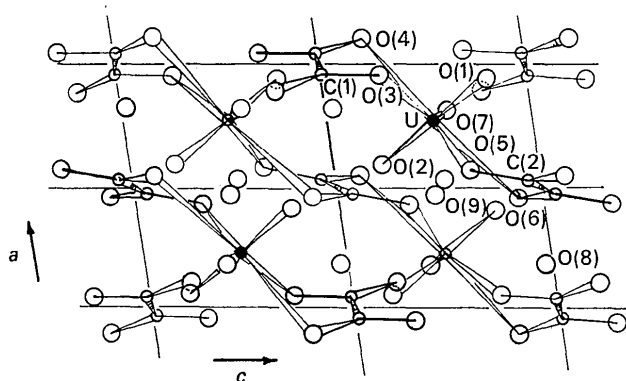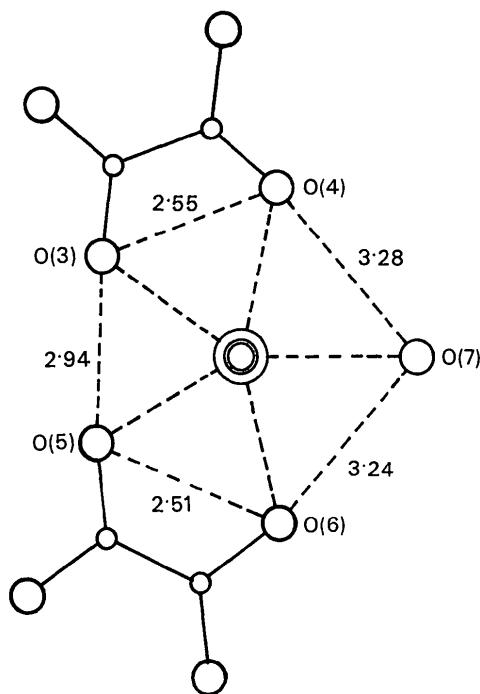

Fig. 1. (010) projection of the unit cell.

Fig. 2. Schematic drawing of the uranyl coordination. The O–U–O axis is perpendicular to the plane of the paper. O(7) is the oxygen atom of the single water molecule coordinated to the uranium atom. The O–O contact distances in Å are shown.

Table 4. Bond distances and bond angles

The superscripts refer to the atoms generated by (i) $1-x$, $-y$, $-z$ and (ii) $-x$, $-y$, $1-z$

Bond distances (Å)

U–O(1)	1·62 (4)	C(1)–O(3)	1·27 (6)
U–O(2)	1·63 (4)	C(1)–O(4^i)	1·15 (6)
U–O(3)	2·38 (4)	C(1)–C(1^i)	1·55 (6)
U–O(4)	2·52 (4)	C(2)–O(5)	1·16 (6)
U–O(5)	2·48 (3)	C(2)–O(6^{ii})	1·25 (6)
U–O(6)	2·56 (4)	C(2)–C(2^{ii})	1·51 (6)
U–O(7)	2·44 (3)		

Bond angles (°)

O(1)–U–O(2)	178 (2)	O(3)—U—O(4)	63 (1)
O(1)–U–O(3)	93 (2)	O(3)—U—O(5)	75 (1)
O(1)–U–O(4)	92 (2)	O(6)—U—O(5)	60 (1)
O(1)–U–O(5)	88 (2)	O(6)—U—O(7)	80 (7)
O(1)–U–O(6)	91 (2)	O(4)—U—O(7)	82 (1)
O(1)–U–O(7)	90 (2)	O(3)—C(1)–O(4^i)	130 (4)
O(2)–U–O(3)	89 (2)	O(3)—U—C(1^i)	108 (4)
O(2)–U–O(4)	88 (2)	O(4^i)–C(1)–C(1^i)	121 (4)
O(2)–U–O(5)	93 (2)	O(5)—C(2)–O(6^{ii})	130 (4)
O(2)–U–O(6)	88 (2)	O(5)—U—C(2^{ii})	119 (4)
O(2)–U–O(7)	88 (2)	O(6^{ii})–C(2)–C(2^{ii})	111 (4)

Table 5. Intermolecular interatomic distances less than 3·0 Å

The superscripts refer to the following transformations:
(iii) $1-x$, $-y$, $1-z$ (iv) $-x$, y, z
(v) x, $\frac{1}{2}-y$, $z-\frac{1}{2}$ (vi) $-x$, $y-\frac{1}{2}$, $\frac{1}{2}-z$
(vii) x, $\frac{1}{2}-y$, $\frac{1}{2}+z$

O(1)–O(1^{iii})	2·77 (5) Å
O(2)–O(4^{iv})	2·76 (5)
O(4)–O(8^v)	2·62 (5)
O(5)–O(9^{vi})	2·78 (4)
O(6)–O(1^{iv})	2·80 (5)
O(7)–O(8)	2·73 (4)
O(7)–O(9)	2·54 (4)
C(2)–O(1^{iii})	2·89 (5)

of values observed in uranyl complexes of similar co-ordination (Åberg, 1969).

The most noticeable feature of the structure is the tetradentate nature of the oxalate groups. Each oxalate group acts as a bridge between two uranyl ions using all the four oxygen atoms for coordination. The oxalate groups occupy centrosymmetric positions and are planar. Recently such tetradentate oxalate groups have been reported to be present in $(NH_4)_2(UO_2)_2(C_2O_4)_3$ (Alcock, 1968) and $K_4Th(C_2O_4)_4.4H_2O$ (Akhtar & Smith, 1969) and are probably responsible for the ready formation of a large number of stable actinide oxalate complexes.

There are two oxalate groups associated with the uranyl ion, each using two oxygen atoms for coordination. One of the three water molecules is also coordinated to the uranyl group through the oxygen atom, thereby making the uranium atom seven coordinated. The five individual U–O distances are not significantly different from the average value of 2·49 (4) Å. The five

oxygen atoms and the uranium atom form a plane,

$$0.6688X - 0.1679Y + 0.7243Z = 2.2837$$

(where X, Y and Z correspond to the a, b and c^* axes respectively) which is perpendicular to the O–U–O axis. The individual deviations in Å of the atoms from the plane are U (0.04), O(3) (−0.06), O(4) (0.00), O(5) (0.08), O(6) (−0.07) and O(7) (0.02).

The bond distances and bond angles of the two independent oxalate groups are the same as those found in many other oxalate compounds (Glen, Silverton & Hoard, 1963; Hansson, 1970). The oxalate groups form stable five-membered rings with the uranium atom, unlike the four-membered rings formed in the acetato, nitrato and carbonato complexes of uranyl (Zachariasen & Plettinger, 1959; Barclay, Sabine & Taylor, 1965; Mazzi & Rinaldi, 1961). Very short 'biting' distances in the latter ligands lead to planar hexagonal coordination. The longer O–O distance of 2.5–2.6 Å of the oxalate group favours pentagonal coordination perpendicular to the O–U–O axis. The O–O contact distances within the pentagon are shown in Fig. 2.

As explained above, two water molecules per formula unit of the compound are not involved in coordination to the uranium atom. The non-bonded O–O distances between the water molecules suggest that these are probably involved in hydrogen bonding. Hydrogen bonding between the free water molecules and the water molecule coordinated to the uranium atoms help to link the different zigzag layers of $[UO_2(C_2O_4).H_2O]_n$ chains, as shown in Fig. 3. In addition, two oxygen atoms of each oxalate group also appear to be hydrogen bonded to the free water molecules in a way similar to that found in $Nd_2(C_2O_4)_3.10.5H_2O$ (Hansson, 1970). The thermal behaviour of uranyl oxalate is in agreement with the differential nature of the water molecules. On heating, two water molecules are lost at 100 °C while the third is lost only at 170 °C (Padmanabhan, Saraiya & Sundaram, 1960).

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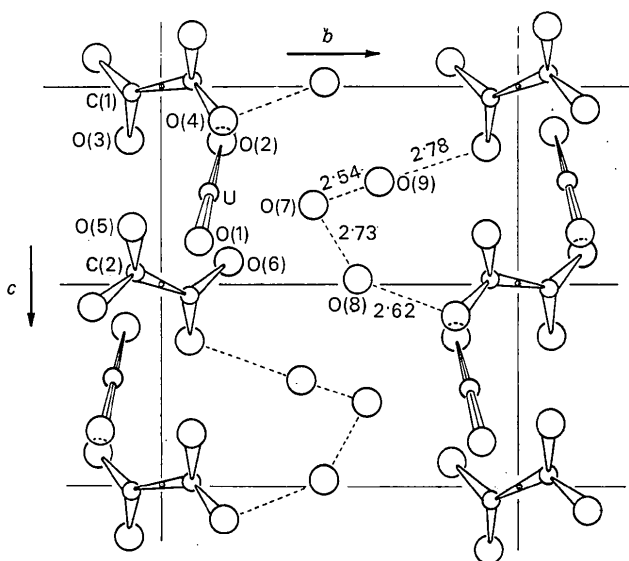

Fig. 3. (100) projection of the unit cell. The broken lines indicate possible hydrogen bonding by the water molecules with O–O distances in Å.

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