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The Crystal and Molecular Structure of Potassium Diuranyl Trisoxalate Tetrahydrate

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$K_2(UO_2)_2(C_2O_4)_3.4H_2O$ is monoclinic, space group $P2_1/n$, with $a=8\cdot85$ (1), $b=19\cdot67$ (1), $c=5\cdot37$ (1) Å, $\beta=91\cdot5$ (2)°, $Z=2$. The structure was refined to a final R of 0·097 with 822 visual reflexions corrected for absorption. The crystal contains K^+ and $[(UO_2)_2(C_2O_4)_3]_n^{2n-}$ ions. The structure of the polymeric anion is different from that in the anhydrous ammonium salt. The linear uranyl ions have six oxalate O atoms at the corners of a puckered hexagon. Mean U–O distances are 1·76 (uranyl) and 2·45 Å (to oxalate). All the oxalate groups are planar and tetradentate.

Introduction

Among the oxalato complexes of uranyl, those with a uranyl-to-oxalate ratio of 1:1·5 are unique in their low solubility in water, low temperature coefficient of solubility and relatively high stability in aqueous solutions despite their dimeric nature (Chernyaev, 1966). Although only K^+ and heavier metal cations formed solid compounds readily, modifications in the experimental procedure made the preparation of the Na^+, NH_4^+ and Li^+ salts possible (Chernyaev, Golovnya, Ellert, Shchelokov & Markov, 1958; Alcock, 1973*a*; Jayadevan, Singh Mudher & Chackraburtty, 1974). The structure of the anhydrous ammonium compound $(NH_4)_2(UO_2)_2(C_2O_4)_3$ (Alcock, 1973*b*) showed that it has a polymeric $[(UO_2)_2(C_2O_4)_3]_n^{2n-}$ anion in which the linear uranyl ions have a planar pentagon of O atoms coordinated to them (Fig. 1). Since the chemical process involved in crystallization is the replacement of the aquo by oxalate ligands, the dimeric structure in solution will have unidentate oxalate groups which are rather unlikely. Further, the normally planar oxalate groups are considerably distorted in the solid compound. Since it is known that such distortions are often caused by the bonding characteristics of the NH_4^+ ion (Jeffrey & Parry, 1952; Robertson, 1965), this study of the K^+ salt $K_2(UO_2)_2(C_2O_4)_3.4H_2O$ was undertaken as a continuation of our work on uranyl oxalate (Jayadevan & Chackraburtty, 1972). The K^+ ion is large enough to form a stable solid compound but is not heavy enough to adversely affect the structure determination.

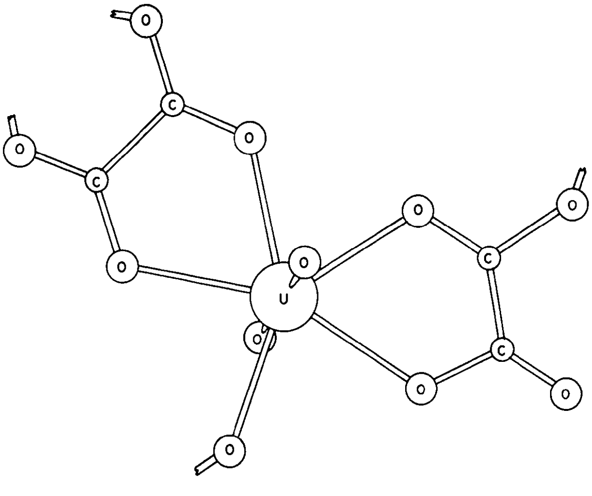

Fig. 1. Coordination of the uranium atom in $(NH_4)_2(UO_2)_2(C_2O_4)_3$.

Preparation

Uranyl oxalate and potassium oxalate in the molar ratio 1:2 were dissolved in the minimum amount of water and the solution heated at 80°C in a water bath for 4 h. Chunky yellow crystals formed on cooling, were filtered and washed with cold water, acetone and ether. The crystals were dried in air.

Chemical analysis of U gravimetrically as U_3O_8, oxalate volumetrically with $KMnO_4$, and water by weight loss at 150°C thermogravimetrically gave the percentages U 50·2 (49·9); C_2O_4 28·3 (27·7); H_2O 7·3 (7·5), where those calculated for the composition $K_2(UO_2)_2(C_2O_4)_3.4H_2O$ are given in parentheses.

Several well-formed crystals were used to determine the density pycnometrically.

X-ray studies

Crystal A, 0·06 × 0·015 × 0·022 cm, was used for layers hkn ($n=0$, 1, 2 and 3) and smaller crystal B, 0·02 × 0·014 × 0·020 cm, for layers nkl ($n=0$, 1, 2). The layers were photographed on sets of three films with Cu $K\alpha$ radiation and the equi-inclination Weissenberg method. The value of 91·5(2)° for β obtained by the least-squares analysis of the powder diffraction data agreed with that calculated from the positions of $00l$ and $h00$ reflexions on the higher-layer festoons (Stout & Jensen, 1968). The crystal data are shown in Table 1. For $Z=2$, the fourfold general positions $\pm(x,y,z)$, $\pm(\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z)$ of the space group $P2_1/n$, a non-standard setting of $P2_1/c$ chosen for the convenience of the almost

Table 1. *Crystal data*

The standard deviations here and in the text given in parentheses refer to the last figure.

$a=8{\cdot}85\ (1)$ Å $\quad D_m=3{\cdot}42\ (1)$ g cm^{-3}
$b=19{\cdot}67\ (1)$ $\quad D_c=3{\cdot}40$ g cm^{-3}
$c=5{\cdot}37\ (1)$ $\quad V=934$ Å^3
$\beta=91{\cdot}5\ (2)°$ $\quad Z=2$

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

orthogonal cell, require the dimeric anion to lie on centres of symmetry.

The intensities were estimated visually with a calibrated wedge prepared from crystal *A* and were converted into structure factors after Lorentz and polarization corrections. Absorption effects ($\mu=678$ cm^{-1}) corrected (*International Tables for X-ray Crystallography*, 1959) assuming crystal *A* to be a cylinder and crystal *B* to be a sphere, both of radius 0·008 cm, were only approximate. *hk*0 photographs taken before and after exposing the crystal to X-rays for about 200 h were identical, indicating the absence of any crystal decomposition as observed in the NH_4^+ salt.

Table 2. *Observed and calculated structure factors* (× 10)

Unobserved reflexions are marked with an asterisk.

H	K	L	FOBS	FCALC	H	K	L	FOBS	FCALC	H	K	L	FOBS	FCALC	H	K	L	FOBS	FCALC
0	4	0	4023	-1869	7	7	0	668	612	2	11	1	857	963	-5	18	1	734	832
0	6	0	3496	2929	7	8	0	469	443	-2	11	1	849	837	-5	19	1	510	-535
0	8	0	2747	-1950	7	9	0	1371	-1298	2	13	1	859	755	5	20	1	588	-490
0	10	0	1967	-1464	7	10	0	542	-493	-2	13	1	1281	1267	-5	20	1	440	-460
0	12	0	2365	2551	7	11	0	429	444	-2	14	1	676	-593	-5	22	1	464	-485
0	14	0	932	-979	7	13	0	513	540	2	15	1	1275	-1284	6	1	1	1134	610
0	16	0	1407	-1919	7	14	0	408	496	-2	15	1	1415	-1649	-6	1	1	1081	975
0	18	0	2031	1871	7	15	0	927	-1132	-2	16	1	651	946	6	2	1	*604	395
0	20	0	469	-548	7	16	0	338	-342	2	17	1	675	608	6	3	1	1859	-1993
0	22	0	524	-519	7	17	0	393	416	-2	17	1	624	567	-6	3	1	1535	-1709
0	24	0	939	836	7	19	0	418	405	2	19	1	846	727	-6	4	1	968	877
1	3	0	2717	1987	8	0	0	1548	1543	-2	19	1	785	989	6	5	1	735	680
1	6	0	*495	464	8	1	0	518	508	-2	20	1	507	-376	-6	5	1	*682	611
1	7	0	2375	2279	8	2	0	980	-612	2	21	1	1049	-961	6	7	1	898	933
1	8	0	*570	639	8	4	0	954	-977	-2	21	1	1109	-1107	-6	8	1	821	-757
1	9	0	3318	-3531	8	5	0	703	-662	-2	22	1	568	407	6	9	1	1364	-1457
1	11	0	1109	1096	8	6	0	1263	1300	2	23	1	427	339	-6	9	1	1164	-1150
1	13	0	1174	1055	8	7	0	748	716	-2	23	1	320	385	-6	10	1	650	749
1	15	0	1520	-1559	8	8	0	696	-729	3	0	1	1922	2136	6	11	1	884	777
1	17	0	782	898	8	10	0	630	-619	-3	1	1	1530	-1668	-6	11	1	579	578
1	19	0	798	848	8	11	0	488	-357	3	2	1	1237	-1368	6	13	1	639	730
1	21	0	1255	-1139	8	12	0	1144	1140	-3	2	1	2039	-2098	-6	13	1	727	689
1	23	0	361	393	8	13	0	318	347	3	3	1	*610	476	-6	14	1	796	-725
2	0	0	2847	3208	8	14	0	816	-813	3	4	1	859	-975	6	15	1	1223	-1236
2	1	0	839	844	8	18	0	371	-406	-3	4	1	1543	-1894	-6	15	1	989	-1084
2	2	0	1111	-1114	8	19	0	337	-339	-3	5	1	1292	1261	-6	16	1	733	646
2	4	0	1668	-1579	9	1	0	828	827	3	6	1	2070	2196	6	17	1	*473	346
2	6	0	2306	2183	9	2	0	558	640	-3	6	1	3123	3349	6	19	1	907	628
2	8	0	1164	-1058	9	3	0	938	-1078	-3	7	1	1034	-965	-6	19	1	560	490
2	10	0	1219	-1195	9	4	0	508	-399	3	8	1	801	-829	-6	20	1	495	-486
2	12	0	2204	2182	9	5	0	597	592	-3	8	1	917	-958	-6	21	1	623	-685
2	13	0	*502	541	9	7	0	498	541	3	10	1	910	-1232	7	0	1	1499	1295
2	14	0	555	-621	9	8	0	539	489	-3	10	1	912	-1021	-7	0	1	1498	1364
2	16	0	719	-921	9	9	0	886	-1094	-3	11	1	769	744	-7	1	1	1059	-889
2	18	0	1328	1384	9	10	0	397	-481	3	12	1	1408	1559	7	2	1	828	-934
2	20	0	466	-460	9	11	0	368	313	-3	12	1	1947	2141	-7	2	1	883	-729
2	22	0	628	-564	9	13	0	434	423	-3	13	1	1074	-1026	7	4	1	771	-929
2	24	0	836	789	9	14	0	461	466	3	14	1	593	-530	-7	4	1	879	-683
3	1	0	1473	1406	10	0	0	1028	1076	-3	14	1	821	-830	-7	5	1	1089	1021
3	3	0	3305	-2787	10	1	0	550	527	3	16	1	790	-654	7	6	1	1339	1324
3	4	0	953	-794	10	2	0	338	-365	-3	16	1	897	-902	-7	6	1	1258	1339
3	5	0	1588	1403	10	4	0	384	-416	-3	17	1	743	677	-7	7	1	1113	-1021
3	7	0	1395	1339	10	5	0	453	-493	3	18	1	1412	1298	7	8	1	617	-537
3	8	0	664	485	10	6	0	659	657	-3	18	1	1206	1226	-7	8	1	834	-703
3	9	0	1624	-1859	0	1	1	1509	1741	-3	19	1	*524	-413	7	10	1	586	-578
3	10	0	*502	-394	0	3	1	2781	-3050	3	22	1	617	-453	-7	10	1	847	-739
3	11	0	935	904	0	4	1	1020	819	-3	22	1	610	-980	-7	11	1	816	876
3	13	0	857	876	0	5	1	1911	1934	-3	23	1	345	332	7	12	1	1179	1159
3	15	0	1701	-1754	0	7	1	1380	1462	4	1	1	1610	1633	-7	12	1	1064	1024
4	0	0	2093	2047	0	8	1	476	-718	-4	1	1	1253	1419	-7	13	1	886	-885
4	1	0	697	602	0	9	1	2898	-3137	-4	2	1	1041	-977	7	14	1	471	-495
4	2	0	1424	-1459	0	11	1	1088	1113	4	3	1	2604	-2759	-7	14	1	593	-485
4	4	0	1262	-1158	0	13	1	1287	1275	-4	3	1	2401	-2925	7	16	1	602	-669
4	5	0	551	-395	0	14	1	683	-533	-4	4	1	1289	1971	-7	16	1	989	-393
4	6	0	2621	2667	0	15	1	1349	-1413	4	5	1	936	791	-7	17	1	523	495
4	7	0	*501	456	0	17	1	979	918	-4	5	1	954	929	7	18	1	769	741
4	8	0	1029	-1118	0	19	1	703	655	4	7	1	999	991	-7	18	1	723	798
4	10	0	936	-1095	0	21	1	1153	-1174	-4	7	1	1196	1087	-7	19	1	406	-812
4	12	0	1697	1833	0	23	1	462	438	-4	8	1	1191	-1133	8	1	1	608	626
4	13	0	490	444	1	4	1	1213	-1019	4	9	1	1686	-1905	-8	1	1	878	713
4	14	0	693	-671	-1	4	1	1904	-1910	-4	9	1	1601	-1771	-8	2	1	1159	-1063
4	16	0	836	-716	1	5	1	*602	297	-4	10	1	1084	1044	8	3	1	1929	-1620
4	18	0	875	1084	-1	5	1	1171	1126	4	11	1	1039	1203	-8	3	1	1148	-1055
4	20	0	539	-608	1	6	1	2419	2473	-4	11	1	1079	997	-8	4	1	918	802
4	22	0	519	-547	-1	6	1	2853	2839	4	13	1	925	891	8	5	1	643	789
5	1	0	828	739	1	7	1	1089	-935	-4	13	1	942	1025	-8	5	1	601	619
5	2	0	673	639	-1	7	1	*687	-403	-4	14	1	736	-714	8	7	1	999	948
5	3	0	2584	-2380	1	8	1	1223	-1230	4	15	1	1518	-1504	-8	7	1	579	490
5	4	0	601	-445	-1	8	1	1029	-932	-4	15	1	1410	-1690	-8	8	1	881	-816
5	5	0	840	724	1	10	1	972	-1102	-4	16	1	677	616	8	9	1	1248	-1131
5	7	0	1021	1029	-1	10	1	970	-937	4	17	1	560	525	-8	9	1	1009	-1249
5	8	0	*500	464	1	11	1	*608	528	-4	17	1	644	471	-8	10	1	811	760
5	9	0	1745	-1781	-1	11	1	976	800	4	19	1	892	663	8	11	1	421	359
5	10	0	*495	-359	1	12	1	1818	1942	-4	19	1	720	544	-8	11	1	484	466
5	11	0	917	961	-1	12	1	1914	2112	-4	20	1	636	-543	8	13	1	543	583
5	13	0	798	749	-1	13	1	768	-636	4	21	1	958	-910	-8	13	1	*510	391
5	14	0	*458	447	1	14	1	828	-832	-4	21	1	820	-909	-8	14	1	801	-750
5	15	0	1397	-1511	-1	14	1	1094	-1149	-4	22	1	475	437	8	15	1	817	-859
5	17	0	474	479	1	16	1	871	-933	5	0	1	2151	2034	-8	15	1	750	-703
5	19	0	500	519	-1	16	1	988	-939	-5	0	1	1381	1137	-8	16	1	607	891
5	20	0	336	307	-1	17	1	574	567	-5	1	1	977	-1028	9	0	1	1130	1036
5	21	0	727	-805	1	18	1	1569	1649	5	2	1	1493	-1454	-9	0	1	997	1137
6	0	0	1482	1269	-1	18	1	1218	1351	-5	2	1	914	-878	-9	1	1	921	-899
6	1	0	533	424	1	20	1	567	-455	5	4	1	1051	-957	9	2	1	462	-375
6	2	0	902	-804	1	21	0	1255	-1137	-5	4	1	915	-884	-9	2	1	475	-400
6	4	0	866	-912	1	22	1	571	-462	-5	5	1	1191	973	9	4	1	969	-684
6	5	0	706	-671	-1	22	1	614	-507	5	6	1	2385	2564	-9	4	1	573	-408
6	6	0	1401	1712	-1	23	1	*421	281	-5	6	1	1984	2126	-9	5	1	710	800
6	7	0	636	519	1	24	1	688	786	-5	7	1	1089	-949	9	6	1	896	875
6	8	0	645	-787	-1	24	1	757	796	5	8	1	953	-906	-9	6	1	728	790
6	10	0	870	-768	2	1	1	1805	2029	-5	8	1	910	-770	-9	7	1	613	-819
6	11	0	663	-624	-2	1	1	1289	1506	5	10	1	1191	-1098	9	8	1	516	-460
6	12	0	1139	1279	2	2	1	848	-718	-5	10	1	1013	-1052	-9	8	1	500	-422
6	13	0	469	-539	2	3	1	1464	-1374	-5	11	1	943	869	9	10	1	*453	-445
6	14	0	450	-511	-2	4	1	1365	1292	5	12	1	1290	1563	-9	10	1	395	-390
6	15	0	668	774	2	5	1	808	969	-5	12	1	1089	1239	-9	11	1	708	741
6	17	0	*466	303	-2	5	1	1541	1823	-5	13	1	766	-765	9	12	1	781	806
6	20	0	415	-413	2	7	1	1004	1205	5	14	1	669	-697	-9	12	1	683	636
7	1	0	1011	827	-2	7	1	1379	1298	-5	14	1	616	-586	-9	13	1	568	-348
7	2	0	930	979	-2	8	1	1199	-1337	5	16	1	689	-733	-9	14	1	406	-335
7	3	0	1829	-1769	2	9	1	2260	-2639	-5	16	1	556	-570	10	1	1	389	369
7	4	0	712	-468	-2	9	1	2203	-2279	-5	17	1	633	596	-10	1	1	*405	332
7	5	0	965	925	-2	10	1	689	602	5	18	1	1006	1031	-10	2	1	897	-791

Table 2 (*cont.*)

H	K	L	FOBS	FCALC	H	K	L	FOBS	FCALC	H	K	L	FOBS	FCALC	H	K	L	FOBS	FCALC
10	3	1	478	-729	4	5	2	678	611	-2	7	3	879	772	-6	2	3	2246	-1938
-10	3	1	785	-731	4	6	2	2139	2019	2	8	3	1156	-1067	6	3	3	1364	-1325
-10	4	1	811	794	4	8	2	998	-1093	-2	8	3	1638	-1805	-6	3	3	1001	-886
10	5	1	419	384	4	10	2	1018	-1252	2	9	3	1240	-1404	6	4	3	808	607
-10	5	1	450	382	4	11	2	658	486	-2	9	3	1500	-1393	-6	4	3	2051	1851
10	7	1	319	285	4	12	2	1323	1432	2	10	3	804	1004	6	5	3	601	471
-10	7	1	470	373	4	16	2	881	-577	-2	10	3	1493	1491	6	7	3	648	693
10	8	1	323	239	-4	17	2	1089	1046	2	11	3	567	643	6	8	3	563	-536
-10	8	1	817	-769	4	18	2	922	1096	2	13	3	757	839	-6	8	3	2245	-1860
10	9	1	635	-687	-4	18	2	818	847	-2	13	3	906	744	6	9	3	985	-1086
-10	9	1	767	-720	-4	19	2	553	-683	2	14	3	943	-1028	-6	9	3	897	-852
-10	10	1	659	653	-4	20	2	479	-419	-2	14	3	1510	-1175	6	10	3	556	476
0	0	2	2330	2439	4	20	2	538	-479	2	15	3	981	-1243	-6	10	3	1663	1414
0	1	2	744	-815	5	1	2	1018	1125	-2	15	3	967	-892	6	11	3	432	422
0	4	2	1403	-1623	5	3	2	1907	-2161	2	16	3	652	856	-6	14	3	1146	-1272
0	5	2	1224	1161	5	4	2	679	626	-2	16	3	1161	1057	6	15	3	618	-480
0	6	2	2163	1940	5	5	2	828	808	2	17	3	491	444	-6	15	3	546	-561
0	7	2	1672	-1403	5	7	2	844	991	2	19	3	483	494	6	16	3	311	270
0	8	2	1174	-868	5	8	2	668	-908	2	20	3	453	-577	-6	16	3	1049	1071
0	10	2	679	-697	5	9	2	1607	-1642	-2	20	3	1024	-830	7	0	3	1089	922
0	11	2	1073	994	5	11	2	771	881	2	21	3	585	-695	-7	0	3	844	639
0	12	2	1911	1842	5	13	2	728	620	-2	21	3	778	-707	-7	1	3	2055	-1836
0	13	2	667	-788	5	15	2	1028	-1209	-2	22	3	621	710	7	2	3	625	-413
0	14	2	808	-857	5	17	2	*671	443	3	0	3	1589	1516	7	4	3	610	-513
0	16	2	767	-728	-5	18	2	613	546	3	1	3	1164	-976	7	5	3	379	302
0	17	2	733	624	-5	20	2	721	-747	-3	1	3	2327	-2020	-7	5	3	2089	1742
0	18	2	770	1026	6	0	2	1487	1550	3	2	3	824	-709	7	6	3	908	790
1	1	2	1685	1399	6	2	2	939	-905	-3	2	3	976	-794	-7	6	3	862	714
1	2	2	1933	-1647	6	4	2	458	-788	-3	4	3	881	-801	7	7	3	358	-216
1	3	2	2888	-2969	6	6	2	1123	1420	3	5	3	1164	1141	-7	7	3	1898	-1618
-1	3	2	2162	-2209	6	10	2	679	-676	-3	5	3	1762	1890	-7	11	3	1484	1493
1	4	2	1587	1272	6	12	2	1049	1207	3	6	3	1769	1855	7	12	3	656	718
-1	4	2	1174	1129	6	18	2	616	778	-3	6	3	1226	1214	-7	12	3	451	634
1	5	2	1799	1713	-6	18	2	807	757	3	7	3	814	-916	-7	13	3	1136	-1194
-1	5	2	1486	1644	-6	19	2	663	-748	-3	7	3	1443	-1464	-8	2	3	1604	-1644
1	7	2	1181	1247	7	3	2	987	-1121	3	8	3	738	-778	8	3	3	894	-793
-1	7	2	1181	1209	7	7	2	592	708	-3	10	3	601	-528	-8	4	3	1638	1667
1	8	2	678	-588	8	0	2	1091	1032	3	11	3	708	914	8	5	5	439	382
-1	8	2	963	-1087	8	2	2	561	-569	-3	11	3	1617	1495	8	7	3	455	454
1	9	2	1926	-2050	8	4	2	469	-584	3	12	3	1021	1093	-8	8	3	1406	-1338
-1	9	2	1363	-1399	9	3	2	868	-926	-3	12	3	993	1016	8	9	3	599	-753
1	10	2	1074	1017	10	0	2	568	688	3	13	3	669	-685	-8	10	3	1099	1203
1	11	2	677	628	0	2	3	1697	-1789	-3	13	3	1517	-1410	9	0	3	1023	886
1	13	2	944	957	0	3	3	1888	-1808	3	16	3	501	-397	-9	1	3	1310	-1296
-1	13	2	1159	935	0	4	3	1557	1539	3	17	3	511	571	9	2	3	567	-659
1	14	2	805	-789	0	5	3	941	1004	-3	17	3	959	1125	9	4	3	371	-401
-1	14	2	1231	-934	0	7	3	983	935	3	18	3	831	844	-9	5	3	1301	1317
1	15	2	1435	-1489	0	8	3	1079	-1109	-3	18	3	610	717	9	6	3	458	483
-1	15	2	1438	-1220	0	9	3	1233	-1295	3	19	3	488	-476	-9	7	3	1068	-1292
1	16	2	620	724	0	10	3	1061	1249	-3	19	3	893	-872	-9	11	3	900	1131
-1	16	2	696	750	0	11	3	657	530	4	1	3	1104	1045	-10	2	3	1014	-1213
1	17	2	593	654	0	13	3	925	862	4	2	3	853	-710	-10	4	3	1019	1175
1	19	2	628	653	0	14	3	1199	-1186	-4	2	3	1803	-1559	0	0	4	1066	1126
1	20	2	565	-497	0	15	3	1088	-960	4	3	3	1591	-1311	0	1	4	2067	-1765
-1	20	2	566	-565	0	16	3	1025	1007	-4	3	3	1283	-1037	0	5	4	1910	1627
1	21	2	859	-914	0	19	3	476	382	4	4	3	936	735	0	6	4	967	883
-1	21	2	994	-930	0	20	3	722	-699	-4	4	3	2076	1865	0	7	4	1787	-1748
2	0	2	2874	3022	0	21	3	781	-729	-4	5	3	613	383	0	11	4	1678	1642
2	1	2	957	-884	0	22	3	538	530	4	7	3	729	514	0	12	4	818	835
2	2	2	1265	-1134	1	0	3	1848	1519	4	8	3	787	-850	0	13	4	1389	-1096
2	3	2	601	597	1	1	3	1689	-1382	-4	8	3	1542	-1770	0	17	4	967	979
2	4	2	1079	-1027	-1	1	3	1538	-1672	4	9	3	1099	-1216	0	19	4	764	-830
2	5	2	761	824	1	2	3	1176	-987	-4	9	3	1024	-1159	1	2	4	1739	-1623
2	6	2	2039	2139	-1	2	3	889	-769	4	10	3	697	644	1	3	4	1108	-1097
2	7	2	1194	-1139	1	4	3	1313	-1225	-4	10	3	1232	1448	1	4	4	1580	1415
2	8	2	1084	-1152	-1	4	3	888	-1064	4	11	3	609	679	1	8	4	1580	-1316
2	10	2	1116	-1154	1	5	3	1961	1737	4	14	3	592	-552	1	10	4	1528	1274
2	12	2	1799	1744	-1	5	3	1539	1578	-4	14	3	996	-1216	1	14	4	1435	-1193
2	11	2	677	794	1	6	3	1948	2144	4	15	3	819	-873	1	16	4	1233	961
2	12	2	1639	1744	-1	6	3	1704	1499	-4	15	3	569	-685	2	0	4	1011	802
2	13	2	663	-579	1	7	3	1599	-1916	4	16	3	455	390	2	1	4	1306	-1287
-2	13	2	1329	-1084	-1	7	3	1460	-1579	-4	16	3	959	974	2	4	4	592	-481
-2	14	2	919	-779	1	8	3	589	-580	4	17	3	478	446	2	5	4	1269	1549
2	16	2	604	-659	1	10	3	742	-671	4	19	3	374	434	2	6	4	1048	1154
-2	16	2	869	-799	-1	10	3	683	-483	-4	20	3	910	-901	2	7	4	1219	-1432
-2	17	2	1006	887	1	11	3	1269	1346	-4	21	3	424	-497	2	11	4	1219	1220
-2	18	2	1151	991	-1	11	3	1352	1276	5	0	3	1566	1411	2	12	4	1041	898
2	19	2	801	-551	1	12	3	1437	1507	-5	0	3	1361	1080	2	13	4	1016	-931
-2	19	2	744	-607	-1	12	3	1290	1160	5	1	3	799	-856	2	18	4	*715	498
-2	20	2	549	-435	1	13	3	1049	-1014	-5	1	3	2315	-2101	2	19	4	777	-647
3	1	2	1671	1572	-1	13	3	1000	-1111	5	2	3	727	-677	0	4	5	1694	1471
3	2	2	1176	-871	1	14	3	528	-615	-5	2	3	809	-631	0	8	5	1469	-1313
3	3	2	2149	-1914	1	17	3	723	738	-5	5	3	1692	1683	0	10	5	1509	1332
3	5	2	680	587	-1	14	3	798	-589	5	6	3	1344	1221	0	14	5	1221	-1135
3	7	2	1174	1235	-1	16	3	800	-789	-5	6	3	840	912	0	16	5	1024	931
3	8	2	676	-633	-1	17	3	1058	905	5	7	3	469	-517	1	1	5	1528	-1350
3	9	2	1793	-2009	1	18	3	670	655	-5	7	3	1645	-1595	1	5	5	1297	1263
3	10	2	676	607	-1	18	3	747	752	5	8	3	687	-625	1	7	5	1166	-1273
3	11	2	668	876	1	19	3	469	-668	5	10	3	584	-675	2	2	5	1219	-1338
3	13	2	648	671	-1	19	3	669	-818	-5	10	3	867	-651	2	8	5	1153	-1188
-3	14	2	1279	-1048	1	22	3	279	-386	-5	11	3	1453	1417	2	10	5	1016	1093
3	15	2	1297	-1306	-1	22	3	338	-391	5	12	3	849	864	2	4	5	1206	1130
-3	15	2	1509	-1437	2	1	3	1501	1456	-5	12	3	800	609	0	1	6	1380	-1380
-3	16	2	1023	836	-2	1	3	767	530	5	13	3	568	-529	0	5	6	1129	1327
3	17	2	*671	509	2	2	3	2088	-1903	-5	13	3	1126	-1260	0	7	6	1098	-1310
3	19	2	795	741	-2	2	3	1717	-1825	5	16	3	438	-361	1	2	6	1169	-1319
-3	20	2	795	-771	2	3	3	2182	-2044	5	17	3	422	474	1	4	6	1156	1157
3	21	2	669	-717	-2	3	3	1715	-1598	-5	17	3	1119	1157	1	8	6	1054	-1101
-3	21	2	921	-854	2	4	3	1163	1458	5	18	3	715	778	1	10	6	904	1030
4	0	2	2635	2669	-2	4	3	1697	1886	-5	18	3	693	617	2	1	6	1196	-1212
4	1	2	839	-669	2	5	3	1118	979	-5	19	3	789	-849					
4	2	2	1078	-1097	-2	5	3	878	891	6	1	3	759	488					
4	4	2	607	-631	2	7	3	670	711	-6	1	3	826	424					
4	4	2	609	-631	2	7	3	670	711	-6	1	3	826	424					

The positions of U and K were derived from a Patterson map and the remaining non-hydrogen atoms from difference maps. The atomic positions, isotropic temperature factors except for U, anisotropic for U, and layer scale factors were refined by the full-matrix least-squares program *LALS* (Gantzel, Sparks & Trueblood, 1961) on a BESM-6 computer. The refinement was stopped at $R_1=[\sum|\Delta F|/\sum F_{\rm obs}]$ of 0·097 and $R_2=[\sum\omega|\Delta F|^2/\sum\omega F^2_{\rm obs}]^{1/2}$ of 0·107 since no parameter changed by more than $\frac{1}{4}$ its standard deviation. The reflexions were given weights $1/\sigma^2$, where σ was assigned in agreement with the accuracy of the measurements as $\sigma=0{\cdot}05F_{\rm obs}$ if $90<F_{\rm obs}<180$; $\sigma=0{\cdot}08F_{\rm obs}$ if $40<F_{\rm obs}<90$ or $180<F_{\rm obs}<250$ and $\sigma=0{\cdot}10F_{\rm obs}$ if $250<F_{\rm obs}$ or $F_{\rm obs}<40$. The 822 reflexions used in the final cycles include 21 unobserved reflexions that alone satisfied the condition $F_{\rm calc}\geq 0{\cdot}5F_{\rm min}$, where $F_{\rm min}$ corresponds to the local minimum observed intensity. The scattering factors for U^{2+} were derived from U° and U^{3+} data of Cromer & Waber (1965), while those for K^+, O and C were from *International Tables for X-ray Crystallography* (1962).

The observed structure factors are compared in Table 2 with those calculated for the final atomic

Table 3. *Atomic parameters*

	x	*y*	*z*	*B*
U	−0·0094 (2)	0·16606 (8)	0·0442 (4)	*
K	0·3944 (22)	0·0995 (9)	0·458 (4)	4·3
O(1)	−0·1283 (43)	0·1755 (21)	−0·222 (9)	2·5
O(2)	0·1046 (38)	0·1555 (17)	0·311 (8)	1·8
O(3)	0·0784 (54)	0·2769 (25)	−0·151 (11)	3·5
O(4)	0·2463 (46)	0·3353 (21)	−0·316 (9)	3·2
O(5)	0·4151 (52)	0·2282 (22)	−0·279 (10)	3·1
O(6)	0·2462 (47)	0·1750 (20)	−0·085 (10)	3·4
O(7)	0·1043 (42)	0·0589 (18)	−0·159 (9)	2·6
O(8)	−0·1071 (54)	0·0529 (24)	0·152 (11)	3·2
O(9)	0·2009 (58)	0·4631 (26)	0·067 (11)	4·1
O(10)	0·0076 (69)	0·4250 (23)	0·497 (13)	4·1
C(1)	0·2004 (84)	0·2807 (40)	−0·238 (20)	4·0
C(2)	0·2974 (71)	0·2249 (32)	−0·176 (15)	2·8
C(3)	0·0747 (74)	0·0008 (40)	−0·063 (17)	3·8

* Anisotropic temperature factors

β_{11}	β_{22}	β_{33}
0·00674 (19)	0·00137 (4)	0·00571 (68)
β_{12}	β_{13}	β_{23}
0·00017 (16)	0·00859 (54)	0·00011 (32)

parameters listed in Table 3. A difference synthesis showed no peaks that could be ascribed to any atom.

Results and discussion

The (001) projection of the unit cell is shown in Fig. 2, where the atoms are numbered to correspond with Table 3. The bond distances and angles are listed in Table 4. Equations for weighted least-square planes are shown in Table 5.

The uranyl ions are linear with O–U–O = 179(2)°. The average U–O distance of 1·76(4) Å for the uranyl ions is longer than that in uranyl oxalate and is reflected by the decrease of about 30 cm^{-1} for the

Table 4. *Bond distances* (Å) *and angles* (°)

The superscripts refer to the following transformations:

(i)	$x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$	(iv)	$\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$
(ii)	$-x, -y, -z$	(v)	$\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$
(iii)	$\frac{1}{2}+x, \frac{1}{2}-y, z-\frac{1}{2}$	(vi)	$-x, 1-y, 1-z$

(*a*) Uranium environment

U——O(1)	1·77 (4)	O(4^{i})–U–O(1)	74 (2)
U——O(2)	1·75 (4)	O(4^{i})–U–O(2)	105 (2)
U——O(3)	2·54 (5)	O(5^{i})–U–O(1)	94 (2)
U——O(4^{i})	2·31 (4)	O(5^{i})–U–O(2)	87 (2)
U——O(5^{i})	2·38 (4)	O(6)–U–O(1)	108 (2)
U——O(6)	2·39 (4)	O(6)–U–O(2)	73 (2)
U——O(7)	2·58 (4)	O(7)–U–O(1)	89 (2)
U——O(8)	2·46 (5)	O(7)–U–O(2)	91 (2)
O(3)···O(5^{i})	2·49 (8)	O(8)–U–O(1)	95 (2)
O(3)···O(6)	2·52 (6)	O(8)–U–O(2)	84 (2)
O(7)···O(6)	2·63 (5)	O(3)–U–O(5^{i})	61 (2)
O(7)···O(8)	2·54 (7)	O(3)–U–O(6)	61 (1)
O(4^{i})···O(8)	2·56 (6)	O(7)–U–O(6)	64 (1)
O(4^{i})···O(5^{i})	2·59 (6)	O(7)–U–O(8)	60 (2)
O(1)–U–O(2)	179 (2)	O(4^{i})–U–O(8)	65 (2)
O(3)–U–O(1)	76 (2)	O(4^{i})–U–O(5^{i})	67 (2)
O(3)–U–O(2)	105 (2)		

(*b*) Oxalate groups

C(1)–O(3)	1·19 (9)	O(3)—C(1)–O(4)	120 (7)
C(1)–O(4)	1·22 (9)	O(3)—C(1)–C(2)	114 (8)
C(1)–C(2)	1·43 (10)	O(4)—C(1)–C(2)	123 (7)
C(2)–O(5)	1·19 (8)	O(5)—C(2)–O(6)	125 (6)
C(2)–O(6)	1·19 (8)	O(5)—C(2)–C(1)	112 (7)
C(3)–O(7)	1·28 (9)	O(6)—C(2)–C(1)	120 (6)
C(3)–O(8^{ii})	1·20 (9)	O(7)—C(3)–O(8^{ii})	125 (6)
C(3)–C(3^{ii})	1·50 (10)	O(7)—C(3)–C(3^{ii})	113 (6)
		O(8^{ii})–C(3)–C(3^{ii})	113 (6)

(*c*) Potassium ion (< 3·2 Å)

K–O(2)	2·89 (4)	K–O(9^{iv})	3·03 (6)
K–O(3^{iii})	2·99 (5)	K–O(9^{v})	2·82 (6)
K–O(5)	2·90 (5)	K–O(10^{iv})	3·08 (7)
K–O(6)	3·17 (5)	K–O(10^{iii})	2·73 (7)

(*d*) Water molecules (< 3·0 Å)

O(9)–O(8^{iii})	2·85 (8)	O(10)–O(5)	2·92 (7)
O(9)–O(10)	2·99 (9)	O(10)–O(10^{vi})	2·95 (8)

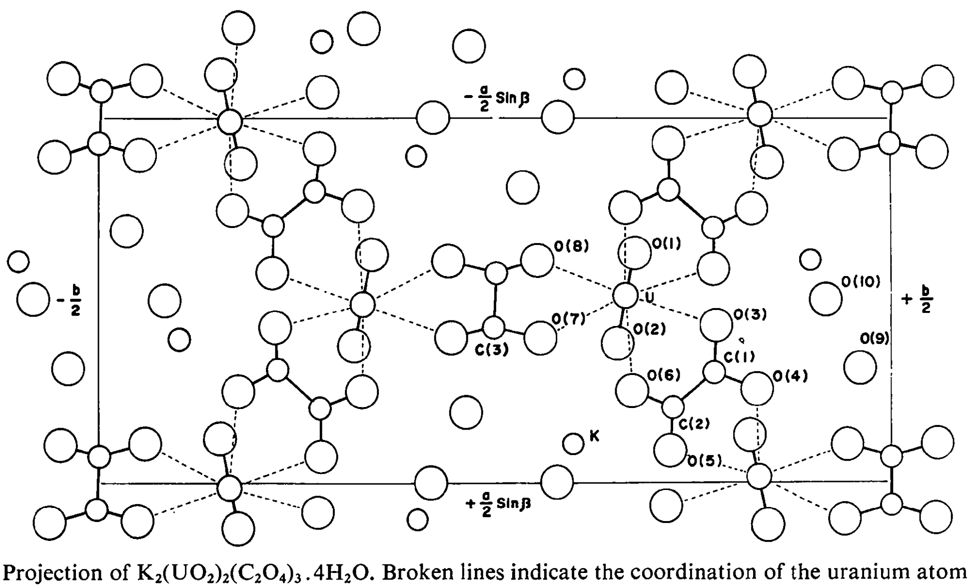

Fig. 2. (001) Projection of $K_2(UO_2)_2(C_2O_4)_3.4H_2O$. Broken lines indicate the coordination of the uranium atom by oxygen atoms of the oxalate groups.

Table 5. *Least-squares planes and interplanar angles*

The orthogonal coordinate system corresponds to the *a*, *b* and *c** axes. Each atom was given a weight equal to $\left[\frac{1}{abc\sigma(x)\sigma(y)\sigma(z)}\right]^{2/3}$ where *a*, *b*, *c* are cell constants and $\sigma(x)$, $\sigma(y)$ and $\sigma(z)$ are deviations of the atomic coordinates. The superscripts are as in Table 4.

Plane	Equation	Atoms included and their deviations (Å)
1	$0{\cdot}4756X - 0{\cdot}0433Y + 0{\cdot}879Z = 0{\cdot}0221$	U, 0·00; O(3), −0·63; O(4^{i}), −0·37; O(5^{i}), 0·42; O(6), 0·47; O(7), −0·38; O(8), 0·19
2	$0{\cdot}3038X + 0{\cdot}3589Y + 0{\cdot}883Z = 1{\cdot}478$	O(3), −0·02; O(4), 0·06; O(5), −0·06; O(6), 0·02; C(1), −0·07; C(2), 0·08
3	$0{\cdot}6310X + 0{\cdot}0246Y + 0{\cdot}775Z = 0{\cdot}002$	Origin, 0·0; O(7), −0·04; O(8), 0·04; C(3), 0·16
4	$0{\cdot}3936X - 0{\cdot}8233Y - 0{\cdot}390Z = -2{\cdot}846$	U; O(1); O(2)

Interplanar angles:

From/To	1	2	3
4	97	122	94
3	11	28	
2	25		

asymmetric stretching frequency of the uranyl group in the infrared spectrum. Six O atoms at an average U–O distance of 2·45(4) Å form a puckered hexagon around the uranyl ion, the O atoms deviating between 0·2 to 0·6 Å from a plane through U (plane 1, Table 5) which is almost perpendicular to the O–U–O axis. Each uranyl ion is thus associated with three oxalate groups forming polymeric anions $[(UO_2)_2(C_2O_4)_3]_n^{2n-}$ that extend throughout the crystal. The K^+ ions fit into the polyhedra formed by O atoms of the oxalate groups and water molecules. There are eight oxygen atoms within a sphere of radius of 3·2 Å about the K^+ ion and, as in many other crystals, the polyhedron is irregular (Palenik, 1967). All the oxalate groups are planar and tetradentate (Table 5) bridging two uranyl ions.

In the NH_4^+ salt, the polymeric anion $[(UO_2)_2(C_2O_4)_3]_n^{2n-}$ has the uranyl ion (U–O = 1·77(6) Å) at the centre of a planar pentagon of O atoms (U–O = 2·38(5) Å) formed by three oxalate groups. One of the oxalate groups is strictly planar and tetradentate while the other two are terdentate with an angle of 12° between two $\genfrac{}{}{0pt}{}{O}{O}\!\!>\!C\text{–}C$ planes. This difference in the conformation seems similar to that found between ammonium oxalate and other oxalates (Robertson, 1965). The twisting of the oxalate ion by 27° about the central C–C bond in the former is caused by hydrogen bonding. A similar requirement of the NH_4^+ ion is sufficient to affect the U coordination in the anhydrous NH_4^+ salt.

Although packing effects are probably responsible for the formation of the polymeric anion on crystallization from the dimeric anion in solution, the planarity of the oxalate group and the puckering of the hexagonal ligand ring around the uranyl ion in the K^+ salt favour the view that the UO_2^{2+} ions are held by the oxalate ion network by essentially electrostatic forces.

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