# Uranyl Oxalate Complexes. Part III.[1] Preparation and Crystal and Molecular Structure of Ammonium Diuranyl Trioxalate

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The crystal structure of the title compound has been determined from photographic and diffractometer data by the heavy-atom method. Crystals are monoclinic, space group $P2_1/n$, $a = 9{\cdot}46(2)$, $b = 13{\cdot}61(2)$, $c = 6{\cdot}12(1)$ Å, $\beta = 92{\cdot}7(1)°$, $Z = 2$. 886 Reflections were refined to a final $R$ of 0·113. The crystal contains $NH_4^+$ and $[(UO_2)_2(C_2O_4)_3]_n^{2n-}$ ions. In the latter, one oxalate group is ter- and one quadri-dentate, giving double chains parallel to $c$. Mean U–O distances are 1·77 (uranyl) and 2·38 Å (to oxalate). The structures and bonding of oxalato- and other complexes of $UO_2^+$ are discussed.

THE low ratio of oxalate to uranium in ammonium diuranyl trioxalate suggests that there may be bridging oxalate groups; this has been confirmed by the present structure determination. A preliminary communication has been published.[2] †

## EXPERIMENTAL

*Crystal Data.*—$C_6H_8N_2O_{16}U_2$, Monoclinic, $a = 9{\cdot}46(2)$, $b = 13{\cdot}61(2)$, $c = 6{\cdot}12(1)$ Å, $\beta = 92{\cdot}7(1)°$, $U = 787{\cdot}1$ Å$^3$, $D_c = 3{\cdot}54$, $Z = 2$, $D_m > 3{\cdot}3$, $F(000) = 740$. $\mu(\text{Cu-}K_\alpha) = 805$, $\mu(\text{Mo-}K_\alpha) = 252$ cm$^{-1}$. Systematic absences $h + l \neq 2n$ for $h0l$ and $0k0 \neq 2n$ indicate space group $P2_1/n$, a non-standard setting of $P2_1/c$, chosen for the convenience of the almost orthogonal cell. This has general positions $\pm(x, y, z)$ and $\pm(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$, and the $(UO_2)_2(C_2O_4)_3{}^{2-}$ units lie on centres of symmetry.

Ammonium uranyl dioxalate $(NH_4)_2UO_2(C_2O_4)_2$ and ammonium diuranyl trioxalate $(NH_4)_2(UO_2)_2(C_2O_4)_3$ were formed together by evaporation on a steam-bath of water (10 ml) containing uranyl oxalate (1·8 g, 4·3 mmol) and ammonium oxalate (0·62 g, 4·3 mmol). Chunky crystals of the diuranyl trioxalate and needle-shaped crystals of the uranyl dioxalate were separated under the microscope. Those of the trioxalate are usually rather elongated blocks bounded by {011} and terminated by {001}.

Data were originally collected photographically but these were superseded by a set collected on a Stoe Weissenberg automatic diffractometer, as described previously.[1] Unit-cell dimensions were determined from high-angle reflections with the standard deviations estimated from the accuracy of the observations. Layers $hk0$—5 were collected, crystal decomposition being monitored with a low-angle reflection on each layer. Slow decomposition was observed and the data were rescaled by factors of the form $(1 + kN)$ for the $N$th reflection on a layer. As with the dioxalate,[1] this compensation was probably not fully satisfactory. Crossing data were provided by procession photographs of layers $h0l$ and $0kl$. Lorentz, polarisation, and absorption corrections were applied, the latter with the program ABSCOR. 886 Reflections were considered observed, having $I/\sigma(I) > 3{\cdot}0$.

The structure was solved by heavy-atom methods by use of the photographic data, and refined to $R$ 0·13. Further refinement by use of the diffractometer data gave $R$ 0·127 with all atoms isotopic and unit weights (which were satisfactory). Final refinement was again[1] with layer temperature factors and with anisotropic temperature factors for the uranium atom to $R$ 0·113. Anomalous dispersion by uranium was allowed for[3] and scattering factors were from ref. 4. The final refinement used the program BAYLS,[5] other computing was with the '*X*-Ray '63' system on the ATLAS computer.[6]

The contents of the unit cell are shown in Figure 1, and Figure 2 gives the atomic numbering, Table 1 the atomic parameters, Table 2 the bond lengths and angles, and Table 3 the mean planes. The final structure factors are listed in Supplementary Publication No. SUP 20707 (3 pp.).‡

## RESULTS

The crystal contains $NH_4^+$ ions and uranyl groups five-co-ordinated by oxalate ions giving approximately penta-

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† The value of β given in ref. 2 is incorrect and the other cell-constant values have been revised.

‡ For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. Items less than 10 pp. are sent as full-sized copies.

[1] N. W. Alcock, Parts I and II, preceding papers.

[2] N. W. Alcock, *Chem. Comm.*, 1968, 1327.

[3] R. B. Roof, *Acta Cryst.*, 1961, **14**, 934.

[4] 'International Tables for *X*-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962.

[5] BAYLS, Refinement program developed by N. A. Bailey and rewritten in Fortran by N. W. Alcock.

[6] 'X-RAY '63' system of programs, J. M. Stewart, University of Maryland Technical Report, TR 64 6.

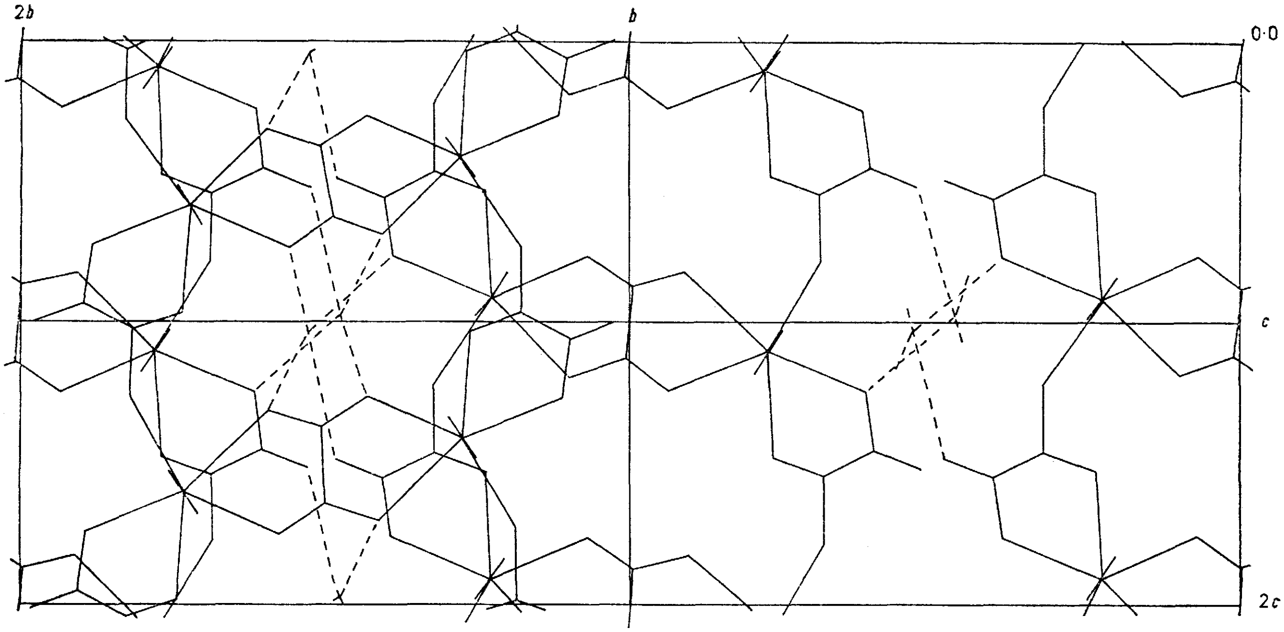

FIGURE 1 Four unit cells of $(NH_4)_2(UO_2)_2(C_2O_4)_3$ projected down *a*. For one set of double chains (heavy lines) uranium atoms are at $x$ ±0·06, for the other set (light lines, drawn for two cells only) at $x$ ±0·56. Hydrogen bonds are shown as dashed lines. The nitrogen atoms are at the intersections of the sets of four hydrogen bonds.

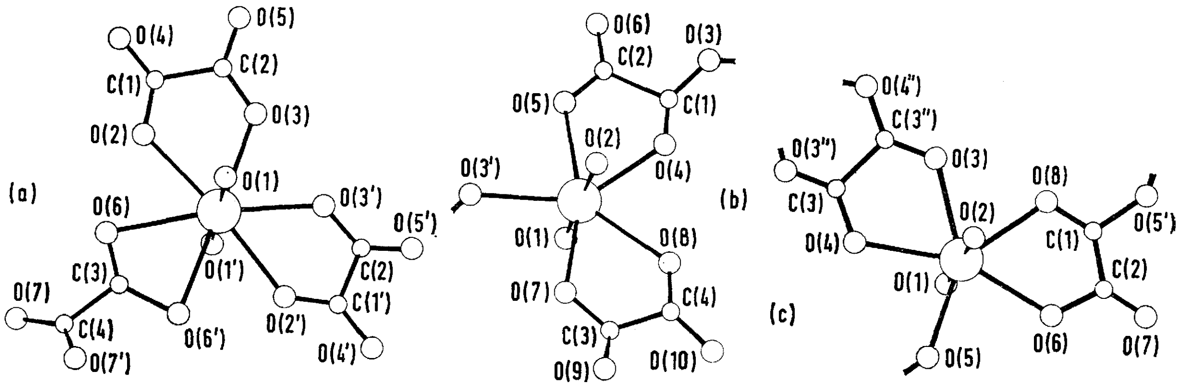

FIGURE 2 The anions of the three uranyl oxalate complexes, viewed nearly normal to the oxalate planes (a), $(UO_2)(C_2O_4)_3^{4-}$; (b), $[(UO_2)(C_2O_4)_2]_n^{2n-}$; and (c), $[(UO_2)_2(C_2O_4)_3]_n^{2n-}$

gonal bipyramidal geometry about the uranium atom. One oxalate group is placed on a centre of symmetry and is quadri-dentate, 1,4-co-ordinated to two uranium atoms. The other is bidentate (1,4) to one uranium atom and unidentate to another. This produces infinite double chains $[C_2O_4(UO_2)C_2O_4(UO_2)C_2O_4]_n^{2n-}$ parallel to *c*. Within one unit cell, there are two chains, with uranium atoms at $x = \pm 0{\cdot}06$ and $\pm 0{\cdot}56$. The mean U–O distances are 1·77 in the $UO_2$ group and 2·38 Å to the oxalate groups. The oxalate group which does not lie on a centre of symmetry is not quite planar, having a dihedral angle of 12° between the O–C–O planes at each end.

TABLE 1

Atomic co-ordinates (× 10³) and temperature factors with standard deviations in parentheses

| Atom | *x* | *y* | *z* | *B* |
|---|---|---|---|---|
| U | 63·9(3) | 226·5(2) | 88·1(4) | * |
| O(1) | −114(6) | 248(4) | −8(10) | 5·9(1·5) |
| O(2) | 241(8) | 206(6) | 169(11) | 9·0(2·0) |
| O(3) | 104(5) | 67(4) | 235(8) | 3·8(1·0) |
| O(4) | 31(5) | 98(4) | −187(8) | 3·8(1·1) |
| O(5) | 93(4) | 322(3) | −222(7) | 3·0(0·9) |
| O(6) | 112(6) | 387(4) | 235(9) | 4·8(1·2) |
| O(7) | 193(6) | 479(4) | 506(9) | 4·4(1·2) |
| O(8) | 63(5) | 234(4) | 468(10) | 3·6(1·3) |
| C(1) | 96(9) | 317(7) | 540(13) | 4·9(1·9) |
| C(2) | 138(8) | 403(5) | 445(12) | 3·6(1·5) |
| C(3) | −2(6) | 8(4) | −128(10) | 2·1(1·0) |
| N | 232(6) | 530(4) | 965(10) | 3·9(1·3) |

* For U: $\exp[-(0{\cdot}0105(5)h^2 + 0{\cdot}0050(2)k^2 + 0{\cdot}015(3)l^2 + 2 \times 0{\cdot}0005(8)kl + 2 \times 0{\cdot}0012(6)hl + 2 \times 0{\cdot}0000(5)hl)]$.

*Packing*.—The nitrogen atom has four oxygen neighbours at 2·82, 2·91, 3·02, and 3·03 Å, some or all of which are presumably hydrogen bonded. It is likely that at least one of the longer distances represents an actual bond, because they are the only possible interchain links. The two shorter distances involve two oxygen atoms on the same chain.

## DISCUSSION

The bond lengths in the three uranyl oxalate complexes are collected in Table 4, together with those of some related compounds. The three complexes are shown, from similar view points, in Figure 2.

The most important difference between them is the change in co-ordination of the $UO_2^{2+}$ group from five to six. The single factor governing this co-ordination number seems from Table 4 and from the geometry of $[UO_2(C_2O_4)_3]^{4-}$ to be the non-bonded O · · · O distances around the ring. Five individual oxygen atoms can be placed comfortably around a $UO_2^{2+}$ group with U–O *ca.* 2·35—2·4 Å and O · · · O 2·7—2·8 Å. Few compounds of this type have been studied, but one example is $[UO_2\{CO(NH_2)_2\}_4(H_2O)](NO_3)_2$.[11] To place six individual oxygen atoms in a regular hexagon would require O · · · O equal to U–O, 2·4 Å which is clearly too small. Six ligands can only be achieved by constraining some oxygen atoms to be closer than 2·7 Å, in a rigid ligand. Examples are: $O\text{–}O^{2-}$ 1·5, $NO_3^-$ 2·1, and $CH_3CO_2^-$ 2·2 Å which form $UO_2L_3$ complexes, while two nitrate groups are sufficient in $UO_2(NO_3)_2(H_2O)_2$ for two individual oxygen atoms. However, O · · · O in a free oxalate group [12] is *ca.* 2·7 Å and so this does not provide any con-

TABLE 2

Bond lengths (Å) and angles (°) with standard deviations in parentheses *

| | | | |
|---|---|---|---|
| (*a*) Uranium environment | | | |
| U–O(1) | 1·78(6) | O(1)–U–O(6) | 97(2) |
| U–O(2) | 1·75(8) | O(1)–U–O(8) | 106(2) |
| U–O(3) | 2·41(5) | O(2)–U–O(3) | 88(3) |
| U–O(4) | 2·44(5) | O(2)–U–O(4) | 100(3) |
| U–O(5) | 2·33(5) | O(2)–U–O(5) | 100(3) |
| U–O(6) | 2·40(6) | O(2)–U–O(6) | 83(8) |
| U–O(8) | 2·33(6) | O(2)–U–O(8) | 77(3) |
| O(3) · · · O(4) | 2·64(7) | O(3)–U–O(4) | 66(2) |
| O(4) · · · O(5) | 3·11(7) | O(3)–U–O(5) | 147(2) |
| O(5) · · · O(6) | 2·94(7) | O(3)–U–O(6) | 136(2) |
| O(6) · · · O(8) | 2·59(8) | O(3)–U–O(8) | 70(2) |
| O(8) · · · O(3) | 2·72(8) | O(4)–U–O(5) | 81(2) |
| | | O(4)–U–O(6) | 158(2) |
| O(1)–U–O(2) | 177(3) | O(4)–U–O(8) | 136(2) |
| O(1)–U–O(3) | 93(2) | O(5)–U–O(6) | 77(2) |
| O(1)–U–O(4) | 79(2) | O(5)–U–O(8) | 143(2) |
| O(1)–U–O(5) | 77(3) | O(6)–U–O(8) | 66(2) |
| (*b*) Oxalate groups | | | |
| C(1)–O(5′) | 1·49(9) | O(5′)–C(1)–O(8) | 112(7) |
| C(1)–O(8) | 1·25(11) | O(5′)–C(1)–C(2) | 114(7) |
| C(1)–C(2) | 1·37(12) | O(8)–C(1)–C(2) | 134(8) |
| C(2)–O(6) | 1·32(9) | O(6)–C(2)–O(7) | 120(7) |
| C(2)–O(7) | 1·21(9) | O(6)–C(2)–C(1) | 104(7) |
| C(3)–O(4) | 1·32(8) | O(7)–C(2)–C(1) | 136(7) |
| C(3)–O(3″) | 1·21(8) | O(4)–C(3)–O(3″) | 130(6) |
| C(3)–C(3″) | 1·58(9) | O(4)–C(3)–C(3″) | 114(5) |
| | | O(3″)–C(3)–C(3″) | 114(5) |
| (*c*) Ammonium ion | | | |
| N · · · O(7) | 2·91(8) | O(7)–N–O($3^{I}$) | 133(3) |
| N · · · O($3^{I}$) | 3·03(8) | O(7) · · · N–O($4^{II}$) | 66(2) |
| N · · · O($4^{II}$) | 3·02(8) | O(7) · · · N–O($6^{III}$) | 112(3) |
| N · · · O($6^{III}$) | 2·82(8) | O(3′)–N–O($4^{II}$) | 72(2) |
| | | O(3′) · · · O($6^{III}$) | 95(2) |
| | | O(4′)–N–O($6^{III}$) | 151(6) |

* O(5′) is related to O(5) by $z + 1$, C(3″) and O(3″) are related to C(3) and O(3) by $-x, -y, -z$.

Roman numeral superscripts refer to the following atom transformations:

I $\frac{1}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$ III $x, y, z + 1$
II $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$

TABLE 3

(*a*) Equations of mean planes in orthogonal (Å) co-ordinates with axes $X = a$, $Y = b$, $Z$ perpendicular. Deviations (Å) of atoms from these planes are given in square brackets

Plane (1): U, O(3)—(6), O(8)

$$0{\cdot}997X - 0{\cdot}205Y + 0{\cdot}058Z = -0{\cdot}035$$

[U 0·0, O(3) −0·03, O(4) 0·03, O(5) −0·02, O(6) 0·01, O(8) 0·01]

Plane (2): C(3), C(3′), O(3), O(3″), O(4), O(4″)

$$0{\cdot}981X - 0{\cdot}178Y + 0{\cdot}075Z = 0{\cdot}0$$

[C(3) −0·06, O(3) −0·02, O(4) 0·02]

Plane (3): C(1), C(2), O(8), O(5′)

$$0{\cdot}953X - 0{\cdot}290Y + 0{\cdot}058Z = -0{\cdot}240$$

[C(1) −0·01, other defining atoms zero; O(6) −0·22; O(7) 0·21]

Plane (4): C(1), C(2), O(6), O(7)

$$0{\cdot}916X - 0{\cdot}390Y - 0{\cdot}084Z = -1{\cdot}275$$

[C(1) 0·0, C(2) −0·02, O(6) 0·0, O(7) 0·01, O(8) 0·21, O(5′) −0·23]

Line (5): U, O(1), O(2) Direction cosines 0·937, −0·164, 0·307

[U 0·03, O(7) 0·01, O(2) 0·01]

(*b*) Angles (deg.) between planes or lines

| | | | |
|---|---|---|---|
| (1)–(2) | 2 | (2)–(4) | 16 |
| (1)–(3) | 4 | (2)–(5) | 14 |
| (1)–(4) | 15 | (3)–(4) | 12 |
| (1)–(5) | 14 | (3)–(5) | 15 |
| (2)–(3) | 6 | (4)–(5) | 26 |

TABLE 4

Comparative interatomic distances (Å) in uranyl complexes; the final column gives the minimum distance between oxygen atoms of different ligands

| Compound | No. of ligand O-atoms | U–O (uranyl) | U–O (ligand) | Min. O · · · O (ligand ring) |
|---|---|---|---|---|
| $(NH_4)_4(UO_2)(C_2O_4)_3$ [a] | 6 | 1·69 | 2·43 * (1,4-)<br>2·57 (1,3-) | 2·52 |
| $(NH_4)_2(UO_2)(C_2O_4)_2$ [a] | 5 | 1·77 * | 2·37 * | 2·78 |
| $(NH_4)_2(UO_2)_2(C_2O_4)_3$ [b] | 5 | 1·77 * | 2·38 * | 2·72 |
| $Na_4(UO_2)(O_2)_3$ [c] | 6 | 1·88 * | 2·28 * | 2·92 |
| $Rb(UO_2)(NO_3)_3$ [d] | 6 | 1·78 | 2·48 | 2·79 |
| $Na(UO_2)(AcO)_3$ [e] | 6 | 1·71 * | 2·49 * | 2·76 |
| $UO_2(NO_3)_2,(H_2O)_2$ [f] | 6 | 1·76 * | 2·45 * ($H_2O$)<br>2·49 * ($NO_3$) | 2·62 |
| $[UO_2\{CO(NH_2)_2\}_4,H_2O](NO_3)_2$ [g] | 5 | 1·78 * | 2·36 * (urea)<br>2·46 ($H_2O$) | 2·73 |
| $UO_2C_2O_4,3H_2O$ [h] | 5 | 1·63 * | 2·48 * | 2·94 |

* Mean value.

[a] Ref. 1. [b] This work. [c] Ref. 7. [d] Ref. 8. [e] Ref. 9. [f] Ref. 10. [g] Ref. 11. [h] N. C. Jayaderan and D. M. Chackraburtty, *Acta Cryst.*, 1972, **B28**, 3178.

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[7] N. W. Alcock, *J. Chem. Soc.* (*A*), 1968, 1588.

[8] G. A. Barclay, T. M. Sabine, and J. C. Taylor, *Acta Cryst.*, 1965, **19**, 205.

[9] W. H. Zachariasen and H. A. Plettinger, *Acta Cryst.*, 1959, **12**, 526.

[10] N. K. Dalley, M. H. Mueller, and S. H. Simonsen, *Inorg. Chem.*, 1971, **10**, 323.

[11] N. K. Dalley, M. H. Mueller, and S. H. Simonsen, *Inorg. Chem.*, 1972, **11**, 1840.

[12] B. Beagley and R. W. H. Small, *Acta Cryst.*, 1964, **17**, 783.

straint. As expected, therefore, the 2 : 3 and 1 : 2 uranyl oxalate complexes have five-co-ordinate $UO_2^{2+}$ groups.* The driving force for the formation of the 1 : 3 complex is the high concentration of oxalate in the solution, but even so, it is surprising and important that a six-co-ordinate complex is formed. A close examination shows that it is under considerable strain, and the structure shows to what extent such strain can be accommodated in a uranyl complex. The first evidence of strain is that one of the oxalate groups is bidentate from adjacent oxygen atoms (1,3-co-ordinated) and its U–O distance is very long (2·57 Å). This must obviously be energetically less favourable than 1,4-co-ordination and it seems that no other example of a bidentate oxalate group of this type is known. Secondly, the non-bonded O · · · O distance has been reduced to 2·52 Å. Thirdly, the angles in the oxalate groups (Figure 3) show very clearly that they are distorted, with the non-bonded interactions forcing the bonded oxygen atoms together.

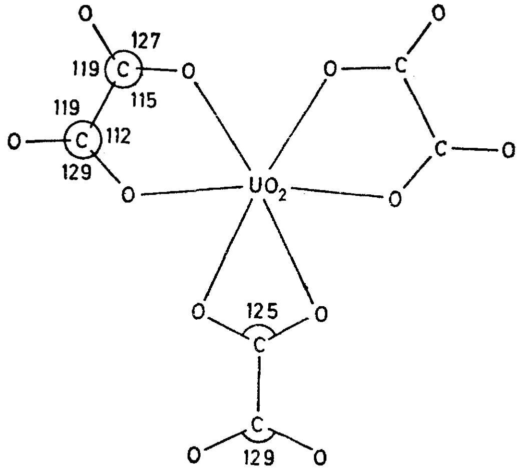


FIGURE 3 Angles in the ring groups of $(UO_2)(C_2O_4)_3{}^{4-}$

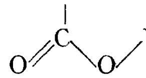
Apart from these distortions, all the oxalate groups have the normal dimensions of the free ion within the experimental accuracy. One possible exception is the C–O distances in the 1,4-co-ordinated oxalate in $UO_2(C_2O_4)_3{}^{4-}$. The mean C–O(co-ordinated) is 1·256 (18, root mean square error of mean), and C–O(free) is 1·221 (18). This suggests that the bonding pattern is to some extent  U. There are also changes of conformation, several of them having dihedral angles (Table 5) significantly different from zero between the $\begin{smallmatrix}O\\O\end{smallmatrix}\!>\!C{-}C$ planes. The largest is 37° in the 1,3-co-ordinated oxalate in $[UO_2(C_2O_4)_3]^{4-}$ apparently caused by particular hydrogen bonds, and the others are probably also due to packing effects. This is similar to the geometry of the free oxalate ion, which in most cases (*e.g.* $Li_2C_2O_4$, ref. 12) is planar, but in ammonium oxalate monohydrate has a dihedral angle of 26·6°, due to hydrogen bonding.[13] Further effects probably due to packing are the inclinations of the closely linear $UO_2$ groups to the closely planar equatorial oxygen atoms which range from 166 to 175·5°.

TABLE 5

Dihedral angles (deg.). Each complex contains two independent oxalate groups

| Complex | Oxalate (1) | Oxalate (2) | $UO_2$–ligand plane |
|---|---|---|---|
| $(UO_2)(C_2O_4)_3{}^{4-}$ | 37 | Very closely planar | 175·5 |
| $(UO_2)(C_2O_4)_2{}^{2-}$ | 14 | 10 | 173 |
| $(UO_2)_2(C_2O_4)_3{}^{2-}$ | 12 | Strictly zero | 166 |

The bonding between $UO_2^{2+}$ and the ligands has normally been thought of as being covalent (*e.g.* refs. 7 and 14) and there is one major piece of evidence in favour of this. However, the opposite view must be considered seriously: that these structures are the result of essentially electrostatic packing around linear $UO_2^{2+}$ groups. The ease with which the angle uranyl-to-ligand-plane alters is consistent with this, as is the way in which the co-ordination number changes under steric control. More puckering of the ligand planes than is found would be expected on this model, however, as there would be no forces other than uranyl-oxygen to ligand-oxygen repulsions tending to keep the ligand-oxygen atoms in a plane. Of the uranyl oxalate complexes only $[UO_2(C_2O_4)_3]^{4-}$ shows significant puckering (±0·08 Å). The strongest evidence against electrostatic bonding comes from the $UO_2$ bond lengths. There is clear evidence that these are variable, and that there is an inverse correlation between the uranyl U–O and the ligand U–O.[15] This can be seen in Table 4, and is true in particular of the uranyl oxalates, where the lengthening of the ligand U–O in $[UO_2(C_2O_4)_3]^{4-}$, probably due to overcrowding (see earlier) to 2·43 and 2·57 Å (*vs.* 2·37, 2·38 Å in the others) is accompanied by a shortening of the uranyl U–O to 1·69 Å (*vs.* 1·77 Å in the others).†

One further aspect of the uranyl oxalate structures is of significance in the 1 : 2 and 2 : 3 complexes: the cross-linking in which some of the oxalate groups have become ter- and quadri-dentate. The chemical process involved here is the replacement, either in solution or on crystallisation, of aquo- by oxalato-ligands. The evidence that $(UO_2)_2(C_2O_4)_3{}^{2-}$ persists in solution as a dimer [16] does not clarify this point because the bridging oxalate group might only be unidentate to two different uranium atoms in solution. It was suggested [2] that the

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* *Note added in proof:* As does uranyl oxalate, $UO_2C_2O_4,3H_2O$, itself, N. C. Jayaderan and D. M. Chackraburtty, *Acta Cryst.*, 1972, **B28**, 3178.

† *Note added in proof*: Similarly, in $UO_2C_2O_4,3H_2O$, with ligand U–O bond length of 2·48 Å, long possibly because of packing constraints, the uranyl U–O bond length is 1·63 Å.

[13] J. H. Robertson, *Acta Cryst.*, 1965, **18**, 410.

[14] C. Panattoni, R. Graziani, V. Croatto, B. Zarli, and G. Bombieri, *Inorg. Chim. Acta*, 1968, **2**, 43.

[15] W. H. Zachariasen, *Acta Cryst.*, 1954, **7**, 795.

[16] I. I. Chernayev, ' Complex Compounds of Uranium,' Israel Program for Scientific Translations, Jerusalem, 1966, pp. 123—126.

tendency to form multidentate oxalate groups might be due to the presence of extended π-interactions in the co-ordination plane. However, the evidence presented here, that most of the oxalate groups are significantly non-planar, argues against this. Also these multidentate oxalate groups are not restricted to uranyl complexes (*contra* ref. 2) but have been found with a number of transition metals,[17] with *X*-ray confirmation for compounds of titanium,[18] iron,[19] nickel,[20] ruthenium,[17] and thorium.[21]

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[17] P. T. Cheng, B. R. Loescher, and S. C. Nyburg, *Inorg. Chem.*, 1971, **10**, 1275.

[18] M. G. B. Drew, G. W. A. Fowles, and D. T. Lewis, *Chem. Comm.*, 1969, 876.

[19] F. Mazzi and C. Garavelli, *Periodico Mineral.* (*Rome*), 1957, **26**, 269 (*Chem. Abs.*, **52**, 6074*d*; **54**, 8476*g*; **55**, 6268*h*).

[20] N. F. Curtis, *J. Chem. Soc.* (*A*), 1968, 1584.

[21] M. N. Akhtar and A. J. Smith, *Chem. Comm.*, 1969, 705.