Uranyl Oxalate Complexes. Part I. Preparation and Crystal and Molecular Structure of Ammonium Uranyl Trioxalate

By **Nathaniel W. Alcock,** *Department of Molecular Sciences, University of Warwick, Coventry CV4 7AL*

The preparation is reported of ammonium uranyl oxalate complexes with $UO_2:C_2O_4$ ratios of 1 : 3, 1 : 2, and 1 : 1·5. The crystal structure and single-crystal visible absorption spectrum of the title compound have been determined. Crystals are monoclinic, space group *C*2/*c*, *a* = 10·031(9), *b* = 11·519(10), *c* = 14·213(10) Å, β = 101·46(6)°, *Z* = 4. 1287 Observed intensities were measured by diffractometer; the structure was solved by the heavy-atom method and refined to a final *R* of 0·072. The crystal contains NH_4^+ and $UO_2(C_2O_4)_3^{4-}$ ions. The latter have two bidentate oxalate groups forming five-membered rings with U–O 2·43 Å, and one such group forming a four-membered ring with U–O 2·57 Å. This oxalate group has its two ends twisted relative to each other by 37°. The uranyl U–O distance is 1·69 Å, and the geometry around the uranium atom is approximately hexagonal bipyramidal.

RECENT structural studies of complexes of the uranyl ion [1] have begun to clarify the principles governing these species. Many of the systems involve chelating ligands and in this context, oxalate is particularly interesting in having the unusually large chelating distance (bite) of *ca.* 2·7 Å, while remaining rigid.

This and the following two papers report structure determinations of three ammonium uranyl oxalates in which the uranyl–oxalate ratio varies from **1 : 3** to **1 : 1·5**. Ammonium was used as the counter ion, partly because as a light atom, it does not decrease the accuracy of the structure determination and partly because it was used extensively in early preparative work on the system. In all cases crystals were prepared by evaporation at 80 °C or over, so that anhydrous species were formed and the complex ions were certain to involve only uranyl and oxalate.

The preparations of all the species are reported here; the geometries of the uranyl complexes are considered in Part III.*

EXPERIMENTAL

Preparations.—Uranyl oxalate, $(UO_2)(C_2O_4),3H_2O$ was prepared by mixing slowly at 90 °C uranyl nitrate (30 g in 50 ml water) and oxalic acid (10 g in 50 ml water), filtering, and drying the resulting light yellow precipitate. Several compounds of the uranyl oxalate–ammonium oxalate system were first prepared by Wyruboff,[2] and examined by optical goniometry. Colani [3] has presented a partial phase diagram. Ammonium uranyl trioxalate $(NH_4)_4(UO_2)(C_2O_4)_3$ can only be made above *ca.* 60 °C and although Wyruboff states that he used an equimolecular mixture of the two oxalates, it seems that much more ammonium oxalate is necessary (possibly his equimolecular is an error for equal weights). A suitable method is to mix uranyl oxalate (8·4 g, 20 mmol) and ammonium oxalate (9 g, 63 mmol) in water (60 ml). This solution was placed in an oven at 90 °C and covered with aluminium foil in which a small hole was pierced, when the slow evaporation provides block-like pale yellow crystals of any desired size up to several mm in overall dimensions. It was sometimes necessary to repeat the evaporation before good crystals were formed. The solid also contained needle-like opaque white crystals, probably of dehydrated ammonium oxalate but these could easily be separated out by hand. When fresh the crystals fracture conchoidally but decompose slowly in air (perhaps by hydrolysis) and then give planar fractures.

The axial ratios found by *X*-ray methods for these crystals (0·871 : 1 : 1·233) correspond precisely to those reported by Wyruboff (ref. 2, p. 361) as does the inter-axial angle. He quotes the angle as γ not β, although his axes correspond to the present ones, and he gives goniometric measurements in agreement with this. The correspondence in axial ratios makes it clear that the two substances are identical and this discrepancy is unresolved. His drawings show faces {010} as the most prominent, with {001} and {110} rather smaller; in the present work, the crystals have always had {110} best developed with {001} completing the polyhedron.

Both ammonium uranyl dioxalate $(NH_4)_2(UO_2)(C_2O_4)_2$ and ammonium diuranyl trioxalate $(NH_4)_2(UO_2)_2(C_2O_4)_3$ were formed during attempts to duplicate Wyruboff's preparation of the trioxalate by evaporation of a solution equimolar in uranyl oxalate and ammonium oxalate; according to Colani [3] this mixture should produce the diuranyl trioxalate alone, but his phase limits do not correspond to the expected stoicheiometries.

Crystal Data.—$C_6H_{16}N_4O_{14}U$, Monoclinic, *a* = 10·031(9), *b* = 11·519(10), *c* = 14·213(10) Å, β = 101·46(6)°, *U* = 1608·3 Å,[3] D_c = 2·50, *Z* = 4, D_m = 2·47 (by flotation in benzene–methylene iodide), *F*(000) = 1136. Mo-K_α radiation, λ = 0·7107 Å; μ(Mo-K_α) = 72·5 cm^{-1}. Systematic

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* Parts II and III, following papers.

[1] See *e.g.* C. Panattoni, R. Graziani, G. Bandoli, B. Zarli, and G. Bombieri, *Inorg. Chem.*, 1969, **8**, 320.

[2] M. G. Wyruboff, *Bull. Soc. France, Minerol.*, 1909, **32**, 340.

[3] A. Colani, *Compt. rend.*, 1961, **165**, 234.

TABLE 1

Atomic co-ordinates and anisotropic * temperature factors ($\times 10^4$), with standard deviations in parentheses

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
U	0	1309·8(6)	2500	35·3(17)	19·7(7)	18·9(5)	0	9·5(5)	0
O(1)	1601(15)	1326(9)	3098(12)	51(16)	42(8)	53(10)	1(9)	40(10)	6(6)
O(2)	916(17)	1447(11)	1039(10)	79(19)	28(9)	23(7)	3(10)	21(10)	3(6)
O(3)	723(17)	−510(11)	1871(11)	83(21)	21(10)	36(9)	6(11)	33(12)	6(7)
O(4)	2020(20)	642(13)	−20(10)	144(27)	42(12)	23(8)	18(14)	43(12)	5(7)
O(5)	1822(21)	−1448(12)	895(13)	123(26)	31(11)	49(11)	11(13)	41(14)	−1(8)
O(6)	429(17)	3351(12)	1844(10)	85(20)	29(9)	31(8)	8(12)	28(11)	−1(7)
O(7)	−280(21)	5685(13)	1696(11)	130(27)	33(11)	34(9)	19(14)	32(13)	10(8)
C(1)	1430(22)	617(16)	652(14)	57(23)	29(13)	11(9)	8(14)	2(12)	−3(9)
C(2)	1324(21)	−573(15)	1178(14)	41(22)	27(13)	27(11)	5(14)	11(13)	−1(9)
C(3)	0	3856(23)	2500	75(37)	31(19)	12(12)	0	11(17)	0
C(4)	0	5219(22)	2500	72(40)	34(18)	24(12)	0	20(18)	0
N(1)	1683(18)	2121(14)	8384(12)	47(19)	34(12)	29(9)	−9(13)	14(10)	−1(8)
N(2)	1040(21)	3689(15)	5172(13)	66(22)	53(16)	27(9)	0(15)	14(12)	−3(9)

* In the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

absences: $h + k \neq 2n$ for hkl and $l \neq 2n$ for $h0l$ indicate space groups $C2/c$ or Cc, the former chosen on the basis of the structure refinement. This choice of space group requires the complex anion $UO_2(C_2O_4)_3^{4-}$ to show either a centre or a two-fold axis of symmetry and the presence of three oxalate groups indicates the latter.

The unit-cell constants and standard deviations were determined by least-squares fit to the reflecting positions of 12 high-angle reflections using the standard program of a Picker FACS 1, and are the means of determinations on two crystals. Data were collected on this instrument by use of Mo-K_α radiation with a graphite monochromator, and θ—2θ scan, 4° take-off angle, and no attenuators, the crystals being enclosed in a Lindemann glass tube. Data were collected to 2θ 50°. Crystal decomposition was monitored with one low- and two high-angle reflections. It was found that the low-angle reflection remained virtually constant, but the high-angle ones showed a steady decrease. After an overall reduction of *ca.* 20% a second crystal was mounted to complete data collection. This decomposition was approximately compensated for by multiplying the net intensity of the Nth reflection recorded by $(1 + kN\theta)$ where θ is the Bragg angle and k was chosen to fit the rate of decomposition. Lorentz and polarisation corrections were applied and the data corrected for absorption with the program ABSCOR; 1287 reflections with $I/\sigma(I) > 3{\cdot}0$ were considered observed.

Data were initially collected with a Stoe Weissenberg diffractometer (*cf.* Part II) and the structure was readily solved by the heavy-atom method, but the refinement was not satisfactory, probably because crystal decomposition was not adequately compensated for. With the new data set and the previous co-ordinated, least-squares refinement rapidly produced R 0·102 with isotropic temperature factors.

A weighting scheme of the form $\sigma^2(F) = 3{\cdot}5F$ was found to be satisfactory, and refinement with all atom thermal parameters anisotropic gave a final R of 0·072, with a significant improvement over refinement with only the uranium atom anisotropic. Anomalous dispersion by uranium was allowed for,[4] but no extinction correction was needed. Scattering factors were from ref. 5. Refinement was not attempted in space group Cc because of the satisfactory results in $C2/c$. All calculations were performed by use of the 'X-Ray '63' system of programs [6] on the SRC ATLAS and on an IBM 7094. Table 1 gives the final atomic co-ordinates and temperature factors, Table 2 the bond lengths and angles, and Table 3 the mean planes.

TABLE 2

Distances (Å) and angles (°) with standard deviations in parentheses

(*a*) Uranium environment			
U–O(1)	1·69(1)	O(1)–U–O(2)	86·3(7)
U–O(2)	2·44(2)	O(1)–U–O(3)	82·0(6)
U–O(3)	2·42(1)	O(1)–U–O(6)	87·5(5)
U–O(6)	2·57(2)	O(2)–U–O(3)	63·1(5)
O(2) ··· O(3)	2·54(2)	O(2)–U–O(6)	60·9(5)
O(6) ··· O(6′)	2·21(2)	O(3)–U–O(3′)	62·8(5)
O(2) ··· O(6)	2·54(2)	O(6)–U–O(6′)	50·9(5)
O(3) ··· O(3′)	2·52(3)		
(*b*) Oxalate groups			
C(1)–O(2)	1·26(3)	O(2)–C(1)–O(4)	129(2)
C(1)–O(4)	1·22(3)	O(2)–C(1)–C(2)	112(2)
C(1)–C(2)	1·56(3)	O(4)–C(1)–C(2)	119(2)
C(2)–O(3)	1·26(3)	O(3)–C(2)–O(5)	127(2)
C(2)–O(5)	1·22(3)	O(3)–C(2)–C(1)	115(2)
		O(5)–C(2)–C(1)	119(2)
C(3)–O(6)	1·24(2)	O(6)–C(3)–O(6′)	125(5)
C(3)–C(4)	1·55(5)	O(6)–C(3)–C(4)	118(1)
C(4)–O(7)	1·24(2)	O(7)–C(4)–O(7′)	129(2)
		O(7)–C(4)–C(3)	115(1)
(*c*) Ammonium ions			
N(1) ··· O(2^{I})	2·92(2)	O(2^{I}) ··· N(1) ··· O(3^{II})	135·8(9)
N(1) ··· O(3^{II})	2·84(2)	O(2^{I}) ··· N(1) ··· O(4^{III})	98·3(7)
N(1) ··· O(4^{III})	2·79(2)	O(2^{I}) ··· N(1) ··· O(7^{IV})	84·9(6)
N(1) ··· O(7^{IV})	2·86(2)	O(3^{II}) ··· N(1) ··· O(4^{III})	101·2(7)
		O(3^{II}) ··· N(1) ··· O(7^{IV})	115·8(7)
		O(4^{III}) ··· N(1) ··· O(7^{IV})	122·6(8)
N(2) ··· O(5^{II})	2·80(2)	O(5^{II}) ··· N(2) ··· O(5^{V})	87·3(8)
N(2) ··· O(5^{V})	2·89(3)	O(5^{II}) ··· N(2) ··· O(6^{VI})	106·8(7)
N(2) ··· O(6^{VI})	2·98(2)	O(5^{II}) ··· N(2) ··· O(7^{VII})	95·3(8)
N(2) ··· O(7^{VII})	2·85(3)	O(5^{V}) ··· N(2) ··· O(6^{VI})	157·9(9)
		O(5^{V}) ··· N(2) ··· O(7^{VII})	77·3(7)
		O(6^{VI}) ··· N(2) ··· O(7^{VII})	122·5(9)

Roman numerals as superscripts refer to the following transformations of the atoms relative to the reference molecule at x, y, z:

I $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$
II $x, -y, \frac{1}{2} + z$
III $x, y, 1 + z$
IV $-x, 1 - y, 1 - z$
V $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$
VI $-x, y, \frac{1}{2} - z$
VII $x, 1 - y, \frac{1}{2} + z$

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

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

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

The atomic numbering is shown in Figure 1. Final structure factors are listed in Supplementary Publication No. SUP 20705 (3 pp., 1 microfiche).*

TABLE 3

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

Plane (1): U, O(2), O(3), O(6)

$$0{\cdot}834X + 0{\cdot}060Y + 0{\cdot}569Z = 1{\cdot}501$$

[U 0·08, O(2) 0·07, O(3) −0·08, O(6) −0·07, C(1) −0·10, C(2) −0·21, C(3) −0·09, O(1) −1·60]

Plane (2): C(1), C(2), O(2)—(5)

$$0{\cdot}760X + 0{\cdot}186Y + 0{\cdot}623Z = 1{\cdot}682$$

[C(1) 0·02, C(2) 0·01, O(2) −0·01, O(3) 0·00, O(4) 0·00, O(5) −0·01]

Plane (3): O(6), C(3), C(4)

$$0{\cdot}828X + 0{\cdot}560Z = 1{\cdot}379$$

[O(7) 0·68]

Plane (4): O(7), C(3), C(4)

$$0{\cdot}998X + 0{\cdot}056Z = 0{\cdot}886$$

[O(6) 0·67]

The line, (5), U–O(1) has direction cosines 0·870, 0, 0·494

(*b*) Angles (°) between plane (line) normals

(1)–(2)	9·2	(2)–(4)	37·5
(1)–(3)	3·5	(2)–(5)	14·3
(1)–(4)	36·9	(3)–(4)	37·5
(1)–(5)	4·5	(3)–(5)	4·5
(2)–(3)	12·0	(4)–(5)	26·5

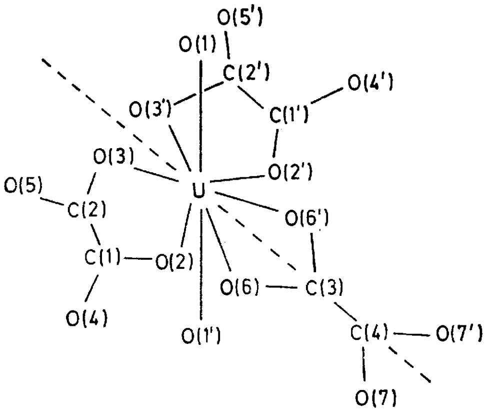

FIGURE 1 Atomic numbering for the $UO_2(C_2O_4)_3^{2-}$ ion. A primed atom is related to an unprimed one by the molecular two-fold axis of symmetry, which is shown dashed

Single-crystal Spectra.—Because the electronic structure of uranyl complexes is of interest and because large crystals could be obtained, the single-crystal visible and u.v. absorption spectrum of ammonium uranyl trioxalate was examined. Measurements were made at 77 K on a Cary 14 recording spectrophotometer with polarised light. The monoclinic symmetry gives three independent absorption spectra. Direction (II) lies along the *b* axis, in the plane of the oxalate groups. Directions (I) and (III) in the *ac* plane lie in the expected directions (*cf.* Figure 2), along the UO_2 direction and in the oxalate plane respectively. There is marked pleochroism, with the crystal almost colourless for light polarised parallel to (I), but bright yellow for (II) and (III). Because the principal faces developed are {110} useful spectra could not be obtained without grinding and polishing artificial faces on the crystals. The crystals used were 1—2 mm across, and they were oriented with a precession camera and glued with Araldite to a glass slide, while one side was ground to maximum cross-section (with carborundum and paraffin oil) and polished; they were then cut off the slide, glued with Araldite to a pierced copper plate or block, ground to a suitable thickness (*ca.* 0·2 mm), and polished. A preliminary examination through the {110} faces of a thin crystal which needed a minimum of treatment gave very fine spectra with many very sharp peaks, but the best results (Table 4) after treatment as described only showed broad peaks. It is clear that the crystal shaping has produced partial decomposition; this was confirmed by the frequent appearance of striae due to linear fractures on the ground crystals (*cf.* earlier). It was also found that light of wavelength *ca.* 300 nm caused rapid decomposition. It is possible that grinding the crystals under rigorously anhydrous conditions or treating them at 90 °C with mother liquor might allow the detailed spectrum to be studied. The results are similar to those previously found for uranyl complexes,[7] showing several vibrational progressions. As a spectrum of good quality could not be obtained, no detailed interpretation was attempted.

TABLE 4

Visible and u.v. single-crystal spectrum (nm) of ammonium uranyl trioxalate (600—300 nm). Peaks are strong unless otherwise marked: m = medium, sh = shoulder, w = weak

Direction (I): Parallel to O–U–O

A progression with doublet peaks of which the shorter wavelength one becomes progressively stronger: 483w, 478w, 456; 451, 447sh; 436, 430; 423, 417; 410sh, 405; 393, 383, 364, 355, 345sh; and a continuous absorption extending to 300.

Direction (II): Parallel to *b* axis

A progression of broad peaks: 485m, 465, 449, 431, 417, 406, 393, 383, 373, 365, 353sh, and a continuous absorption extending to 300, much more intense than for direction (I).

Direction (III): Perpendicular to *b* axis and O–U–O

A progression of peaks, each probably an unresolved multiplet tailing towards short wavelength, with a spread of *ca.* 80 nm (540 and 526w, uncertain) 484w, 478w, 465, 450, 436; a plateau with peaks at: 423, 410, 399; 379, 364, 355, 346sh; and a continuous absorption extending to 300, of similar intensity to direction (II).

RESULTS AND DISCUSSION

The crystal contains discrete NH_4^+ and $UO_2(C_2O_4)_3^{4-}$ ions. The latter is considered in detail in Part III, but the most significant features are summarized here. Two of the oxalate groups are co-ordinated to give five-membered rings (1,4-co-ordinated), the third to give a

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* 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 supplied as full size copies).

[7] E. Rabinowitch and R. L. Belford, 'Spectroscopy and Photochemistry of Uranyl Compounds,' Pergamon Press, Oxford, 1964.

four-membered ring (1,3-co-ordinated). The U–O distances are 1·69 in the UO_2 group, 2·43 (mean) to the 1,4-co-ordinated oxalate, and 2·57 Å to the other. This oxalate group has a 37° twist between the O–C–O planes at each end. The geometry around the uranium atom is approximately hexagonal bipyramidal.

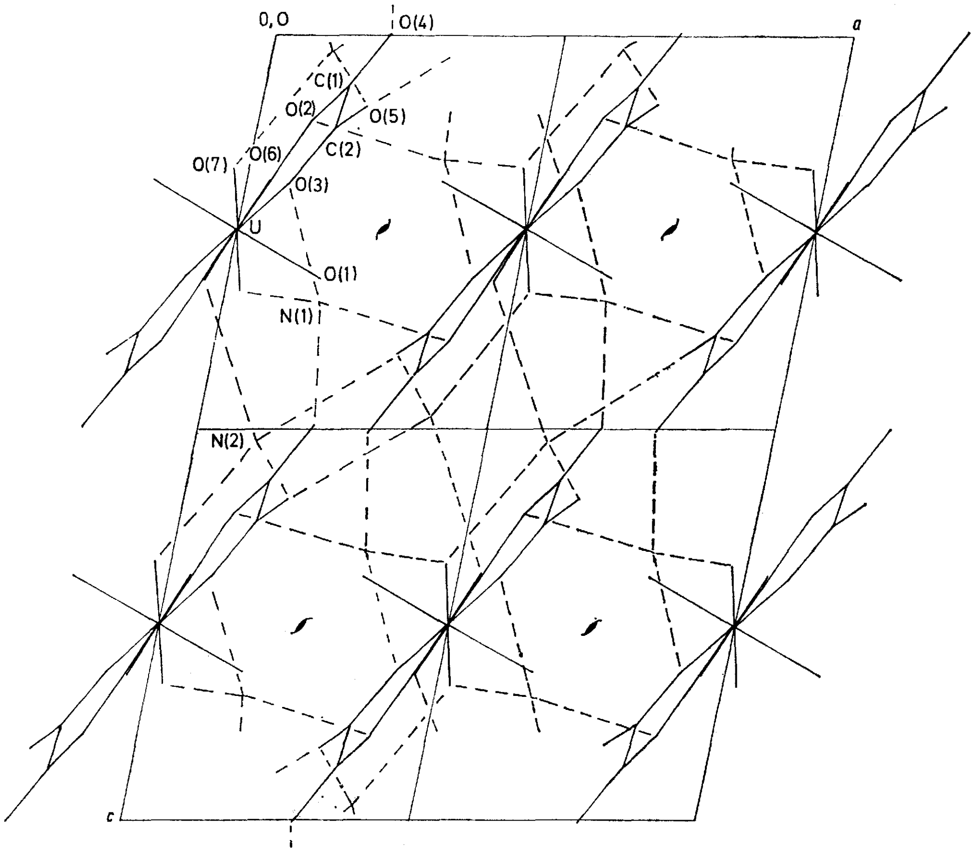

FIGURE 2 Packing of the crystal, viewed down *b*. Alternate uranium atoms are at $y = 0{\cdot}13$ and 0·63. In the upper row the 1,3-co-ordinated oxalate groups are above the uranium atoms [C(3) at $y = 0{\cdot}39$ and 0·89]; in the lower row these oxalate groups are below the uranium atoms. Hydrogen bonds are shown as dashed lines and the nitrogen atoms are located at the intersections of these lines.

Packing.—Both nitrogen atoms have four oxygen neighbours in approximately tetrahedral arrangements with N–O 2·79—2·98 Å. All these are probably involved in hydrogen bonds. Some of the unlocated hydrogen atoms must lie rather far from N–O lines to judge from the deviations of the O–N–O angles from 109°. These hydrogen bonds link the anions in a three-dimensional array (Figure 2 and Table 2). The presence of this three-dimensional network may account for the remarkable conchoidal fractures shown by the crystals.

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