Uranyl Oxalate Complexes. Part II.[1] Preparation and Crystal and Molecular Structure of Ammonium Uranyl Dioxalate

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The crystal structure of the title compound has been determined from diffractometer data by the heavy-atom method. Crystals are triclinic, space group $P\bar{1}$, $a = 12{\cdot}91(2)$, $b = 7{\cdot}20(1)$, $c = 6{\cdot}31(1)$ Å, $\alpha = 110{\cdot}56(5)$, $\beta = 107{\cdot}85(5)$, $\gamma = 84{\cdot}25(5)°$, $Z = 2$. 1351 Reflections were refined by least squares to a final R of 0·130. The crystal contains NH_4^+ and $[(UO_2)(C_2O_4)_2]_n^{2n-}$ ions. In the latter one oxalate group is bidentate, and one bidentate to one uranium atom and unidentate to another, giving chains parallel to c. Mean distances are U–O(uranyl) 1·77, and U–O(oxalate) 2·37 Å.

THE uranyl oxalate complex with a uranium–oxalate ratio of 1 : 2 should have a structure without either overcrowding or extensive cross-linking. Its crystal structure has been determined.

EXPERIMENTAL

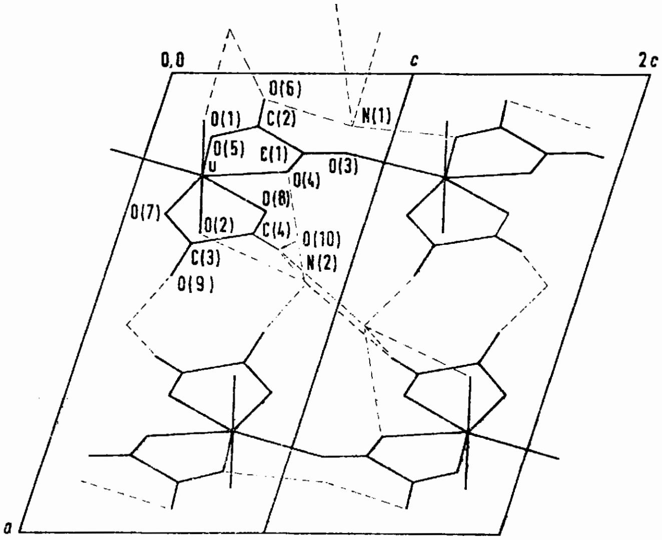
Crystal Data.—$C_4H_8N_2O_{10}U$, Triclinic, $a = 12{\cdot}91(2)$, $b = 7{\cdot}20(1)$, $c = 6{\cdot}31(1)$ Å, $\alpha = 110{\cdot}56(5)$, $\beta = 107{\cdot}85(5)$, $\gamma = 84{\cdot}25(5)°$, $U = 522{\cdot}3$, $D_c = 3{\cdot}06$, $Z = 2$, $D_m = 3{\cdot}0$. $F(000) = 436$. Space group $P\bar{1}$ was assumed and shown to be satisfactory by the refinement. Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; $\mu(\text{Cu-}K_\alpha) = 633$ cm^{-1}.

Crystals of 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 dioxalate, elongated along c, frequently appeared as twins with a common c axis and with 110 and $\bar{1}\bar{1}0$ parallel.

Data were collected on a Stoe Weissenberg automatic diffractometer by use of Cu-K_α radiation with β-filter, θ—2θ scan, and no attenuators. Unit-cell dimensions were determined from high-angle reflections of crystals mounted about two different directions, and their standard deviations estimated from the accuracy of the observations. Crystal decomposition was monitored with a low-angle reflection on each layer; slow decomposition was observed and three crystals were used in all. Two were mounted about c and used for the collection of layers $hk0$—2 and $hk3$—5; one was mounted about 111 and used for zero, first, and second layers. To correct for the decomposition the data were rescaled by factors of the form $(1 + kn)$ for the n reflection on a layer. Lorentz, polarisation, and absorption corrections were applied, the latter with the program ABSCOR. From the later experience with the trioxalate,[1] it seems likely that the decomposition was more complicated than was realised, and the compensation not fully satisfactory. Data were placed approximately on a common scale by comparison of identical reflections but no merging was done, all occurrences of the same reflection being retained with individual layer scale factors (*cf.* ref. 2). 1671 Reflections with $I/\sigma(I) > 3{\cdot}0$ were considered observed.

A Patterson synthesis showed the U · · · U vectors clearly and the light atoms were readily located on successive Fourier syntheses. It was found that $hk2$ and the final layer for the second crystal setting had exceptionally high R factors, probably caused by decomposition effects; these layers were removed, reducing the total number of reflections to 1351. Refinement proceeded to R 0·138 with anisotropic temperature factors for the uranium atom with unit weights which were satisfactory.

For further refinement an attempt was made to correct for the crystal decomposition assuming this to be similar to that found for the uranyl trioxalate complex. Decreasing intensities for high-angle reflections correspond to increasing atomic temperature factors, and to compensate for this an overall temperature factor (B_j) was applied to each layer with the nth reflection on the jth layer being multiplied by $\exp(B_j \sin^2 \theta_n/\lambda^2)$. B_1 Was given the value zero, *i.e.* all the layers were corrected relative to the first layer.[3] Refinement in this way gave a final R of 0·130. Anomalous dispersion by uranium was allowed for,[4] and scattering factors were from ref. 5. All computing except the final refinement was with the '*X*-Ray '63' program system on the ATLAS computer.[6]



The structure projected down b, giving the atomic numbering. Dashed lines represent possible hydrogen bonds and the nitrogen atoms are at the intersections of these lines.

The Figure gives the atomic numbering, Table 1 the atomic positions and temperature factors, Table 2 the bond

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[1] Part I, N. W. Alcock, preceding paper.

[2] 'Crystallographic Computing,' ed. F. Ahmed, Munksgaard, Copenhagen, 1970, p. 183.

[3] 'BAYLS' a least-squares program developed by N. A. Bailey, and rewritten in FORTRAN by N. W. Alcock.

[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, J. M. Stewart, University of Maryland Technical Report, TR 64 6.

TABLE 1

Atomic co-ordinates ($\times 10^3$) and temperature factors, with standard deviations in parentheses

Atom	x	y	z	B
U	221·5(2)	168·2(3)	268·4(3)	*
O(1)	969(4)	295(7)	199(9)	2·9(10)
O(2)	344(4)	44(8)	344(9)	3·2(10)
O(3)	166(3)	−12(6)	845(7)	1·1(7)
O(4)	213(2)	146(4)	626(5)	0·1(5)
O(5)	136(4)	−116(6)	256(8)	1·9(8)
O(6)	54(4)	−269(7)	423(8)	2·4(9)
O(7)	301(3)	381(5)	168(6)	0·5(6)
O(8)	299(3)	466(6)	583(7)	1·3(7)
O(9)	439(5)	608(9)	278(11)	4·5(12)
O(10)	383(4)	757(8)	701(9)	3·2(10)
C(1)	170(4)	35(7)	663(9)	0·2(8)
C(2)	113(4)	−136(7)	425(9)	0·5(8)
C(3)	367(5)	536(10)	320(11)	1·9(11)
C(4)	351(4)	588(8)	560(9)	0·6(8)
N(1)	884(4)	430(7)	184(8)	1·2(8)
N(2)	452(5)	174(10)	853(12)	3·4(12)

* For U: $\exp[-(0{\cdot}0024(2)h^2 + 0{\cdot}0044(8)k^2 + 0{\cdot}0013(18)l^2 - 2 \times 0{\cdot}0031(3)hk + 2 \times 0{\cdot}0002(4)hl - 2 \times 0{\cdot}0054(8)kl)]$.

TABLE 2

Distances (Å) and angles (°), with standard deviations in parentheses. O(3′) is at (z − 1) in relation to O(3)

(a) Uranium environment

U–O(1)	1·78(5)	O(1)–U–O(2)	178(3)
U–O(2)	1·75(5)	O(1)–U–O(4)	98(2)
U–O(4)	2·35(4)	O(1)–U–O(5)	94(2)
U–O(5)	2·39(5)	O(1)–U–O(7)	88(2)
U–O(7)	2·28(4)	O(1)–U–O(8)	90(2)
U–O(8)	2·40(3)	O(1)–U–O(3′)	83(2)
U–O(3′)	2·43(4)	O(2)–U–O(4)	80(2)
O(4) ··· O(5)	2·42(4)	O(2)–U–O(5)	85(2)
O(4) ··· O(8)	2·78(6)	O(2)–U–O(7)	93(2)
O(5) ··· O(3′)	3·07(8)	O(2)–U–O(8)	90(2)
O(7) ··· O(8)	2·48(6)	O(2)–U–O(3′)	98(2)
O(7) ··· O(3′)	3·15(5)	O(4)–U–O(5)	61(1)
		O(4)–U–O(8)	72(1)
		O(5)–U–O(3′)	79(2)
		O(7)–U–O(8)	64(1)
		O(7)–U–O(3′)	84(1)

(b) Oxalate groups

C(1)–O(3)	1·32(8)	O(3)–C(1)–O(4)	139(4)
C(1)–O(4)	1·14(7)	O(3)–C(1)–C(2)	109(5)
C(1)–C(2)	1·59(6)	O(4)–C(1)–C(2)	111(5)
C(2)–O(5)	1·25(8)	O(5)–C(2)–O(6)	128(4)
C(2)–O(6)	1·27(8)	O(5)–C(2)–C(1)	110(5)
C(3)–O(7)	1·35(7)	O(6)–C(2)–C(1)	122(5)
C(3)–O(9)	1·25(12)	O(7)–C(3)–O(9)	126(6)
C(3)–C(4)	1·50(10)	O(7)–C(3)–C(4)	109(6)
C(4)–O(8)	1·22(8)	O(9)–C(3)–C(4)	125(5)
C(4)–O(10)	1·24(7)	O(8)–C(4)–O(10)	129(6)
		O(8)–C(4)–C(3)	115(4)
		O(10)–C(4)–C(3)	116(6)

(c) Ammonium ions

N(1) ··· O(1^{I})	2·81(7)	O(1^{I}) ··· N(1) ··· O(5^{II})	75(2)
N(1) ··· O(5^{II})	2·86(8)	O(1^{I}) ··· N(1) ··· O(6^{III})	64(2)
N(1) ··· O(6^{III})	2·90(6)	O(1^{I}) ··· N(1) ··· O(6^{IV})	77(2)
N(1) ··· O(6^{IV})	2·96(8)	O(5^{II}) ··· N(1) ··· O(6^{III})	126(3)
		O(5^{II}) ··· N(1) ··· O(6^{IV})	110(2)
		O(6^{III}) ··· N(1) ··· O(6^{IV})	92(2)
N(2) ··· O(2)	2·92(8)	O(2) ··· N(2) ··· O(4)	54(2)
N(2) ··· O(4)	2·97(7)	O(2) ··· N(2) ··· O(9^{V})	80(3)
N(2) ··· O(9^{V})	2·68(12)	O(2) ··· N(2) ··· O(10^{VI})	72(2)
N(2) ··· O(10^{VI})	2·95(9)	O(2) ··· N(2) ··· O(10^{VII})	161(3)
N(2) ··· O(10^{VII})	2·88(8)	O(4) ··· N(2) ··· O(9^{V})	115(3)
		O(4) ··· N(2) ··· O(10^{VI})	71(2)
		O(4) ··· N(2) ··· O(10^{VII})	143(3)
		O(9^{V}) ··· N(2) ··· O(10^{VI})	138(3)
		O(9^{V}) ··· N(2) ··· O(10^{VII})	92(3)
		O(10^{VI}) ··· N(2) ··· O(10^{VII})	105(3)

TABLE 2 (*Continued*)

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

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

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 the planes are given in square brackets.

Plane (1): U, O(4), O(5), O(7), O(8), O(3′)

$$0{\cdot}827X - 0{\cdot}476Y + 0{\cdot}297Z = 1{\cdot}858$$

[U 0·0, O(4) 0·05, O(5) 0·02, O(7) 0·12, O(8) −0·11, O(3′) −0·07, O(1) −1·77, O(2) 1·73]

Plane (2): C(1), C(2), O(3), O(4)

$$0{\cdot}819X - 0{\cdot}531Y + 0{\cdot}218Z = 1{\cdot}545$$

[C(1) 0·05, C(2) 0·01, O(3) −0·02, O(4) −0·02, O(5) −0·23, O(6) 0·14]

Plane (3): C(1), C(2), O(5), O(6)

$$0{\cdot}734X - 0{\cdot}573Y + 0{\cdot}363Z = 1{\cdot}969$$

[O(3) −0·03, O(4) 0·09, defining atoms zero]

Plane (4): C(3), C(4), O(7), O(9)

$$0{\cdot}559X - 0{\cdot}668Y + 0{\cdot}491Z = 0{\cdot}459$$

[C(3) 0·05, C(4) −0·01, O(7) −0·01, O(9) −0·02, O(8) −0·33, O(10) 0·38]

Plane (5): C(3), C(4), O(8), O(10)

$$0{\cdot}756X - 0{\cdot}412Y + 0{\cdot}508Z = 2{\cdot}241$$

[C(3) 0·01, C(4) −0·03, O(8) 0·01, O(10) 0·01, O(7) −0·38, O(9) 0·36]

Line (6): U, O(1), O(2) has direction cosines 0·772, −0·478, 0·419
[U 0·01, O(1) O(2) 0·01]

(b) Angles (°) between planes or lines

(1)–(2)	6	(3)–(4)	14
(1)–(3)	9	(3)–(5)	13
(1)–(4)	22	(3)–(6)	7
(1)–(5)	14		
(1)–(6)	7		
		(4)–(5)	19
(2)–(3)	10	(4)–(6)	17
(2)–(4)	23		
(2)–(5)	18	(5)–(6)	6
(2)–(6)	12		

lengths and angles, and Table 3 the mean planes. Final structure factors are listed in Supplementary Publication No. SUP 20706 (4 pp., 1 microfiche).*

RESULTS AND DISCUSSION

The crystal contains NH_4^+ ions and uranyl groups, five-co-ordinated by oxalate ions giving approximately pentagonal bipyramidal geometry about the uranium atom. These are considered in detail in Part III † but the most significant features are summarized here. One oxalate group is bidentate (1,4-co-ordinated) and the other is bidentate to one uranium atom (1,4-co-ordinated) and unidentate to another. This produces

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* For details 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).

† Following paper.

infinite chains $[(UO_2)(C_2O_4)_2]_n^{2n-}$ parallel to *c*. Mean U–O distances are 1·77 (uranyl) and 2·37 Å (oxalate). Neither of the oxalate groups is quite planar, with dihedral angles of 10 and 19° between the O–C–O planes at each end.

Packing.—Both the nitrogen atoms have oxygen neighbours at distances between 2·68 and 2·97 Å. Most of these are probably involved in hydrogen bonding, but some of the O–N–O angles are rather far from tetrahedral, while N(2) has five near oxygen atoms (all $<3·0$ Å). It is therefore difficult to decide which of these distances correspond to strong hydrogen bonds, but it is clear that they link the uranyl oxalate chains into a three-dimensional array (Figure).

I thank the S.R.C. for a grant jointly with Dr. D. Russell, for purchase of a Stoe diffractometer.

[2/2689 *Received, 27th November*, 1972]