Crystal Structure of Tetra(glycolato)uranium(IV) Dihydrate † a Photoreduction Product of Uranyl Ions in the Presence of Glycolic Acid

By **Nathaniel W. Alcock** * and **Terence J. Kemp**, Department of Chemistry and Molecular Sciences, University of Warwick, Coventry CV4 7AL
Silvana Sostero and **Orazio Traverso**, Istituto Chimico dell'Universita de Ferrara, Via Borsari 46, 44100 Ferrara, Italy

The crystal structure of the title compound has been determined as the first example of a monomeric carboxylato-complex of U^{IV}. The crystals are monoclinic, $P2_1/a$, with $a = 6.555(6)$, $b = 17.652(13)$, $c = 8.008(2)$, $\beta = 128.52(4)$, and $Z = 2$. The structure has been solved by the heavy-atom method and refined to $R = 0.057$ for 1 031 observed reflections. The uranium atoms are ten-co-ordinate, with bicapped square-antiprismatic geometry [U–O 2.38(2)—2.55(1) Å], and the glycolate anions are planar, 1 : 4 co-ordinated.

THERE has been a continuing active interest in the structure and chemistry of carboxylato-complexes of uranium in view both of their tendency to display high co-ordination number and of their utilisation in separation and extraction procedures. Most attention has been focused on complexes of U^{VI} as the $[UO_2]^{2+}$ ion, *e.g.* with formate,[1-4] acetate,[5,6] oxydiacetate,[7] iminodiacetate,[8] oxalate,[9] glutarate,[10] succinate,[11] and glycolate [12-14] ligands, from which it has become clear from crystallographic studies that the principal common features are (*i*) that the linear O–U–O group has either five or six additional oxygen atoms co-ordinated to the U atom to yield slightly irregular bipyramids and (*ii*) that the ligands are frequently linked to form infinite chains. Attempts to deduce molecular structures solely from i.r. data [12] have not always been substantiated by subsequent *X*-ray investigation.[13]

Much less information is available on the analogous uranium(IV) complexes, and only the crystal structure of tetra(acetato)uranium(IV) is available.[15] Little attention has also been paid to the corresponding thorium(IV) complexes, despite their greater tractability. It has now become possible to prepare a number of uranium(IV) counterparts,[12] and we have undertaken an *X*-ray analysis of one example of these, tetra(glycolato)uranium(IV) dihydrate, as being the only one that has so far provided suitable crystals for investigation: the uranium(VI) analogue, $[UO_2(HOCH_2CO_2)_2]$, has recently been examined both by *X*-ray [13,14] and i.r.[12,13] methods, and its structure has proved controversial.[12,13] Glycolic acid complexes are themselves of interest because of the polyfunctional nature of the ligand.

EXPERIMENTAL

Crystals were obtained from the preparation described in ref. 12, and consisted of rather irregular flakes. It was found that most have very high mosaic spread, making them useless for data collection. Eventually, one more suitable was found, and indexed (with the standard Syntex programs) with the approximately orthorhombic cell I (Table 1). It was not clear whether all the deviations in angle from 90° were real, or whether they were caused by centring problems associated with the mosaic spread (as observed with other materials). Therefore, a full triclinic data set was collected ($\pm h$, $\pm k$, l) of 3 642 reflections. The scan rate was 1—29° min^{-1} (2θ), depending on the intensity of a 2 s pre-scan, $2\theta_{max.} = 50°$, and the scan range (2θ) was 1.25° each side of the $K_{\alpha1}$ and $K_{\alpha2}$ positions. Three check reflections, monitored every 100 reflections, showed a slow decrease which was compensated for by rescaling. Corrections for Lorentz, polarisation, and absorption effects were made (the last with the program ABSCOR[16]).

Weissenberg and precession photographs were then taken of the crystal, revealing as expected complex lineage and twinning effects. In particular, on layers with *h* even, the condition $k + l = 2n$ was satisfied, apart from a few very faint spots; each reflection contained three components, a doublet and a single spot. On layers with *h* odd, the doublet and singlet were recorded separately, and the condition was not satisfied. This could be interpreted in terms of a centred cell of half the original volume, twinned with $a' = a$, $b' = -b$, and with the stronger component (A) itself showing doubled spots (cell II) in Table 1. It was clear from the photographs that true *mmm* symmetry was not present. Cell II showed apparent $2/m$ symmetry, but it was not certain whether this was perfect. A primitive triclinic cell was therefore also considered (cell III).

TABLE 1

Alternative cell parameters * and crystal data

Cell constants	I	II	III
a/Å	8.009(2)	6.555(6)	9.421(8)
b/Å	10.258(3)	17.652(13)	17.652(13)
c/Å	17.677(9)	8.008(2)	8.008(2)
α/°	89.25(3)	88.85(4)	88.85(4)
β/°	91.13(3)	128.52(4)	103.61(5)
γ/°	89.17(2)	90.10(4)	159.64(2)
U/Å³	1 451.7(9)	724.8(6)	362.4(3)
Space group		(a) $C2/m$ (b) $P2_1/a$	$P\bar{1}$

Transformation matrices:

$$\text{I—II} \begin{pmatrix} -\frac{1}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & -1 \\ 1 & 0 & 0 \end{pmatrix} \quad \text{I—III} \begin{pmatrix} -\frac{1}{4} & -\frac{1}{4} & \frac{1}{2} \\ 0 & 0 & -1 \\ 1 & 0 & 0 \end{pmatrix}$$

Crystal data: $C_8H_{16}O_{14}U$, Monoclinic, $P2_1/a$ (for cell II), $D_c = 2.59$ g cm^{-3} for $Z = 2$, Mo-K_α radiation, $\lambda = 0.710\ 69$, μ(Mo-K_α) $= 106.6$ cm^{-1}, $F(000) = 536$

* Least-squares refinement from 10 to 15 high-angle reflections.

Analysis of this confused set of data proceeded in four stages. Initially, separation of those reflections *apparently* uniquely produced by A from those uniquely produced by B showed an A : B ratio of *ca.* 4 : 1 (in *F*); however, cal-

---

† More systematically, diaquatetra(glycolato-*OO'*)uranium(IV).

culation of a precise ratio was obviously very sensitive to differential recording of these reflections, and so depended on angle. It also became apparent that individual intensities were very similar, as might be expected with a very heavy atom at the origin. Thus, to a first approximation, a reflection with contribution from A and B would have intensity $I_A + (1/16I_A)$. No correction for twinning was therefore made, but instead the reflections were divided into three categories, A + B, A alone, and B alone. The last were discarded, and the others were put into separate scale groups.

The reflections were first studied in the triclinic cell (III) with U at the origin; this gave a satisfactory agreement, and showed light atoms in the co-ordination sphere of U. These atoms, however, conformed to symmetry $2/m$. The data were therefore converted into monoclinic cell II, giving space group $C2/m$. Refinement in this system proceeded to $R = 0.087$, showing a $[\mathrm{U(OH_2)_2(HOCH_2CO_2)_4}]$ unit of site symmetry $2/m$. This had, however, disordered glycolate ligands.

TABLE 2

Atomic co-ordinates ($\times 10^4$) with standard deviations in parentheses

Atom	*X*	*Y*	*Z*
U	0	0	0
O(1)	4 958(13)	101(5)	2 508(11)
O(2)	1 987(20)	−582(6)	3 417(17)
O(3)	3 127(21)	−1 579(6)	5 469(17)
O(4)	−1 981(19)	−1 167(6)	151(16)
O(5)	1 903(20)	−560(6)	−1 434(16)
O(6)	3 154(24)	−1 606(7)	−2 032(19)
O(7)	−2 142(20)	−1 097(6)	−2 176(17)
C(1)	1 684(26)	−1 237(8)	3 804(22)
C(2)	539(30)	1 691(8)	−1 916(24)
C(3)	1 595(29)	−1 242(8)	−2 017(24)
C(4)	−889(42)	−1 601(12)	−2 684(34)
O(12)	−1 960(124)	−514(36)	−3 513(102)
O(13)	3 290(134)	1 635(39)	5 544(111)
O(14)	−2 573(122)	1 270(34)	−500(98)
O(15)	1 997(92)	538(27)	−1 435(76)
O(16)	3 178(135)	1 678(39)	−2 164(111)
O(17)	−2 202(136)	1 207(39)	−2 244(112)
C(11)	1 440(268)	1 519(77)	3 475(221)
C(12)	−1 293(123)	1 567(35)	1 755(101)
C(13)	1 724(92)	1 216(27)	−1 818(76)
C(14)	−77(205)	1 891(58)	−1 585(167)

Atoms O(12) to C(14) have 0.25 occupancy

It was therefore possible that the true space group was $P2_1/a$, with the reflections previously studied being those to which the uranium atom contributed. Finally, therefore, the weak reflections indexable on cell II but not satisfying $h + k = 2n$ were included. This could not be done completely as on layers with odd *h* (cell I) the cell II reflections coincide with the strong reflections of cell II′. Further, on layers of even *h*, these weak cell II reflections coincide with the weak cell II′ reflections. Separation of them is no longer fairly straightforward as there is no approximate intensity relationship between them. However, the simple assumption used for the separation of strong reflections was still applied, but omitting entirely the weak reflections for layers of odd *h*.

The effect of omitting reflections should only be significant in Fourier syntheses, where they will impose pseudo-C-centring, making the apparent site symmetry at the origin $2/m$, rather than $\bar{1}$. However, the inclusion of any atom will have the effect of removing both its peak and that of the pseudo-symmetry-related one from the difference map. With refinement under these conditions, two individual co-ordinated molecules of glycolic acid could be located, but weak peaks in approximate, but not precise, mirror-relationship were still present. Their inclusion at 0.25 occupancy and final refinement with anisotropic temperature factors for U only reduced *R* to 0.057 for 1 031 observed reflections $[I/\sigma(I) > 3.0]$. In what follows, the discussion of the structure ignores these minor peaks. It is in any case not possible to be certain whether the disorder occurs within individual crystals or is a consequence of partially corrected twinning. The satisfactory refinement confirms the final choice of $P2_1/a$ for the space group.

TABLE 3

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

U–O(1)	2.549(8)	C(1)–C(2)	1.49(2)
U–O(2)	2.404(13)	C(2)–O(4)	1.44(2)
U–O(4)	2.506(16)	O(5)–C(3)	1.27(2)
U–O(5)	2.382(16)	C(3)–O(6)	1.23(4)
U–O(7)	2.411(10)	C(3)–C(4)	1.51(4)
O(2)–C(1)	1.28(3)	C(4)–O(7)	1.38(4)
C(1)–O(3)	1.22(2)		

O(2)–C(1)–O(3)	124(2)	O(5)–C(3)–O(6)	124(2)
O(2)–C(1)–C(2)	116(2)	O(5)–C(3)–C(4)	114(2)
O(3)–C(1)–C(2)	119(2)	O(6)–C(3)–C(4)	122(2)
C(1)–C(2)–O(4)	109(2)	C(3)–C(4)–O(7)	111(2)

Contact distances in the co-ordination sphere to 3.3 Å (primed atoms generated by the centre at U)

O(1)–O(2)	2.75(2)	O(2)–O(5′)	2.82(2)
O(1)–O(5)	2.72(1)	O(2)–O(7′)	3.15(2)
O(1)–O(4′)	2.59(1)	O(4)–O(5′)	3.23(2)
O(1)–O(7′)	2.46(2)	O(5)–O(7)	2.53(2)
O(2)–O(4)	2.53(1)		

The scattering factors for neutral U, O, and C used in the refinement were from ref. 17 in the analytical form. Computing was carried out with the ' *X*-RAY '76 ' program [18] on a Burroughs B6700 computer. Final positional parameters for all atoms are listed in Table 2. The thermal parameters and final structure factors are available as Supplementary Publication No. SUP 22756 (9 pp.).† Bond lengths and angles are in Table 3 and information on molecular planes in Table 4.

TABLE 4

Equations of the least-squares mean planes $PI + QJ + RK = S$ in orthogonal Angström space and deviations (Å) of atoms in square brackets. Atoms defining each plane are marked with an asterisk

	P	*Q*	*R*	*S*
Plane (1)	−0.918	0.311	0.244	0.600
[O(2) * −0.01, O(3) * −0.01, C(1) * 0.03, C(2) * −0.01, O(4) 0.05, U −0.60]				
Plane (2)	−0.174	−0.302	0.937	−0.877
[O(5) * −0.01, O(6) * −0.03, C(3) * 0.03, C(4) * −0.01, O(7) 0.24, U 0.88]				
Plane (3)	0.789	−0.026	0.614	1.022
[O(5) * 0.01, O(2) * −0.01, O(4′) −0.02, O(7′) * 0.002, U −1.02]				

Angles (°) between plane normals:

1–[plane normal to U–O(1) line] 33.3; 1–2 72.8; 1–3 54.3;
2–[plane normal to U–O(1) line] 24.8; 2–3 63.5

DISCUSSION

Uranium(IV) glycolate dihydrate is the first complex of this polyfunctional ligand with either an *f*-block or

---

† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

transition element to be fully characterised structurally, and the first to contain a discrete molecular species, rather than one with multiple bridging by the ligand between the metal ions. In this, it also differs from most uranium(VI) carboxylates and from uranium(IV) acetate.[1-14] The uranium ion achieves a co ordination number of 10 (Figure 1) by means of the four glycolate anions and two water molecules. The geometry around uranium corresponds quite closely to the ideal for this co-ordination number, the bicapped square antiprism. The two water molecules form the caps, with close approaches to four coplanar glycolate oxygen atoms [plane (3) in Table 4]. The O–O contacts in the co-ordination sphere fall in the expected range, although O(1)–O(7′) is rather less than the normal minimum of 2.5—2.6 Å. The two long distances of 3.15 and 3.23 Å show that the complex is not over-crowded.

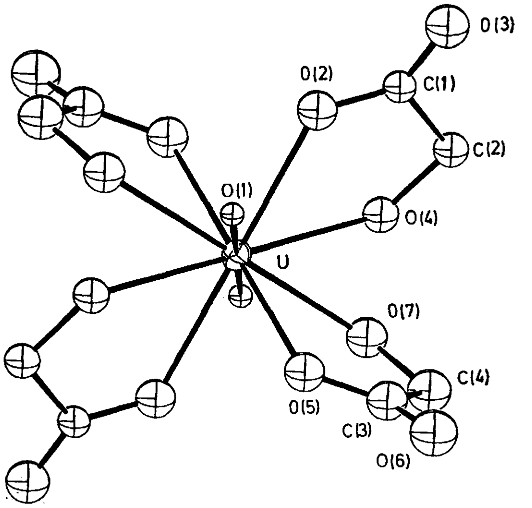

FIGURE 1 The $U(C_2H_3O_3)_4\cdot 2H_2O$ molecule, showing the atomic numbering

TABLE 5

Glycolate ion dimensions (Å)

Compound	C–O(–M)	C=O	C–C	C–OH	Ref.
$Li(C_2H_3O_3)\cdot H_2O$	1.22(1)	1.26(1)	1.54(1)	1.39(1)	*a*
$Li(C_2H_2DO_3)$	1.255(2)	1.254(2) [b]	1.525(2)	1.415(2)	*c*
$KH(C_2H_3O_3)_2$					
(anion)	1.24(1)	1.25(1)	1.51(1)	1.42(1)	*d*
(neutral)	1.21(1)	1.28(1)	1.53(1)	1.39(1)	
$RbH(C_2H_3O_2)_2$					
(anion)	1.26(1)	1.24(1)	1.52(2)	1.43(1)	*e*
(neutral)	1.21(1)	1.31(1)	1.47(2)	1.44(1)	
$U(C_2H_3O_2)_4\cdot$	1.28(3)	1.22(2)	1.49(2)	1.44(2)	*f*
$2H_2O$	1.27(2)	1.23(4)	1.51(4)	1.38(4)	*f*

[a] R. H. Colton and D. E. Henn, *Acta Cryst.*, 1965, **18**, 820. [b] Also co-ordinated to metal. [c] E. J. Gabe and M. R. Taylor, *Acta Cryst.*, 1966, **21**, 418. [d] R. F. Mayers, E. T. Keve, and A. C. Skapski, *J. Chem. Soc.* (*A*), 1968, 2258. [e] L. Golic and J. C. Speakman, *J. Chem. Soc.*, 1965, 2521. [f] This work.

The carboxylate planes [planes (1) and (2)] are twisted relative to the H_2O–U–OH_2 axis by 25 and 35° to produce the antiprismatic geometry. They are also tipped, so that the uranium atom lies 0.6—0.9 Å off the planes. However, the hydroxyl oxygen atoms are only slightly displaced, *i.e.* the glycolate anions are virtually planar.

The only comparable glycolate compounds are those of three alkali metals (Table 5). The lithium salts show the same 1 : 4 chelating geometry, but for the K^+ and Rb^+ acid salts only the neutral molecule is bound like this, and the anion, although bidentate, is bridging. It is also significant that these neutral molecules are twisted about the C–C bond, while the anions are planar [with a maximum displacement of the OH of 0.17 Å reported for $Li(C_2H_2DO_3)$]. Within the rather limited accuracy of the present determination, the glycolate dimensions correspond to those previously found.

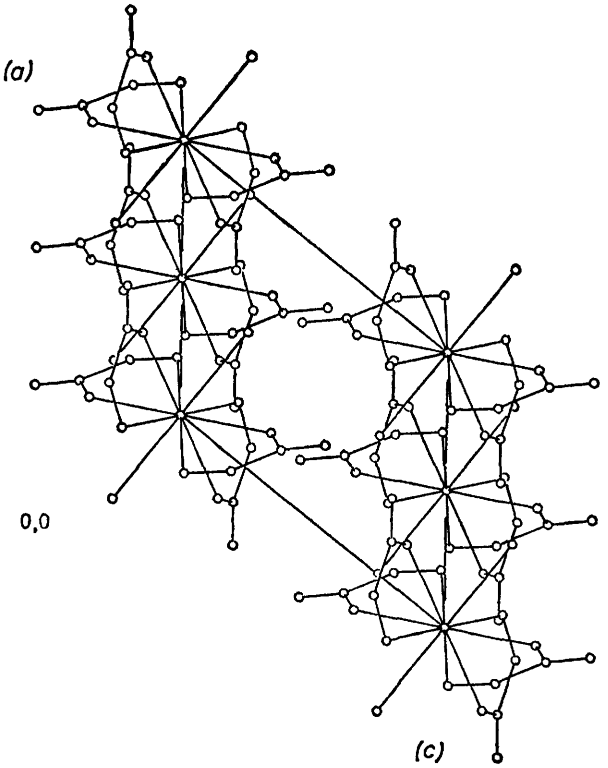

FIGURE 2 Packing diagram, viewed down *b*

The molecules pack in the crystal (Figure 2) in layers in the *a*–*b* plane, with only distant contacts between the layers. This accounts both for the flaky nature of the crystals, and their propensity to twin.

We thank N.A.T.O. and C.N.R. (Italy) for furthering the Warwick-Ferrara collaboration.

[9/1608 *Received*, 10*th October*, 1979]

REFERENCES

[1] B. F. Mentzen, J. P. Puaux, and H. Loiseleur, *Acta Cryst.*, 1977, **B33**, 1848.

[2] B. F. Mentzen, J. P. Puaux, and H. Sautereau, *Acta Cryst.*, 1978, **B34**, 1846.

[3] B. F. Mentzen, J. P. Puaux, and H. Sautereau, *Acta Cryst.*, 1978, **B34**, 2707.

[4] B. F. Mentzen, *Acta Cryst.*, 1978, **B33**, 2546.

[5] J. Howatson, D. M. Grev, and B. Morosin, *J. Inorg. Nuclear Chem.*, 1975, **37**, 1933.

[6] C. Pannatoni, R. Graziani, G. Bandoli, B. Zarli, and G. Bombieri, *Inorg. Chem.*, 1969, **8**, 320.

[7] G. Bombieri, U. Croatto, R. Graziani, E. Forsellini, and L. Magon, *Acta Cryst.*, 1974, **B30**, 407.

[8] G. Bombieri, E. Forsellini, G. Tomat, L. Magon, and R. Graziani, *Acta Cryst.*, 1974, **B30**, 2659.

[9] N. W. Alcock, *J.C.S. Dalton*, 1973, 1610, 1614, 1616.

[10] F. Benetollo, G. Bombieri, J. A. Herrero, and R. M. Rojas, *J. Inorg. Nuclear Chem.*, 1979, **41**, 195.

[11] G. Bombieri, F. Benetollo, A. Del Pra, and R. M. Rojas, *J. Inorg. Nuclear Chem.*, 1979, **41**, 201.

[12] G. Sbrignadello, G. Tomat, G. Battiston, P. A. Vigato, and O. Traverso, *J. Inorg. Nuclear Chem.*, 1978, **40**, 1647.

[13] B. F. Mentzen and H. Sautereau, *Inorg. Chim. Acta*, 1979, **35**, L347.

[14] J. Polonio, M. A. Olivares, and R. M. R. Lopez, *Anales Real Soc. Espan. Fis. Quim.*, 1969, **65**, 213.

[15] I. Jelenić, D. Grdenić, and A. Bezjak, *Acta Cryst.*, 1964, **17**, 758.

[16] N. W. Alcock, 'The Analytical Method for Absorption Correction,' in 'Crystallographic Computing,' ed. F. Ahmed, Munksgaard, Copenhagen, 1970.

[17] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[18] '*X*-RAY '76,' J. M. Stewart, Technical Report TR-446, the Computer Science Center, University of Maryland, March 1976.