# Crystal Structure of Tetra-ammonium Uranyl Tricarbonate

By **R. Graziani**, Facoltà di Chimica Industriale, Università di Venezia, Italy
**G. Bombieri** * and **E. Forsellini**, Laboratorio di Chimica e Tecnologia dei Radioelementi del C.N.R., 35100 Padova, Italy

Crystals of the title compound are monoclinic, $a = 10{\cdot}68$, $b = 9{\cdot}38$, $c = 12{\cdot}85$, $\beta = 96°\ 27'$, $Z = 4$, space group $C2/c$. The structure was solved by Patterson and electronic-density syntheses by use of three-dimensional counter data, and refined by least-squares to $R$ 0·076 for 1833 reflections. The uranium(VI) atom is in an eight-co-ordinate distorted hexagonal environment. The linear uranyl group is perpendicular to the equatorial plane in which three carbonate groups are chelated. The $NH_4^+$ groups which fill holes in the structure link the anions through hydrogen bonding.

THE carbonate ligand exhibits both bi- and uni-dentate characteristics and may be characterized as being ' quasi-bidentate '. There is extensive literature on the carbonate complexes of $U^{VI}$, some of which have been investigated and discussed in view of their importance in uranium metallurgy. Among these studies, $X$-ray work has shown that in rutherfordine,[1] the naturally occurring mineral $UO_2CO_3$, and in crystals of synthetic $UO_2CO_3$,[2] the $CO_3^{2-}$ groups are stacked in layers and the $UO_2^{2+}$ ions lie normal to these planes. The uranium atoms occupy hexagonal holes forming six non-equivalent bonds with oxygen atoms from four carbonate groups. Two other structures are known [3,4] in which the equatorial co-ordination of three bidentate carbonate groups to the uranyl ion has been established.

In a preliminary $X$-ray investigation [5] on crystals of $K_4[(UO_2)(CO_3)_3]$ and $[NH_4]_4[(UO_2)(CO_3)_3]$ cell constants and space groups were determined but no structural information has been reported. There appears to be a lack of structural data on these types of compound in the solid state. In view of this and of the considerable interest in hydrogen bonding in crystalline materials we have determined the $X$-ray crystal structure of the ionic complex $[NH_4]_4[(UO_2)(CO_3)_3]$.

## EXPERIMENTAL

Well formed lemon-yellow crystals were prepared by the method of ref. 5. A preliminary study was made using oscillation, Weissenberg, and precession photographs. The unit-cell parameters, subsequently refined with counter data by use of a least-squares program are only slightly different from those of ref. 5.

*Crystal Data.*—$C_3H_{16}N_4O_{11}U$, $M = 522$, Monoclinic, $a = 10{\cdot}68(1)$, $b = 9{\cdot}38(1)$, $c = 12{\cdot}85(1)$ Å, $\beta = 96°\ 27'(5)$, $U = 1279$ Å$^3$, $D_m = 2{\cdot}72$ (by flotation), $Z = 4$, $D_c = 2{\cdot}71$. Mo-$K_\alpha$ radiation, $\lambda = 0{\cdot}7107$ Å; $\mu(\text{Mo-}K_\alpha) = 189\ \text{cm}^{-1}$. Space group $C2/c$ or $Cc$ shown to be the former by the subsequent successful analysis.

The selected single crystal specimen was ground into a sphere *ca.* 0·05 mm in radius and mounted with the [001] direction parallel to the $\phi$-axis of the goniometer. A total of 1833 independent reflections were collected on a computer-controlled Siemens diffractometer using the $\theta$—$2\theta$ scan and the five-point measuring procedure. Intensities were measured with the Mo-$K_\alpha$ radiation and a Na(Tl)I scintillation counter up to $2\theta_{\text{max.}}$ 60°. The 58 reflections with intensities $I < 2\sigma(I)$ were considered unobserved and were given zero weight in the subsequent refinement.

All intensities were corrected for absorption for spherical specimens,[6] assuming $\mu R = 3{\cdot}2$. Structure factors were calculated using scattering factors for neutral atoms,[7] and for uranium, the real part of the correction for the anomalous scattering [8] was applied.

The calculations were carried out on the CDC 6600 computer using the programs system of ref. 9.

TABLE 1

Atomic positional ($\times 10^4$) and thermal parameters, with estimated standard deviations in parentheses

| | $x$ | $y$ | $z$ | $B$/Å$^2$ |
|---|---|---|---|---|
| U | 5000 | 6928(1) | 2500 | * |
| O(1) | 5389(14) | 9261(16) | 1715(11) | 2·2(2) |
| O(2) | 5965(11) | 6797(14) | 868(10) | 1·7(2) |
| O(3) | 5706(12) | 4747(15) | 1665(10) | 1·8(2) |
| O(4) | 5000 | 1333(25) | 2500 | 2·7(4) |
| O(5) | 6743(14) | 4748(17) | 258(12) | 2·5(2) |
| O(6) | 6532(13) | 6945(15) | 3228(11) | 2·0(2) |
| C(1) | 5000 | 38(31) | 2500 | 2·1(4) |
| C(2) | 6171(17) | 5400(20) | 910(14) | 1·7(3) |
| N(1) | 6776(17) | 3359(20) | 3528(14) | 2·4(3) |
| N(2) | 6061(17) | 8289(20) | 5398(14) | 2·3(3) |

* Anisotropic thermal parameters ($\times 10^4$)

| | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|
| U | 44(1) | 46(1) | 23(1) | 0 | 5(1) | 0 |

from the expression: $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

*Determination of the Structure.*—The structure was solved by the heavy-atom method. The atomic co-ordinates with isotropic vibration parameters and one overall scale-factor were subjected to several cycles of block-diagonal least-squares refinement in the centric space group $C2/c$. The function minimized was $\Sigma w[|F_o| - |F_c|]^2$ with $w = 1$. In this model the molecule has crystallographic $C_2$ symmetry and the U, C(1), and O(4) atoms lie on the two-fold axis corresponding to the special position $4(e)$. The uranium atom was then assigned an anisotropic temperature factor and refinement was continued with full-matrix least-squares. This resulted in convergence at $R$ 0·076. In the

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[1] C. L. Christ, Toan R. Clarck, H. T. Evans, jun., *Science*, 1955, **121**, 472.

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[5] Stiepan S. Malcic, *Bull. Inst. Nuclear Sci. ' Boris Kidrich,'* 1958, **8**, 95.

[6] ' International Tables for $X$-Ray Crystallography,' vol. 2, 302, Kynoch Press, Birmingham, 1962.

[7] Ref. 6, vol. 3, pp. 202 and 212.

[8] Ref. 6, vol. 3, p. 215.

[9] J. M. Stewart, F. A. Kundell, and J. C. Baldwin, '**$X$**-Ray '63 ' System of Crystallographic Programs, University of Maryland, Technical Report TR 64 6, revised version (1970).

TABLE 2

Bond distances and angles with estimated standard deviations in parentheses *

(*a*) Bond lengths (Å)

| | | | |
|---|---|---|---|
| U–O(1) | 2·46(1) | O(1)–C(1) | 1·34(2) |
| U–O(2) | 2·44(1) | O(2)–C(2) | 1·33(2) |
| U–O(3) | 2·46(1) | O(3)–C(2) | 1·29(2) |
| U–O(6) | 1·79(1) | O(4)–C(1) | 1·22(3) |
| | | O(5)–C(2) | 1·25(3) |

(*b*) Bond angles (°)

| | | | |
|---|---|---|---|
| O(1)–U–O($1^{I}$) | 54·7(5) | U–O(2)–C(2) | 96(1) |
| O(2)–U–O(3) | 53·5(5) | U–O(3)–C(2) | 95(1) |
| O(1)–U–O(6) | 91(1) | O(1)–C(1)–O($1^{I}$) | 114(2) |
| O(2)–U–O(6) | 90(1) | O(2)–C(2)–O(3) | 115(2) |
| O(3)–U–O(6) | 86(1) | O(1)–C(1)–O(4) | 123(1) |
| U–O(1)–C(1) | 95(1) | O(2)–C(2)–O(5) | 123(2) |
| | | O(3)–C(2)–O(5) | 122(2) |

* Roman numerals as superscripts refer to the following transformations relative to the reference *x*, *y*, *z*:

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

TABLE 3

Contacts $<3·5$ Å between ' hydrogen-donor–acceptor ' atoms, and some related angles, with estimated standard deviations

(*a*) Distances (Å)

| | | | |
|---|---|---|---|
| N(1) ··· O(3) | 2·85(2) | N(2) ··· O($2^{I}$) | 2·92(2) |
| N(1) ··· O($3^{I}$) | 2·94(2) | N(2) ··· O($1^{VII}$) | 2·99(2) |
| N(1) ··· O($1^{IV}$) | 3·19(2) | N(2) ··· O($4^{VIII}$) | 3·06(2) |
| N(1) ··· O($2^{IV}$) | 2·86(2) | N(2) ··· O($5^{IX}$) | 2·92(3) |
| N(1) ··· O($2^{V}$) | 3·22(2) | N(2) ··· O($5^{V}$) | 2·95(3) |
| N(1) ··· O($4^{VI}$) | 2·90(2) | N(2) ··· O(6) | 3·15(2) |
| N(1) ··· O($5^{V}$) | 2·85(2) | N(2) ··· O($6^{X}$) | 2·96(2) |
| N(2) ··· O($1^{I}$) | 3·11(2) | | |

(*b*) Angles (°)

| | |
|---|---|
| N($1^{III}$) ··· O(1) ··· N($2^{I}$) | 82(1) |
| N($1^{III}$) ··· O(2) ··· N($2^{I}$) | 76(1) |
| N(1) ··· O(3) ··· N($1^{I}$) | 98(1) |
| O(3) ··· N($1^{I}$) ··· O($3^{I}$) | 57(1) |
| O(1) ··· N($2^{I}$) ··· O(2) | 52(1) |
| O(1) ··· N($1^{III}$) ··· O(2) | 52(1) |

Roman numerals refer to the following equivalent positions relative to atoms at *x*, *y*, *z*:

IV $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$
V $x, \bar{y} - 1, \frac{1}{2} + z$
VI $x, y - 1, z$
VII $x, 1 - y, z - \frac{1}{2}$
VIII $1 - x, \bar{y}, 1 - z$
IX $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$
X $\frac{3}{2} - x, \bar{y} - \frac{1}{2}, 1 - z$

last cycle no parameter shift was $>0·1\sigma$. Attempts to locate the hydrogen atoms from difference-Fourier syntheses were unsuccessful. The final co-ordinates and vibration parameters are given in Table 1 with their standard deviations as derived from the least-squares calculations. Bond distances and bond angles are given in Table 2, contacts and related angles in Table 3. Observed and calculated structure factors are listed in Supplementary Publication No. 20436 (3 pp., 1 microfiche).*

## DISCUSSION

*The anion.*—Figure 1 shows the structure together with the atom numbering scheme used. The uranium atom is eight-co-ordinate, the linear uranyl group being equatorially surrounded by an irregular hexagon of six oxygen atoms from three bidentate carbonate groups. Although the only crystallographic symmetry element present in the molecule is a two-fold rotation axis through the U, C(1), and O(4) atoms, the complex anion as well as the surrounding ammonium groups can be considered to have approximately distorted hexagonal $D_{3h}$ symmetry. The uranyl U–O distance [1·79(1) Å] may be compared with that [1·78(2) Å] in rubidium uranyl nitrate.[10] The three non-symmetry-related U–O-(carbonate) bond distances [2·46(1), 2·44(1), and 2·46(1) Å] are not very different from the corresponding distances found in $Na(UO_2)(OAc)_3$ [11] [2·49(1) Å], and in $Rb(UO_2)(NO_3)_3$ [2·48(1) Å], the small differences being probably related to the larger negative charge of the carbonate ion with respect to acetate and nitrate.

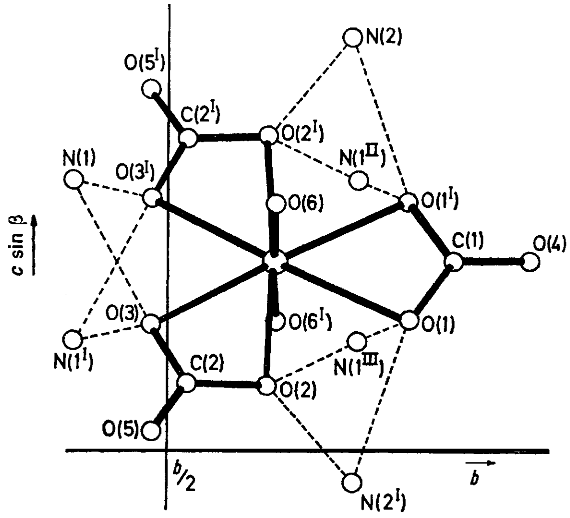

FIGURE 1 The structure viewed along the *a* axis

The carbonate groups are planar but their symmetry is affected by co-ordination. The fact that the C–O distances to the unco-ordinated oxygen atoms [1·22(2) and 1·25(2) Å] are distinctly different from the C–O distances to the co-ordinated oxygen atoms [mean 1·32(3) Å] reveal non-equivalence of one oxygen from the other two on each carbonate. Distortions are also apparent in the O–C–O angles so that the $D_{3h}$ symmetry of the free carbonate groups is lowered to $C_{2v}$ in the complex, thus confirming what has been amply supported by spectral studies.

The two independent O–O distances [O(1) ··· O($1^{I}$) and O(2) ··· O(3)] across the chelated anions [2·26(2) and 2·21(2) Å] are comparable to the analogous distances in $Na(UO_2)(OAc)_3$ and in $[(UO_2(OAc)_2(Ph_3PO)]_2$ [12] [2·19 and 2·16 Å respectively], and the O ··· O approach for the adjacent carbonate groups [mean 2·70 Å] is slightly

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are supplied as full size copies).

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

[11] W. Zachariasen and H. Plettiger, *Acta Cryst.*, 1959, **12**, 526.

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

shorter than the sum of van der Waals radii [13] [2·8 Å]. However this has no apparent influences on the co-ordinated atoms which are coplanar within experimental error (see Table 4).

TABLE 4

Equation of the equatorial least-squares best plane and, in square brackets, deviations (Å) of the relevant atoms from the plane. The equation is in the form $Ax + By + Cz = D$ where $x$, $y$, and $z$ are fractional co-ordinates referred to the crystallographic axes

| Plane: | *A* | *B* | *C* | *D* |
|---|---|---|---|---|
| U, O(1)—(3), O($1^{I}$), O($2^{I}$), O($3^{I}$) | 9·013 | 0·000 | 5·638 | 5·916 |

[O(1) −0·09, O(2) −0·05, O(3) 0·15, C(1) 0·0, O(4) 0·0, C(2) 0·15, O(5) 0·30, N(1) 2·18, N(2) 2·59, N($1^{II}$) 2·33]

The σ of the atoms (defining the plane) from the plane is 0·10 Å.

*The Cations.*—Figure 2 shows the compact packing of the layers in the crystal seen down the *b* axis. The $NH_4^+$ groups are accommodated in a series of connected holes which form parallel chains and which extend through the structure along the [302] direction, normal to the layers of the complex anions. Each series is interrupted after every four ammonium groups by a unit of the complex, so that the chains could be described by a sequence of the type ABBBBABBBB. . . . Five members of this sequence are indicated with letters in Figure 2. The distances between successive members of the sequence are *ca.* 4·7 Å.

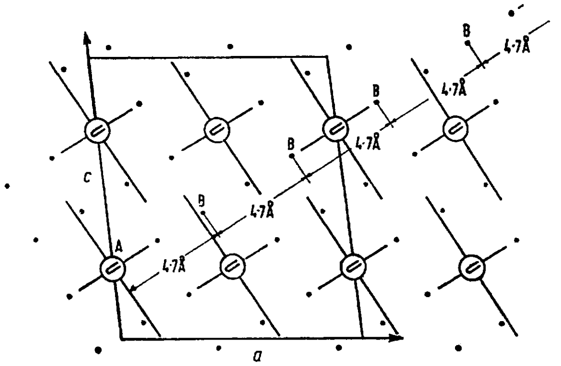

FIGURE 2 Projection of the structure on (010)

*Hydrogen Bonds.*—As a result of the structural arrangement each anion is immediately surrounded by six ammonium ions, only four of which can be considered to belong to the same structural formula unit. They are symmetrically located above and below the equatorial plane so that each ammonium group can make two relatively short contacts with two oxygen atoms of the same anion (Figure 1).

These are not the only short N · · · O contacts. As shown in Table 3, there are a number of oxygen atoms around each of the nitrogen atoms with N · · · O distances 2·85—3·22 Å, most of which lie in the range of the N–H · · · O bond lengths.

The oxygen atoms of the anion serve as acceptors of the hydrogen bonds from the $NH_4^+$ groups, and so the adjacent chains are held together by hydrogen bonding to form an infinite three-dimensional network. There is a wide range of values for the O · · · N · · · O angles relative to each ammonium group and because it was impossible to determine the positions of the hydrogen atoms, it is very difficult to decide which of these N · · · O contacts are to be considered actual hydrogen bonds.

However, by considering the arrangement of the oxygen atoms around the $NH_4^+$ groups it seems that more than four oxygen atoms could take part in hydrogen bonds. The existence of five or more N · · · O distances consistent with hydrogen bond distances instead of the chemically expected four, could be associated with the presence of bifurcated bonds in addition to the normal N–H · · · O bonds, or could indicate some disordering of the hydrogen atoms in the $NH_4^+$ group.

We thank Mrs. Milena Magnabosco and Franco Benetollo for helpful assistance with data reduction.

[2/577 *Received, 13th March,* 1972]

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[13] N. L. Allinger, M. A. DaRooge, and R. B. Neumann, *J. Org. Chem.*, 1961, **26**, 3626.