

The structure is a three-dimensional framework with channels parallel to [001] at $x \simeq 0.0$ and $y \simeq 0.0$ etc. The Na atoms are located within these channels. The structure of $\text{NaCu}_4(\text{AsO}_4)_3$ shown in Fig. 1 is drawn as a projection onto (001).

The author wishes to thank Professor Dr J. Zemann (Vienna) for many helpful discussions. The assistance of Dr H. Effenberger (Vienna) and the financial support of the Hochschuljubiläumsstiftung der Stadt Wien is gratefully acknowledged.

References

- HERITSCH, H. (1938). *Z. Kristallogr.* **99**, 466–479.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
 PERTLIK, F. (1977). *Z. Anorg. Allg. Chem.* **436**, 201–206.
 PERTLIK, F. (1986). *Acta Cryst.* **C42**, 774–776.
 TOMAN, K. (1977). *Acta Cryst.* **B33**, 2628–2631.
 WALITZI, E. M. (1962). *Tschermaks Mineral. Petrogr. Mitt.* **8**, 275–280.
 WALITZI, E. M. (1963). *Tschermaks Mineral. Petrogr. Mitt.* **8**, 614–624.
 ZACHARIASEN, W. A. (1967). *Acta Cryst.* **23**, 558–564.

Acta Cryst. (1987). **C43**, 383–384

Structure of Diammonium Tetrabromodioxouranate(VI) Dihydrate

BY G. VAN DEN BOSSCHE

Institut de Physique B5, Université de Liège au Sart Tilman, B-4000 Liège, Belgium

M. R. SPIRLET

Physique expérimentale B5, Université de Liège au Sart Tilman, B-4000 Liège, Belgium

J. REBIZANT

Commission of the European Communities, JRC Karlsruhe, Postfach 2266, D-7500 Karlsruhe, Federal Republic of Germany

AND J. GOFFART*

Institut de Radiochimie B16, Université de Liège au Sart Tilman, B-4000 Liège, Belgium

(Received 18 June 1986; accepted 19 September 1986)

Abstract. $[\text{NH}_4]_2[\text{UO}_2\text{Br}_4] \cdot 2\text{H}_2\text{O}$, $M_r = 661.7$, triclinic, $P\bar{1}$, $a = 6.8850$ (9), $b = 6.887$ (1), $c = 7.7370$ (7) Å, $\alpha = 94.44$ (1), $\beta = 98.78$ (1), $\gamma = 116.79$ (1)°, $V = 319$ (1) Å³, $Z = 1$, $D_x = 3.44$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 24.44$ mm⁻¹, $F(000) = 290$, $T = 295$ (1) K, $R = 0.030$ for 1027 observed reflections. The structure is composed of $[\text{UO}_2\text{Br}_4]^{2-}$ and $[\text{NH}_4]^+$ ions. U is octahedrally coordinated and the symmetry of $[\text{UO}_2\text{Br}_4]^{2-}$ is approximately D_{4h} with U–O = 1.766 (6) Å and average U–Br = 2.813 (1) Å.

Introduction. A large number of uranyl tetrahalide complexes of the type $M_2\text{UO}_2X_4$ ($M =$ univalent cation, $X = \text{Cl}, \text{Br}$) are known; among them the structures of $\text{Cs}_2\text{UO}_2\text{Cl}_4$ (Hall, Rae & Waters, 1966), $\text{Cs}_2\text{UO}_2\text{Br}_4$ (Mikhailov & Kuznetsov, 1971), $[\text{N}(\text{CH}_3)_4]_2[\text{UO}_2\text{Cl}_4]$ and $[\text{N}(\text{CH}_3)_4]_2[\text{UO}_2\text{Br}_4]$ (Di Sipio, Tondello, Pelizzi,

Ingletto & Montenero, 1974a; Jensen & Dickerson, 1974), $[\text{N}(\text{C}_2\text{H}_5)_3]_2[\text{UO}_2\text{Cl}_4]$ (Bois, Nguyen Quy Dao & Rodier, 1976), $[\text{N}(\text{C}_3\text{H}_7)_4][\text{UO}_2\text{Cl}_4]$ (Di Sipio *et al.*, 1974d), $[\text{N}(\text{C}_3\text{H}_7)_4][\text{UO}_2\text{Br}_4]$ (Di Sipio *et al.*, 1974b), $[\text{N}(\text{C}_2\text{H}_5)_4][\text{UO}_2\text{Cl}_4]$ (Di Sipio *et al.*, 1974c), $[\text{N}(\text{C}_2\text{H}_5)_4][\text{UO}_2\text{Br}_4]$ (Di Sipio *et al.*, 1977) have been determined.

Experimental. Crystals of the title compound obtained by slow cooling of a boiling solution of UBr_4 in methyl nitrite. Single crystal (0.2 × 0.3 × 0.2 mm) suitable for X-ray analysis sealed in a thin-walled glass capillary under an inert atmosphere. Enraf CAD-4 X-ray diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Cell parameters refined by least squares from angle data of 25 reflections. Space group $P1$ or $P\bar{1}$ with $P\bar{1}$ consistent with statistics. 2247 reflections collected (θ - 2θ scan mode) in range $4 \leq 2\theta \leq 50^\circ$, 2142 considered observed [$I \geq \sigma(I)$], $\pm h$, $\pm k$, $\pm l$; index range $h - 8/8$, $k - 8/8$, $l - 9/9$], averaged to 1118 unique reflections ($R_{\text{int}} = 0.008$).

* Chercheur qualifié FNRS.

Three reflections monitored periodically showed no significant deviations from mean. Intensities corrected for Lorentz-polarization effects; empirical absorption corrections (transmission factors range from 43.63 to 99.70%). Structure solved by direct methods and Fourier techniques; full-matrix least-squares refinement [minimizing $\sum(\Delta F)^2$] on 1027 independent reflections with $F^2 \geq 3\sigma(F^2)$. Anisotropic thermal parameters. $R = 0.030$, $wR = 0.036$, $w = 1$, $S = 1.76$, $(\Delta/\sigma)_{\max} = 0.01$. Since hydrogen atoms could not be located on the final difference map, they were not included in the calculations. Maximum and minimum $\Delta\rho$ in final difference Fourier map, 1.866 and $-1.415 \text{ e } \text{\AA}^{-3}$, are about 1 Å from U. Atomic scattering factors and anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974). Enraf-Nonius (1981) SDP programs, Fig. 1 drawn with ORTEP (Johnson, 1965).

Discussion. The crystal structure is illustrated by Fig. 1. Table 1* contains final atomic positional parameters for non-H atoms. Selected interatomic distances and angles are listed in Table 2. The uranium atom has octahedral coordination in the $[\text{UO}_2\text{Br}_4]^{2-}$ anion with four Br atoms at the corners of a rectangular plane [Br(1)–Br(2) = 4.018 (1); Br(1)–Br(2ⁱⁱ) = 3.939 (2) Å and Br(2)–Br(1)–Br(2ⁱ) = 90.07 (3)°] while the UO_2 is linear by symmetry and almost perpendicular [88.7 (5)°] to the rectangular plane.† The approximate symmetry of the ion is thus D_{4h} . The U–O distance 1.766 (6) Å falls within the range of values reported in the literature for dioxouranium compounds with four-fold equatorial coordination, 1.52–2.05 Å (*Gmelin's Handbook of Inorganic Chemistry*, 1983). The bonding

* Lists of structure amplitudes and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43415 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† (i) $-x, -y, -z$; (ii) $-x, 1-y, -z$; (iii) $-1+x, y, 1+z$.

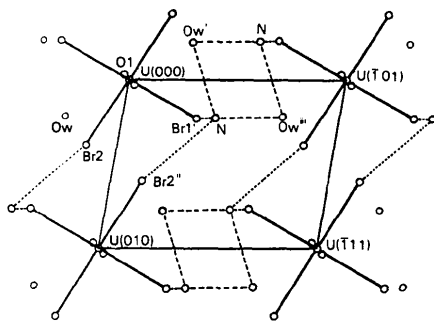


Fig. 1. Projection of the structure along [100]. Symmetry codes are defined in a footnote to the main text.

Table 1. Atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses

	$B_{\text{eq}} = \frac{1}{3} \text{trace } \tilde{B} (\text{\AA}^2)$			B_{eq}
	<i>x</i>	<i>y</i>	<i>z</i>	
U	0.0	0.0	0.0	1.504 (9)
Br(1)	0.2284 (2)	0.2322 (2)	0.3438 (1)	2.89 (2)
Br(2)	0.1765 (2)	0.3923 (2)	-0.1435 (1)	2.66 (2)
O(1)	0.2344 (9)	-0.032 (1)	-0.0279 (9)	2.2 (1)
O(w)	0.566 (1)	0.221 (1)	-0.262 (1)	2.9 (2)
N	-0.245 (1)	0.230 (1)	0.430 (1)	2.3 (2)

Table 2. Selected interatomic distances (Å) and angles (°) with e.s.d.'s in parentheses

U–O(1)	1.766 (6)	O(1)–Br(1)	3.298 (7)
U–Br(1)	2.812 (1)	O(1)–Br(2)	3.294 (8)
U–Br(2)	2.815 (1)		
O(1)–U–Br(1)	89.2 (2)		
O(1)–U–Br(2)	88.9 (2)		
Br(1)–U–Br(2)	91.14 (3)		

between the $[\text{NH}_4]^+$ and $[\text{UO}_2\text{Br}_4]^{2-}$ ions involves two short $\text{N}\cdots\text{Br}$ contacts, $\text{N}\cdots\text{Br}(1)$ and $\text{N}\cdots\text{Br}(2^{\text{ii}})$, which are 3.418 (7) and 3.465 (8) Å respectively. Through these short contacts with the $[\text{NH}_4]^+$ cations, the anionic groups form chains parallel to **b** (Fig. 1). The distances $\text{N}\cdots\text{O}(w^{\text{i}})$ 2.92 (1) Å and $\text{N}\cdots\text{O}(w^{\text{iii}})$ 2.88 (1) Å and the angle $\text{O}(w^{\text{i}})\cdots\text{N}\cdots\text{O}(w^{\text{iii}})$ 95.5 (3)° show that the $[\text{NH}_4]^+$ ions and the water molecules are distributed at the corners of a planar, almost square rhomb which links the anionic chains in the (101) plane. The angle between this rhomb and the four-bromine plane of the anion is 40.8 (8)°.

References

- BOIS, C., NGUYEN QUY DAO & RODIER, N. (1976). *J. Inorg. Nucl. Chem.* **38**, 755–757.
- DI SIPIO, L., TONDELLO, E., PELIZZI, G., INGLETTO, G. & MONTENERO, A. (1974a). *Cryst. Struct. Commun.* **3**, 297–300.
- DI SIPIO, L., TONDELLO, E., PELIZZI, G., INGLETTO, G. & MONTENERO, A. (1974b). *Cryst. Struct. Commun.* **3**, 301–303.
- DI SIPIO, L., TONDELLO, E., PELIZZI, G., INGLETTO, G. & MONTENERO, A. (1974c). *Cryst. Struct. Commun.* **3**, 527–530.
- DI SIPIO, L., TONDELLO, E., PELIZZI, G., INGLETTO, G. & MONTENERO, A. (1974d). *Cryst. Struct. Commun.* **3**, 731–734.
- DI SIPIO, L., TONDELLO, E., PELIZZI, G., INGLETTO, G. & MONTENERO, A. (1977). *Cryst. Struct. Commun.* **6**, 723–726.
- Enraf-Nonius (1981). *Structure Determination Package*. Version 18. Enraf-Nonius, Delft.
- Gmelin's Handbook of Inorganic Chemistry* (1983). 8th edition. *Uranium*: Suppl. Vol. A6, pp. 41–42. Berlin: Springer Verlag.
- HALL, D., RAE, A. D. & WATERS, T. N. (1966). *Acta Cryst.* **20**, 160–162.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- JENSEN, W. & DICKERSON, D. (1974). *Acta Cryst.* **B30**, 840–841.
- JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- MIKHAILOV, YU. N. & KUZNETSOV, V. G. (1971). *Russ. J. Inorg. Chem.* **16**, 1340–1342.