

## The Crystal Structure of Uranium Tetrabromide by X-ray and Neutron Diffraction

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Uranium tetrabromide,  $\text{UBr}_4$ , is monoclinic, space group  $C2/m$  ( $C_{2h}^3$ , No. 12), with  $a=10.92$  (2),  $b=8.69$  (3),  $c=7.05$  (1) Å and  $\beta=93.9$  (1)°,  $Z=4$ ,  $D_m=5.35$ ,  $D_x=5.55$  g cm<sup>-3</sup>. The crystal structure was solved with the aid of X-ray and neutron powder diffraction data, and refined with the neutron powder data by the profile-fitting technique. The final  $R$  was 0.15 for 274 measured intensities. The configuration around the uranium atom is a pentagonal bipyramid of bromine atoms, and the bipyramids are linked into infinite two-dimensional sheets by double bromine-bridging of the uranium atoms. There are only van der Waals attractions between sheets. The interatomic distances and angles within and between sheets are normal.  $\text{UBr}_4$  appears to be the only actinide halide  $\text{MX}_n$  (where  $n$  is 3 to 6) which has a pentagonal bipyramidal configuration around uranium, except for  $\beta\text{-UF}_5$  and  $\text{PaCl}_5$ . It is apparently the only actinide tetrahalide studied so far in which the coordination number is less than eight.

### Introduction

Douglass & Staritzky (1957) indexed the X-ray powder pattern of  $\text{UBr}_4$  on a  $C$ -centred monoclinic cell with  $a=10.92$  (2),  $b=8.69$  (3),  $c=7.05$  (1) Å and  $\beta=93.9$  (1)°, and four formula units per cell. Since that time the crystal structure of  $\text{UBr}_4$  has remained unsolved, perhaps for the reason that single crystals for X-ray structural work are not readily obtainable. The present study was undertaken with powders, and the neutron data were collected to make use of the more favourable neutron scattering factors for uranium and bromine (8.5 fm and 6.8 fm). X-ray diffraction studies suffer from the overwhelming scattering by uranium and from absorption and extinction effects; however, it was thought that the X-ray data of Douglass & Staritzky (1957) would be useful in determining the position of the uranium atom. Various crystal data for  $\text{UBr}_4$ , taken mainly from Douglass & Staritzky (1957), are collected in Table 1.

Table 1. Crystal data for  $\text{UBr}_4$

Values are taken from Douglass & Staritzky (1957). Monoclinic, space group  $C2/m$  ( $C_{2h}^3$ ),  $a=10.92$  (2),  $b=8.69$  (3),  $c=7.05$  (1) Å,  $\beta=93.9$  (1)°, M.W. 557.7,  $U=667$  Å<sup>3</sup>,  $D_m=5.35$ ,  $D_x=5.55$  g cm<sup>-3</sup>

### Experimental

Uranium tetrabromide was prepared by thermally decomposing uranium pentabromide at 200°C for several hours (Blair & Ihle, 1973). The uranium pentabromide for the above reaction was formed by direct reaction of uranium metal turnings and bromine using a few drops of acetonitrile as catalyst (Lux, Wirth & Bagnall, 1970).

The  $\text{UBr}_4$  sample (20 g) was packed into a 12 mm diameter vanadium can using dry-box methods. A neutron-diffraction powder pattern was collected, on the AAEC research reactor HIFAR, over the range  $5^\circ < 2\theta < 35.3^\circ$  with  $\lambda=1.077$  Å by using the elastic diffraction technique (Caglioti, 1970). The pattern is shown in Fig. 1.

A least-squares lattice-constant refinement based on the neutron pattern gave  $a=11.04$  (2),  $b=8.76$  (2),  $c=7.04$  (1) Å and  $\beta=94.05$  (8)°, in general agreement with the earlier work of Douglass & Staritzky (1957).

### Analysis and results

A search of the literature showed that  $\text{UBr}_4$  did not conform to any known  $\text{AB}_4$  structure type. The structure, therefore, had to be solved directly from the X-ray and neutron powder data without the help of the conventional powerful X-ray single-crystal methods.

It was possible to extract 15 unsuperposed  $F_0^2(hkl)$  values from the X-ray powder data of Douglass & Staritzky (1957). These were used in the calculation of a three-dimensional Patterson synthesis, which was a very diffuse distribution giving peaks only at  $y=0$  and  $y=\frac{1}{2}$ . One of the larger vectors was consistent with a uranium location of (0.20, 0, 0.40) giving U-U distances which were sensible in terms of bromine bridging. The possible space groups were  $C2$ ,  $Cm$  and  $C2/m$ , and it seemed reasonable to commence with the higher-symmetry space group  $C2/m$ .

Various refinements with the above X-ray data and structure models involving close-packed anion layers or eight-coordination of uranium met with no success. In all cases, however, the worsened agreement when uranium was left out of the calculated structure factors suggested strongly that, at least, the uranium atom was in the correct location.

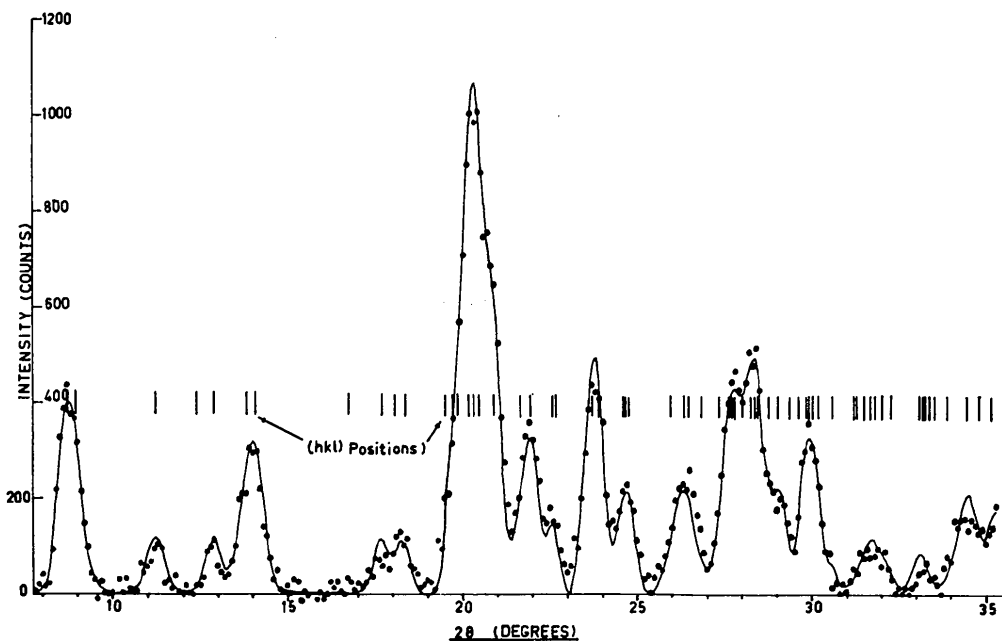


Fig. 1. Observed and calculated neutron-diffraction pattern profiles for uranium tetrabromide.

The correct model was arrived at by abandoning the above concepts and carefully considering the U positions in a three-dimensional model. It was found that if all the U-U approaches of less than 5 Å were double-bromine bridged, a pentagonal bipyramid of bromine atoms could be described about each uranium atom. The new model refined smoothly with the neutron powder data and the least-squares profile-fitting method of Rietveld (1967) to a value of

$$R = \sum_i (|I_{oi} - I_{ci}|) / \sum_i I_{oi} \text{ of } 0.15,$$

where  $I_{oi}$  is one of the 274 background-corrected intensities in the neutron pattern. The final value of  $\chi = [\sum w(I_{oi} - I_{ci})^2 / (NO - NV)]^{1/2}$  was 1.01, also indicating good agreement between theory and experiment. The neutron scattering lengths assumed were those quoted above (Neutron Diffraction Commission, 1972), and an overall isotropic Debye-Waller factor was assumed. As a satisfactory solution of the structure was found in the higher-symmetry space group  $C2/m$  there was no need to consider further the lower-symmetry space groups. The positional parameters are given in Table 2 and the interatomic distances and angles in Table 3. The accuracy of the results is

Table 2. Positional parameters of the atoms in the uranium tetrabromide structure ( $\times 10^3$ )

Debye-Waller $\bar{B} = 4.6$ (3) Å <sup>2</sup> .				
	Position	x	y	z
U	4(i)	192 (2)	000	432 (3)
Br(1)	4(i)	442 (2)	500	247 (3)
Br(2)	4(i)	828 (2)	500	142 (3)
Br(3)	8(j)	863 (1)	311 (2)	670 (2)

comparable with that obtainable in careful X-ray single-crystal studies of the actinide structures. The observed and calculated neutron-diffraction pattern profiles are shown in Fig. 1.

### Discussion

The uranium tetrabromide structure, shown in Fig. 2, is a new  $MX_4$  structure type: the configuration around the uranium atom is a pentagonal bipyramid. The U-Br distances for the bromine atoms in the pentagonal ring lie between 2.85 (2) and 2.95 (2) Å (Table 3). One apical bromine atom, Br(2), is terminal, with the U-Br(2) distance 2.61 (4) Å. The other apical atom, Br(1), has a dual function, in that it is the equatorial atom of an adjoining bipyramid; the apical U-Br(1) distance is 2.78 (3) Å. The axial Br(1)-U-Br(2) angle is 177 (1)°. The pentagonal bipyramids are linked into infinite chains parallel to **b** by sharing Br(3)-Br(3) edges (Fig. 2). These chains are further cross-linked into infinite sheets parallel to (001) by edge-sharing involving the dual-purpose Br(1) atoms. The uranium atoms in the network are all doubly bromine-bridged.

The infinite sheets of fused polyhedra in  $UBr_4$  pack as shown in Fig. 3. The smallest Br-Br separations between layers are similar to those found in adjacent dodecahedra in  $PaBr_4$  (Brown, Petcher & Smith, 1971). It is apparent from Figs. 2 and 3 that the uranium tetrabromide structure is not based on closest packing of the anions.

The inter-chain bridging of the dual-function atom Br(1) distorts the pentagonal ring system from planarity. The best least-squares plane through the uranium atom at (0.308, 0.500, 0.568) and its five equatorial

Table 3. *Interatomic distances and angles in uranium tetrabromide*

U-Br in pentagonal ring of bipyramid	
U-Br(1)	2.95 (2) Å
U-Br(3) (2 ×)	2.85 (2)
U-Br(3) (2 ×)	2.93 (2)
U-Br to apical bromines of bipyramid	
U-Br(1)	2.78 (3) Å
U-Br(2)	2.61 (4)
U-U in bridges	
U-U [bridged by Br(3)]	4.61 (1) Å
U-U [bridged by Br(1)]	4.36 (3)
Br-Br (edges of pentagonal ring)	
Br(1)-Br(3) (2 ×)	3.46 (2) Å
Br(3)-Br(3) (2 ×)	3.49 (2)
Br(3)-Br(3)	3.29 (3)
Apical-equatorial Br-Br approaches in polyhedron	
Br(1)-Br(1)	3.71 (4) Å
Br(1)-Br(3) (2 ×)	4.16 (2)
Br(1)-Br(3) (2 ×)	3.80 (2)
Br(2)-Br(1)	4.33 (3)
Br(2)-Br(3) (2 ×)	3.72 (2)
Br(2)-Br(3) (2 ×)	4.06 (3)
Interlayer Br-Br approaches (see Fig. 3)	
Br(1)-Br(1) (across 2-axis)	3.79 (4) Å
Br(1)-Br(2)	3.89 (3)
Br(2)-Br(3)	3.76 (3)
Br(2)-Br(2) (across 2-axis)	4.37 (4)
U-Br-U bridge angles	
U-Br(1)-U	99.3 (6)°
U-Br(3)-U	105.7 (4)
Pentagonal angles in polyhedron (theoretically 72°)	
Br(1)-U-Br(3) (2 ×)	73.4 (4)°
Br(3)-U-Br(3) (2 ×)	74.3 (4)
Br(3)-U-Br(3)	68.2 (5)
(Apical Br)-U-(equatorial Br) angles (theoretically 90°)	
Br(1)-U-Br(1)	80.7 (6)°
Br(1)-U-Br(3) (2 ×)	95.2 (5)
Br(1)-U-Br(3) (2 ×)	83.4 (6)
Br(2)-U-Br(1)	102.3 (8)
Br(2)-U-Br(3) (2 ×)	85.7 (6)
Br(2)-U-Br(3) (2 ×)	94.1 (6)

bromine neighbours was calculated by the method of Schomaker, Waser, Marsh & Bergman (1959). The equation of the plane, in perpendicular form with absolute coordinates, is  $-0.6069X + 0.8342Z = 1.1935$ . The Br(1) atom is distant  $-0.46 (2) \text{ \AA}$  from this plane, while the other deviations are  $0.10 (2) \text{ \AA}$  for the uranium atom and  $-0.16 (2) \text{ \AA}$  ( $2 \times$ ) and  $0.34 (2) \text{ \AA}$  ( $2 \times$ ) for the Br(3) atoms. The least-squares plane makes an angle of  $91.7^\circ$  with the line joining the two apical bromine atoms.

Pentagonal bipyramids also occur in the anhydrous  $\text{UO}_2\text{Cl}_2$  structure (Taylor & Wilson, 1973*a*). In  $\text{UO}_2\text{Cl}_2$  the uranium atoms are double chlorine-bridged to give infinite chains similar to those in  $\text{UBr}_4$ . The oxygen atom in  $\text{UO}_2\text{Cl}_2$  also has a dual role, being apical in one

polyhedron and equatorial in a neighbouring polyhedron. However, the dual-purpose oxygen atoms in  $\text{UO}_2\text{Cl}_2$  form linear U-O-U bridges, linking the chains in a three-dimensional fashion. Thus the resulting  $\text{UO}_2\text{Cl}_2$  structure is quite different from the  $\text{UBr}_4$  structure-type.

Uranium tetrabromide appears to be the only actinide halide  $\text{MX}_n$ , where  $n$  is 3 to 6, which has a pentagonal bipyramidal configuration around uranium apart from  $\beta\text{-UF}_5$  (Zachariasen, 1949) and  $\text{PaCl}_5$  (Dodge, Smith, Johnson & Elson, 1967). The only actinide tetrahalide with a coordination number less than eight. The other actinide tetrahalides have complex square-antiprismatic or dodecahedral structures, as exemplified by  $\text{UF}_4$  (Larson, Roof & Cromer, 1964),  $\text{ThI}_4$

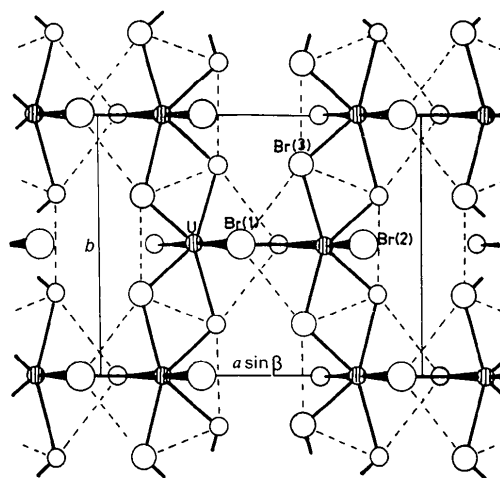


Fig. 2. The crystal structure of uranium tetrabromide seen in the  $ab$  projection, illustrating the bonding of the pentagonal bipyramids into infinite sheets.

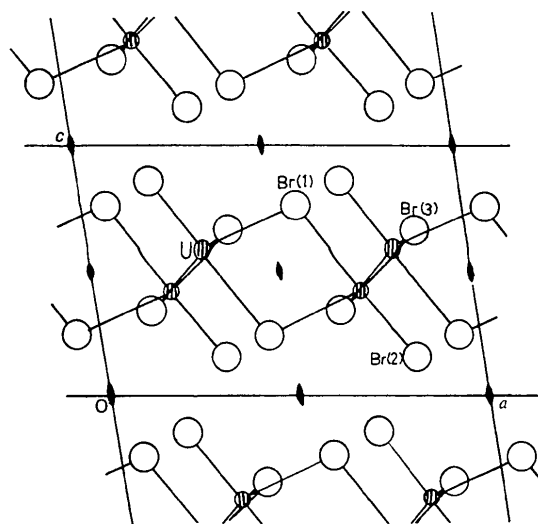


Fig. 3. The structure of uranium tetrabromide as viewed down  $b$ , illustrating the packing of the  $\text{UBr}_4$  sheets.

(Zalkin, Forrester & Templeton, 1964),  $\text{UCl}_4$ ,  $\text{ThCl}_4$ ,  $\text{PaCl}_4$  and  $\text{NpCl}_4$  (Taylor & Wilson, 1973*b*) and  $\text{PaBr}_4$  (Brown, Petcher & Smith, 1971). Uranium tetrabromide is thus a further example of the diversity of crystal structures found in the actinide tetrahalide series.

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## Structure Cristalline de $\text{K}_6\text{MgO}_4$

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Crystals of  $\text{K}_6\text{MgO}_4$  have been prepared by the action of melted  $\text{K}_2\text{O}$  on  $\text{MgO}$ . The symmetry is hexagonal, space group  $P6_3mc$ ; the unit cell parameters are:  $a = 8.47_8 \pm 0.005$ ,  $c = 6.58_5 \pm 0.003$  Å,  $Z = 2$ . The structure contains regular  $\text{MgO}_4$  tetrahedra and can be described as being made up of two types of antiprisms linked by short O–K bonds.

L'action du monoxyde de potassium  $\text{K}_2\text{O}$  sur les oxydes alcalinoterreux semble n'avoir fait l'objet d'aucune étude approfondie. Cependant dans une note récente Bardin, Avallet & Cassou (1974) ont révélé l'existence d'une phase  $\text{K}_6\text{MgO}_4$  qu'ils ont caractérisée par analyses chimique et radiocristallographique. Ils proposent une indexation du spectre de poudre, en attribuant à la phase une symétrie hexagonale.

Nous avons préparé  $\text{K}_6\text{MgO}_4$  à 800°C sous atmosphère d'azote anhydre par action de  $\text{K}_2\text{O}$  sur  $\text{MgO}$  en proportions stoechiométriques. La réaction est complète au bout de trois heures et laisse apparaître par refroidissement lent des aiguilles monocristallines de  $\text{K}_6\text{MgO}_4$ .

### Etude radiocristallographique

Le monocristal choisi pour l'étude structurale avait la forme d'une aiguille de 0,9 mm de longueur dont la base triangulaire mesurait en moyenne 0,2 mm de côté. Compte tenu de son hygroscopicité, le monocristal a

été introduit dans un tube capillaire de 0,3 mm de diamètre.

Les diagrammes de Bragg et de Weissenberg établis suivant l'axe  $Oz$  ont permis de déterminer la symétrie et les paramètres cristallins.  $\text{K}_6\text{MgO}_4$  cristallise dans le système hexagonal, les paramètres  $a = 8,47_8 \pm 0,005$  et  $c = 6,58_5 \pm 0,003$  Å ont été affinés à partir du spectre de poudre.

La seule condition d'existence relevée sur les clichés de Weissenberg et de Buerger,  $hh\bar{2}hl$ :  $l = 2n$ , est compatible avec les groupes d'espace  $P6_3mc$ ,  $P\bar{6}2c$  et  $P6_3/mmc$ . La densité mesurée par Bardin, Avallet & Cassou (1974) impliquait deux motifs  $\text{K}_6\text{MgO}_4$  par maille.

### Détermination de la structure cristalline

Les intensités des diverses réflexions  $hkl$  ont été mesurées à l'aide d'un diffractomètre automatique Enraf-Nonius CAD 3. Les 643 réflexions indépendantes sélectionnées