The Uranium Tetrabromide Structure: A New MX_4 Structure Type

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Summary UBr_4 is a new MX_4 structure type, the configuration around the uranium atom being the pentagonal bipyramid [UBr $Br_{6/2}$].

DOUGLASS and STARITZKY[1] found with *X*-ray powder diffraction that UBr_4 was monoclinic with $a = 1092(2)$, $b = 869(3)$, $c = 705(1)$ pm, $\beta = 93{\cdot}9(1)°$ and $Z = 4$. The space group was either $C2$ (C_2^3), No. 5, Cm (C_s^3), No. 8, or $C2/m$ (C_{2h}^3), No. 12. In the present work, the uranium atoms were located in positions 4(*i*), $\pm$ (x, 0, z) + F.C., in a Patterson synthesis of the previous *X*-ray powder data.[1] The bromine atoms were located by trial-and-error with the help of a neutron powder diffraction pattern, a satisfactory structure being found in the space group $C2/m$. Refinement with the neutron data and the least-squares profile-

fitting technique converged to $R = 0{\cdot}15$ over the 274 background-corrected pattern intensities.

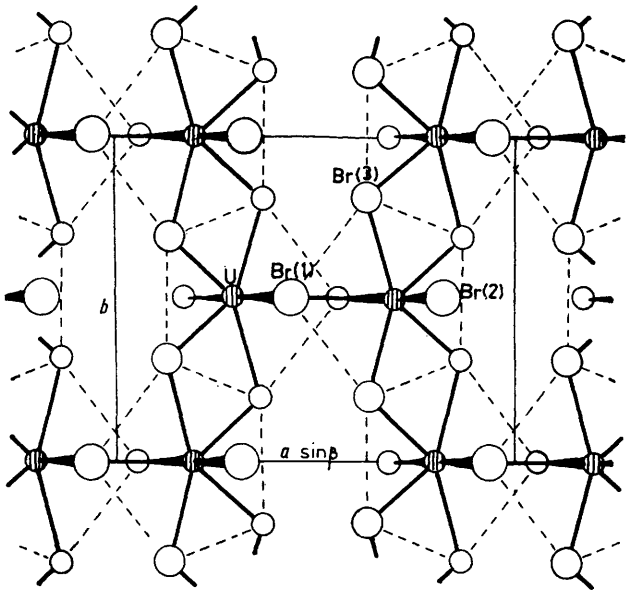

FIGURE. The crystal structure of uranium tetrabromide.

Each uranium atom is bonded to seven bromine atoms in the pentagonal bipyramidal configuration [UBr $Br_{6/2}$], as shown in the Figure, and the equatorial pentagons are edge-fused to form endless chains of polyhedra parallel to *b*. The chains are cross-linked into sheets, through a bridging bromine atom which is an equatorial atom in one chain and an apical bromine in an adjacent chain. Six of the U–Br distances in the polyhedron are between 278(3) and 295(2) pm while the seventh, to a truly terminal apical bromine atom is 261(4) pm. The uranium atoms in adjacent polyhedra are double bromine-bridged.

The Br–U–Br angle for the axial atoms is 177 (1)° and the line through the axial bromine atoms makes an angle of 91·7° with the best least-squares plane through the uranium atom and the equatorial pentagonal ring. The equatorial system is not strictly coplanar because one equatorial bromine atom is an axial atom of an adjacent polyhedron; the latter atom is distant 0·46 (2) Å from the plane. The deviations of the other equatorial atoms from the least-squares plane are 0·10 (2)—0·34 (2) Å.

The actinide tetrahalides usually form square antiprismatic (*e.g.* UF_4, ThI_4) or dodecahedral (*e.g.* UCl_4, $ThCl_4$, $PaBr_4$) co-ordination polyhedra.[2] Uranium tetrabromide is the only actinide tetrahalide so far found to have a co-ordination number of less than eight.

(*Received, 17th April* 1974; *Com.* 431.)

[1] R. M Douglass and E. Staritzky, *Anal. Chem.*, 1957, **29**, 459.
[2] D. Brown, 'Halides of the Lanthanides and Actinides,' Wiley, New York, 1968.