531. *The Crystal Structure of Thorium Tetrabromide.*

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The crystal structure of thorium tetrabromide has been determined by means of *X*-ray powder diffraction photographs. The structure is body-centred tetragonal, space group $D_{4h}^{19} - I4/amd$, with a, c, c/a, and ρ (calc.) equal to 8·945 A., 7·930 ± 0·005 A., 0·887, and 5·69 g./c.c., respectively. There are 4 molecules per unit cell.

Positions have been found for the atoms such that the calculated are in good agreement with the observed intensities. The Th–Br (nearest neighbour) distance is 2·57 A. and Th–Br (second nearest neighbour) is 3·31 A. It would appear that the bromide, like the chloride, is partially covalent in character. The arrangement of the four nearest bromine atoms around the thorium atom is shown to be a distorted square or an extremely flattened tetrahedron with Br–Th–Br angles 93·8° and 150·2°.

The crystal structure of thorium tetrachloride has been found by Mooney (*Acta Cryst.*, 1949, **2**, 189) to be a body-centred tetragonal lattice with cell dimensions $a = 8·473$, $c = 7·468$ A. The number of molecules per unit cell is 4, and the space group is $D_{4h}^{19} - I4/amd$. It was found that this chloride was isomorphous with uranium tetrachloride. The structure of thorium tetrabromide has not been worked out hitherto, but it is now found that this compound is isostructural with the tetrachloride.

Experimental.

Thorium tetrabromide was prepared by direct union of the elements *in vacuo*. A sample was transferred, *in vacuo*, to thin-walled Pyrex *X*-ray capillary tubes of approx. 0·3 mm. diameter. Powder diffraction photographs were taken in the usual manner by use of standard *X*-ray equipment, a 9-cm. Unicam camera, and filtered Cu-$K\alpha$ radiation. The resulting photographs were measured by using a steel scale and vernier, and the intensities were visually estimated.

From the Bragg relationship $\lambda = 2d \sin \theta$, the interplanar spacings d were calculated. By use of a Bunn chart, the diffraction pattern was successfully indexed on the basis of tetragonal cell of axial ratio, c/a, approx. 0·9. The cell constants a and c were then calculated to be 8·945 and 7·930 A. ± 0·005 A., respectively ($c/a = 0·887$). The density, calculated on the assumption that there are 4 mols. per unit cell, is 5·69 g./c.c., which is in close agreement with the experimentally determined value of 5·67 g./c.c. (Moissan and Martinsen, *Compt. rend.*, 1905, **140**, 1513).

From consideration of the indices of the planes the following regularites were observed :

(hkl) present if $h + k + l = 2n$
($hk0$) ,, $h = 2n$ and $k = 2n$
($0kl$) present if $k + l = 2n$
(hhl) ,, $l = 2n$ and $2h + l = 4n$

This indicates a body-centred tetragonal cell of space group $D_{4h}^{19} - I4/amd$. For this space group the positions of the atoms, as given in Internationale Tabellen, Vol. 1, are :

4-fold sets	(*a*) and (*b*)	parameters	000 or $00\frac{1}{2}$		16-fold sets	(*f*) and (*g*)	parameters	$x\frac{1}{4}\frac{1}{8}$ or xxo
8- ,,	(*c*) ,, (*d*)	,,	$0\frac{1}{4}\frac{1}{8}$ or $0\frac{1}{4}\frac{5}{8}$		16- ,,	(*h*)	,,	oyz
8- ,,	(*e*)	,,	$00z$					

The four thorium atoms are necessarily in one of the four-fold sets (*a*) and (*b*). If set (*a*) is chosen, these atoms will have the positions 000, $0\frac{1}{2}\frac{1}{4}$, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, and $\frac{1}{2}0\frac{3}{4}$.

Thorium with parameters 000 makes no contribution to planes with $2h + l = 4n + 2$, whereas for planes with $2h + l = 4n$, $2h + l = 4n \pm 1$ the contributions are respectively $A = 4f_{Th}$ and $B = 0$, $A = 2f_{Th}$ and $B = -A$, and $A = B = 2f_{Th}$, where f_{Th} is the scattering factor for thorium.

Plane (202) is of medium intensity, whereas planes (402), (422), and (314) are definitely not observed. The thorium contribution to these planes is zero; thus it is possible to eliminate any set of positions for bromine atoms which does not give a moderate structure amplitude for (202) and a very small amplitude for (402). This at once eliminates the 16-fold set (*g*) with parameters xxo.

If the bromine atoms were distributed as in the 8-fold set (*e*) with parameters $00z$, the bromine contribution must necessarily reinforce the thorium contribution for planes ($hk0$). All observed ($hk0$) planes were either very weak or absent, indicating that the bromine contribution must be near maximum and out of phase with the thorium contribution. This therefore eliminates the possibility of two 8-fold sets (*e*) or a combination of an 8-fold set (*e*) with either an 8-fold set (*c*) or (*d*). More detailed consideration of the 8-fold sets (*c*) and (*d*) rules out the possibility of bromine being in either of these two sets. Also it is found that the *z* parameter cannot be $\frac{1}{8}$ or $\frac{5}{8}$, which eliminates the 16-fold set (*f*) as well.

We are left therefore with the 16-fold set (*h*) with parameters oyz. Rough values for *y* and *z* were obtained by comparing observed and calculated structure amplitudes for planes ($hk0$). These values were refined by further comparison of calculated and observed amplitudes for all the sensitive planes. The final values arrived at were : $y = 100°$ and $z = 330°$. The bromine atoms are accordingly in positions :

$0yz$; $0\bar{y}z$; $y0\bar{z}$; $\bar{y}0\bar{z}$; 0, $\frac{1}{2} + y$, $\frac{1}{4} - z$; 0, $\frac{1}{2} - y$, $\frac{1}{4} - z$; y, $\frac{1}{2}$, $\frac{1}{4} + z$; $\bar{y}$, $\frac{1}{2}$, $\frac{1}{4} + z$ (all + $\frac{1}{2}\frac{1}{2}\frac{1}{2}$).

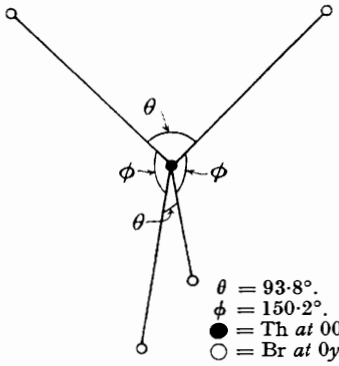
It is seen from the table that the calculated intensities I_c, where $I_c \propto F^2 m$, F being the structure factor and *m* the multiplicity constant, are in good agreement with the observed intensities. In comparing intensities of reflections at widely different scattering angles allowance should, however, be made for the effects of absorption and polarization. The calculated values of interplanar planar spacing d_c are seen to be in agreement with the observed values.

θ	hkl	$d_{obs.}$	$d_{calc.}$	$I_{obs.}$	$I_{calc.}$		θ	hkl	$d_{obs.}$	$d_{calc.}$	$I_{obs.}$	$I_{calc.}$	
7·71	101	5·78	5·93	W	13·8		32·6	611	1·4363	1·4458	VVW	6·4	
10·19	200	4·39	4·47	W	12·0			334		1·4443		0·0	
13·45	112	3·343	3·359	W—	15·3		33·32	523	1·4084	1·4064	M—S	14·4	41·0
15·23	202	2·959	2·967	M	29·3			424		1·4081		26·6	
16·28	301	2·772	2·791	M—	28·4		35·29	622	1·3381	1·3321	W+	1·5	36·3
17·93	103	2·523	2·535	M	30·6			325		1·3363		34·8	
19·26	321	2·354	2·367	M—	26·8		36·05	631	1·3134	1·3149	W—	20	22·4
19·8	312	2·292	2·302	M	42·5			514		1·3137		2·4	
20·47	213	2·2198	2·2064	W	39·8		36·46	116	1·3004	1·2938	VW+	18	
20·47	400	2·2198	2·2361	W	42·3		37·03	415	1·2831	1·2804	M	30·4	46·8
21·71	411	2·0979	2·0925	VVW	16·4			613		1·2850		16·4	
23·01	420	1·9844	2·000	VVW	12·1		38·78	543	1·2332	1·2350	M—	43·6	46·4
	004		1·9826	Abs	0·4	3·8		444		1·2360		2·8	
	303		1·9780		3·4		39·57	721	1·2123	1·2140	VW+	28·0	30·0
24·66	332	1·8586	1·8614	M—	27·1			534		1·2133		2·0	
25·29	323	1·8147	1·8089	VVW	0·01	14·21	40·33	604	1·1931	1·1915	VW	7·2	10·4
	204		1·8126		14·2			435		1·1868		3·2	
	503		1·4815		29·9		43·44	336	1·1221	1·1198	M—	1·2	17·8
31·51	433	1·4812	1·4815	S—	17·4	49·4		107		1·1240		16·6	
	404		1·4834		2·1								

Discussion.

From the above evidence it would appear that thorium tetrabromide, like the chloride (Mooney, *loc. cit.*), has a body-centred tetragonal type structure with unit cell dimensions as given above. The thorium atom is surrounded by eight bromine atoms, four at distances of 2·57 A. and four at 3·31 A. The smallest Br–Br distance is 3·34 A. Covalency being assumed for thorium tetrabromide and tetrachloride, the atomic radius of thorium can be calculated as 0·9 A. and 0·86 A., respectively. Pauling's values being assumed for the ionic radius of chlorine and bromine, and a pure ionic nature assumed for both halides, the radius of thorium can be calculated as 0·62 A. and 0·65 A. for the chloride and bromide, respectively. In the completely ionic structure, ThO_2, the ionic radius for Th^{4+} is 1·02 A. On the basis, therefore, of the bromine atoms' not being in a close-packed arrangement around the thorium atom, indicated by the unequal

Th–Br distances, and the significantly smaller radius of thorium in the chloride and bromide than in the dioxide, it is reasonable to assume that the bromide, like the chloride, is, at least, partially covalent in character.



The four nearest bromine atoms (Br–Br = 3·76 A.) form a configuration around the thorium atom which can be described as a rhombic bisphenoid (see figure). The halogen–Th–halogen angles calculated from the observed data are 93·8° and 150·2° for the tetrabromide and 93·4° and 149° for the tetrachloride.

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