Structural Parameters and Unit Cell Dimensions for the Tetragonal Actinide Tetrachlorides (Th, Pa, U, and Np) and Tetrabromides (Th and Pa)

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Comparison of crystal structure parameters obtained for $ThCl_4$ from quantitative X-ray powder data with those available from single-crystal studies has shown that it is possible to obtain reliable parameters from powder studies on simple compounds. Structure refinement based on powder data for $ThCl_4$ (R = 8·9%), $PaCl_4$ (R = 7·6%), UCl_4 (R = 9·5%), $NpCl_4$ (R = 9·1%), and $ThBr_4$, (R = 11·3%) has yielded crystal structure parameters, and bond lengths for these isostructural compounds. Accurate unit cell dimensions are also reported.

STRUCTURAL parameters deduced by Mooney[1] for $ThCl_4$ and UCl_4 on the basis of X-ray powder diffraction data have recently been discredited by single-crystal diffractometer studies[2] on $ThCl_4$, the results justifying the earlier criticism by Zachariasen[3] concerning the surprisingly large difference between the two sets of bond lengths deduced originally.[1] Positional parameters are also available for $PaBr_4$[4] which is isostructural with the actinide tetrachlorides (Th—Np) possessing tetragonal symmetry, space group $D_{4h}^{19} - I4_1/amd$. However, Scaife[5] has criticised earlier work[6] on $ThBr_4$ which indicated that this compound crystallised in the same space group. He reports that $ThBr_4$ is dimorphic and that the high-temperature (β) form although possessing a unit cell very similar to that deduced previously, gives three weak reflections which break the space group conditions for $D_{4h}^{19} - I4_1/amd$ ($hkl, h + k + l = 2n : hko, h(k) = 2n : 0kl, k + l = 2n : hhl, l = 2n$ and $2h + l = 4n$). The low-temperature (α) form appears to possess a completely different structure and is not isostructural with monoclinic UBr_4 and $NpBr_4$.[7]

As pointed out previously[4] the published structural parameters for UCl_4 and $ThBr_4$ must be considered unreliable in the light of the new $ThCl_4$ and $PaBr_4$ results. No data are available for $PaCl_4$ whilst Zachariasen,[3] without presenting quantitative supporting evidence, has reported values for $NpCl_4$.

The present paper describes an evaluation of the reliability of structural parameters obtained by refinement of quantitative X-ray powder data by comparison of the results for $ThCl_4$ with those obtained from the single crystal study.[2] Positional parameters for the isostructural tetrachlorides $PaCl_4$, UCl_4, and $NpCl_4$ obtained by the ' powder ' method are reported. Attempts to repeat the preparation of α- and β-$ThBr_4$ described by Scaife[5] have been unsuccessful, all products being completely isostructural with the above tetrachlorides, and new positional parameters are also reported for this compound.

The tetrahalides obtained during this investigation gave high quality X-ray powder photographs, and in view of the differences between the compiled lists[8-10] of unit cell dimensions and the fact that the availability of computer programmes for processing X-ray powder diffraction data has increased the precision with which cell dimensions can be determined, these have been redetermined. The redetermination of the unit cell dimensions is also of interest because of the apparent lack of change in the c_0 values for the first three tetrachlorides ($ThCl_4$, $PaCl_4$, and UCl_4) and the sharp fall which occurs at $NpCl_4$.[8]

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EXPERIMENTAL

Unit Cell Dimensions.—The tetrachlorides and tetrabromides were prepared as described previously [11-14] and purified by repeated sublimation *in vacuo* in silica tubes. Analytical results are provided in Table 1. Samples were mounted in thin-walled silica or Lindemann glass capillaries (internal diameter 0·01 or 0·015 cm) in a nitrogen atmosphere box (water content <20 p.p.m.; oxygen content <20 p.p.m.).

TABLE 1

Analytical results

	Found (%) *		Required (%)	
Compound	M	X	M	X
$ThCl_4$	62·1	38·0	62·06	37·94
$PaCl_4$	61·8	38·0	61·96	38·04
UCl_4	62·7	37·3	62·66	37·34
$NpCl_4$	62·5	37·4	62·56	37·44
$ThBr_4$	42·1	57·9	42·06	57·94

* M, metal; X, halogen: determined as described previously, see refs. 7, 11, and 12.

Films were recorded using a 19 cm Debye–Scherrer camera with nickel-filtered copper radiation and exposure times of 12—16 h (35 kV, 15 mA). Positions of both α_1 and α_2 reflections were measured where possible (α_1/α_2 splitting was generally observed for θ values >15°), each film being measured by two people, with a line position accuracy of ±0·03 mm. Since the structure-type was known (tetragonal, space group $D_{4h}^{19} - I4_1/amd$) it was possible to calculate the approximate powder pattern using the programme Genstruck [15] and then index the observed reflections by comparison with the calculated pattern. The indexed reflections were refined by a least-squares method using the programme Cohen [15] with the appropriate wavelength (Cu-α_1, 1·54051 Å or Cu-α_2, 1·54433 Å). The agreement limit was set to 0·0004 for values of $\sin^2\theta$ and two cycles of refinement were sufficient to ensure the correct indexing of the film. Results for different samples and for α_1 and α_2 sets of reflections agreed within the error limits (2σ) quoted in Table 2. The unit cells listed are based on refinement of reflections with θ values >30°, the upper limit of θ being *ca.* 70°, above which value the lines became a little diffuse and therefore could not be measured accurately. Between 60 and 70 reflections were included in each refinement. Checks on the reliability of the camera constants employed have been described recently.[16]

Packing Densities.—By utilising the radioactivity associated with ^{231}Pa and ^{237}Np it was possible to measure packing densities directly for $PaCl_4$ and $NpCl_4$. The sample diameter and length were measured under magnification (×5) following which the capillaries were crushed under concentrated nitric acid in 1 ml graduated flasks and the solution made up to the mark. The concentrations of ^{231}Pa and ^{237}Np were determined by α-assay using the specific activities $1{\cdot}062 \times 10^8$ and $1{\cdot}562 \times 10^6$ αd min^{-1} mg^{-1}, respectively.[17,18] Using *X*-ray densities of 4·72 and 4·96 g cm^{-3} for $PaCl_4$ and $NpCl_4$, respectively, the packing densities 37% ($PaCl_4$) and 47% ($NpCl_4$) were obtained. The mean value 42% was employed for all the tetrahalides investigated.

Crystal Data.—$ThCl_4$, $PaCl_4$, UCl_4, $NpCl_4$, and $ThBr_4$, all tetragonal, space group $D_{4h}^{19} - I4_1/amd$ (No. 141); Cu-K_α radiation $\lambda\alpha_1 = 1{\cdot}54051$ Å. Unit cell dimensions are listed in Table 2.

Structure Determination.—The intensities of powder lines for each compound were measured by scanning both halves of the 19 cm Debye–Scherrer films several times at 5 : 1 linear magnification with a Joyce–Loebl double-beam recording microdensitometer using a 0·39D wedge. In order to minimise film background and to improve the reliability of the measurements it was necessary to scan films recorded for samples contained in Lindemann rather than silica capillaries.

Peak heights were measured for each scan and the mean values corrected for varying overlap of α_1 and α_2 reflections by dividing by a factor of $1 + 0{\cdot}5\cos(F\theta)$, where $F = 90/\theta_S$, θ_S being the angle of the first reflection for which α_1 and α_2 were completely resolved. Above the values of θ_S, which were 18, 21, 21, 13, and 20° for $ThCl_4$, $PaCl_4$, UCl_4, $NpCl_4$, and $ThBr_4$, respectively, only the α_1 reflections were used. The resulting values were corrected in the usual way for geometrical, Lorentz polarisation, and multiplicity factors. An absorption correction was applied (PTMLPCOR [19]) using a packing density of 42% with μ/ρ for Th = 401 cm^2 g^{-1}, Pa = 398 cm^2 g^{-1}, U = 396 cm^2 g^{-1} and Np = 454 cm^2 g^{-1}. Values for Th and U are the experimental figures of Roof [20] whilst those for Pa and Np are interpolated from the values for Th, U, and Pu. μ/ρ values for Cl (106) and for bromine (99·6) were taken from Tables.[21]

TABLE 2

Unit cell dimensions for the actinide tetrachlorides and tetrabromides [a]

	Lattice parameters (Å) [b]		Density [c]	Cell
Compound	a_0	c_0	/g cm^{-3}	volume
$ThCl_4$	8·491	7·483	4·60	539·5
$PaCl_4$	8·377	7·481	4·72	525·0
UCl_4	8·302	7·481	4·89	515·6
$NpCl_4$	8·250	7·457	4·96	507·5
$ThBr_4$	8·931	7·963	5·77	635·2
$PaBr_4$ [d]	8·824	7·957	5·90	619·5

[a] All possess tetragonal symmetry, space group $D_{4h}^{19} - I4_1/amd$. [b] Error limits, 0·001 Å (to give 95% confidence) are 2σ where σ is the e.s.d. obtained from a comparison of the results from different films and, where appropriate, from α_1 and α_2 sets of reflections. Unit cell dimensions listed were obtained by refinement of reflections with θ values >30°. [c] Calculated from the *X*-ray data. [d] Data from ref. 4.

The positions of all possible reflections were calculated

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[11] D. Brown and P. J. Jones, *J. Chem. Soc.* (*A*), 1967, 719.

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[21] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

and those showing any possibility of overlap were rejected. The structures were refined using 25, 26, 26, 29, and 25 line intensities for $ThCl_4$, $PaCl_4$, UCl_4, $NpCl_4$, and $ThBr_4$, respectively.

Recent theoretical values for both real and imaginary parts of the anomalous dispersion corrections were applied [22] to all scattering factors, the latter being taken from the compilation by Hanson *et al.*[23] Positional parameters for $ThCl_4$ [2] were used initially in all cases, and block-diagonal least-squares refinements using the programme NRC-10 by Ahmed [24] rapidly led to the parameters and R values shown in Table 3. The final shifts in all parameters were less than 0·1 σ. Lists of observed and calculated structure amplitudes are provided in Table 4. Bond lengths and angles were calculated using the programme NRC-12.[25]

TABLE 3

Structural parameters for the tetrahalides in $I4_1/amd$ (origin at centre of symmetry $2/m$) with standard deviations in parentheses

	Metal *	Halogen				
Compound	B_{ISO}	x/a	y/b	z/c	B_{ISO}	R(%)
$ThCl_4$ [a]	*c*	0	0·5633(8)	0·7992(8)	*c*	3·8
$ThCl_4$	0·3(3)	0	0·561(6)	0·795(9)	1·21(1·7)	8·9
$PaCl_4$	0·9(3)	0	0·557(7)	0·795(6)	1·39(1·5)	7·6
UCl_4	2·6(3)	0	0·556(7)	0·796(7)	2·68(1·3)	9·5
$NpCl_4$	1·5(2)	0	0·558(7)	0·796(8)	2·13(1·3)	9·1
$ThBr_4$	0·5(3)	0	0·561(3)	0·796(5)	4·71(1·0)	11·3
$PaBr_4$ [b]	*c*	0	0·557(3)	0·804(4)	*c*	12·3

* Positional parameters for the metal atom are $x/a = 0$, $y/b = 0·25$, and $z/c = 0·875$.

[a] Single crystal data from ref. 2. [b] Data from ref. 4. [c] Anisotropic temperature factors given in ref. quoted.

Patterson and Fourier maps were also obtained for $ThCl_4$ using the programme NRC-8 by Ahmed.[26]

RESULTS AND DISCUSSION

Tetrachlorides.—Comparison of our positional parameters obtained by refinement of quantitative *X*-ray powder data for $ThCl_4$ (Table 3) with those from the single crystal diffractometer investigation illustrates the reliability of ' powder ' results when care is exercised in handling the data. The M–A and M–B bond lengths (Table 5) from the two results agree within the e.s.d. values (0·06 and 0·05 Å, respectively) for the powder results. Similar agreement is found for the two sets of halogen–halogen contacts and various angles within an isolated dodecahedron (Table 5). The difference between the two values for the M–A bond length (0·05 Å) is a consequence of the difference between the z/c positional parameters for the chlorine atom because of the four M–A bonds two are parallel to the z direction of the cell and two are at an angle of 33·0° (θ_A) to this direction. A combination of the very slight variation in the z/c parameter for the chlorine atoms in the four tetrachlorides, the M–A bond direction, and the lack of variation in c_0 (Table 2) accounts for the identical M–A bond lengths obtained for $ThCl_4$, $PaCl_4$, and UCl_4. The M–B bond lengths, on the other hand, decrease successively for these three compounds (*cf.* the a_0 values in Table 2). The fact that the M–B bond lengths are virtually identical for UCl_4 and $NpCl_4$ suggests that some errors remain in the data. These may be a consequence of residual absorption errors due to the use of an average packing density or lack of uniformity in the internal diameter of individual capillaries.

Nonetheless, on the whole our results show that for simple compounds the powder method allows the determination of reliable structural parameters relatively rapidly and economically and that compounds with very large linear absorption coefficients present no extraordinary problems. In addition, we were particularly encouraged to find that, despite the small number of reflections (25) a Patterson function calculated using our $ThCl_4$ data showed sufficient resolution to make the location of the heavy atom a trivial problem. The resolution on a Fourier difference synthesis was, however, not as good, and obviously in those instances where a single atom, *e.g.* Th, dominates the phases of the structure factors of the compound the additional factors of packing and space group positions must be considered if the structure is to be completely solved from powder data.

It is interesting to note that the c_0 values for the unit cells of $ThCl_4$, $PaCl_4$, and UCl_4 (Table 2) are virtually constant within the standard deviations quoted. Thus, the uniform decrease in unit cell volume (Table 2) with increasing atomic number of the metal atom (*i.e.* decreasing ionic radius) is a consequence of the change in a_0 within this series. These results confirm the earlier values tabulated by Zachariasen [8] rather than those compiled by other authors.[9–11] Our new values for the unit cell dimensions of $NpCl_4$ are slightly lower than those recorded previously.[8]

The unit cell dimensions obtained during the present investigation are based on data of similar quality to those shown in Table 6 for thorium tetrabromide. The α_1/α_2 splitting was generally discernible above *ca.* 15° for the various compounds and both α_1 and α_2 sets of line positions were used in individual refinements with the appropriate wavelength. It was found that inclusion of reflections below a θ value of 30° resulted in slightly larger unit cell dimensions (0·001—0·002 Å) whereas refinement with reflections above θ values of 30, 40, and 50°, respectively, gave virtually constant values with slightly increasing values of standard deviations. In view of these observations the unit cells listed in Table 2 are those obtained from refinements involving all lines above 30°.

Thorium Tetrabromide.—The reflections measured on

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[22] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[23] H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, 1964, **17**, 1040.

[24] F. R. Ahmed, NRC Crystallographic Programme No. 10 (1968).

[25] M. E. Pippy and F. R. Ahmed, NRC Crystallographic Programme No. 12 (1968).

[26] F. R. Ahmed, NRC Crystallographic Programme No. 8 (1968).

TABLE 4

Structure amplitudes for the tetragonal actinide tetrahalides

h	*k*	*l*	$\|F_{\mathrm{obs}}\|$	$\|F_{\mathrm{calc}}\|$	α_c	*h*	*k*	*l*	$\|F_{\mathrm{obs}}\|$	$\|F_{\mathrm{calc}}\|$	α_c
(a) ThCl$_4$											
1	0	1	215·0	219·3	8·73	4	2	0	239·0	207·3	192·00
2	0	0	309·4	344·8	8·19	3	3	2	362·5	320·5	189·29
2	1	1	123·8	154·6	11·37	5	1	2	187·0	193·0	12·77
1	1	2	269·4	257·2	10·12	4	4	0	235·4	239·9	11·17
2	0	2	162·2	141·3	183·27	6	0	0	268·1	327·6	9·53
3	0	1	350·5	310·0	7·36	6	1	1	160·3	149·6	12·17
1	0	3	334·5	284·4	187·82	5	3	2	186·5	223·7	191·80
3	2	1	237·3	250·6	188·48	6	2	0	239·8	220·4	191·94
3	1	2	290·9	294·5	9·49	1	1	6	265·1	251·0	191·22
4	0	0	353·6	352·9	8·58	6	1	3	213·8	188·6	10·89
2	1	3	188·4	165·8	11·01	4	1	5	165·0	151·1	192·32
4	1	1	173·8	158·6	11·36	6	4	0	227·4	243·5	11·50
						7	2	1	157·2	156·6	192·16
(b) PaCl$_4$											
1	0	1	190·0	224·7	8·91	4	2	0	220·0	205·6	192·28
2	0	0	315·8	341·9	8·55	3	0	3	220·0	188·9	190·38
1	1	2	248·5	259·9	10·37	3	3	2	298·6	306·9	189·61
2	1	1	139·3	156·6	11·64	2	0	4	255·3	232·2	191·37
2	2	0	166·8	145·7	196·10	2	2	4	270·8	269·7	10·42
2	0	2	156·5	141·8	183·27	4	1	3	184·9	183·2	10·67
3	0	1	307·4	303·7	7·65	5	1	2	163·8	180·1	13·39
1	0	3	303·8	280·3	188·05	6	1	1	158·5	137·5	12·72
3	2	1	229·0	241·9	188·82	5	3	2	160·5	204·4	192·35
3	1	2	298·2	288·7	9·82	3	2	5	166·9	171·3	11·22
4	0	0	375·8	353·2	8·72	1	1	6	216·8	227·6	191·63
2	1	3	191·8	158·2	11·58	3	1	6	163·9	158·3	194·42
4	1	1	170·4	158·2	11·58	5	2	5	169·0	161·9	11·67
(c) UCl$_4$											
1	0	1	209·7	275·6	9·16	2	0	4	217·3	204·4	191·68
2	0	0	277·9	336·0	8·83	2	2	4	237·9	230·9	10·74
2	1	1	146·4	153·3	12·01	4	1	3	145·5	157·5	10·98
1	1	2	247·0	253·1	10·69	5	1	2	134·7	150·0	13·95
2	0	2	137·4	135·4	183·31	6	1	1	124·6	109·8	13·23
3	0	1	296·4	287·4	7·87	5	3	2	171·1	162·5	192·82
1	0	3	328·4	263·8	188·27	3	2	5	142·0	135·0	11·50
3	2	1	235·3	222·8	189·12	4	1	5	100·7	98·0	193·65
3	1	2	284·2	266·9	10·10	6	1	3	113·6	125·1	11·86
4	0	0	339·7	326·4	8·95	7	3	2	120·7	142·9	192·75
2	1	3	167·6	143·8	12·04	2	1	7	130·9	105·3	192·35
4	1	1	180·6	144·4	11·94	6	5	3	127·0	100·9	12·34
3	3	2	242·7	270·2	189·90	8	2	4	86·8	100·4	14·22
(d) NpCl$_4$											
1	0	1	202·5	231·9	9·41	5	1	2	177·2	177·1	14·04
2	0	0	294·0	350·8	9·01	6	1	1	161·3	131·3	13·45
2	1	1	136·5	163·5	12·14	5	3	2	202·6	194·2	193·09
1	1	2	258·6	268·4	10·86	3	2	5	171·9	159·1	11·95
2	2	0	153·4	158·0	196·27	1	1	6	260·0	211·4	192·35
2	0	2	169·3	136·7	183·31	6	3	1	161·4	170·7	191·44
3	0	1	314·7	303·7	8·06	4	1	5	121·7	123·3	193·84
1	0	3	343·3	280·5	188·48	4	4	4	196·3	167·5	194·11
3	2	1	240·6	241·0	189·31	3	1	6	149·0	147·7	195·20
3	1	2	309·2	289·7	10·32	7	3	2	156·1	180·2	193·27
4	1	1	167·0	158·9	12·16	2	1	7	142·1	133·7	192·93
3	3	2	286·7	299·2	190·17	8	3	1	100·8	114·4	193·92
2	0	4	261·6	230·2	191·92	4	1	7	95·9	96·0	195·37
2	2	4	258·5	260·8	11·04	7	5	2	109·7	126·5	15·96
4	1	3	190·0	176·8	11·30						
(e) ThBr$_4$											
1	0	1	203·8	211·9	8·91	3	2	1	286·4	305·2	187·28
1	0	3	468·4	377·7	186·42	3	2	5	217·5	195·6	9·70
1	1	2	209·2	209·6	11·66	3	3	2	345·6	382·5	187·91
1	1	6	359·2	257·8	190·10	4	0	0	437·5	434·8	7·27
2	0	0	310·8	377·6	7·64	4	1	1	132·9	127·1	13·04
2	0	2	301·1	289·2	182·94	4	1	3	179·3	196·8	9·64
2	0	4	311·1	225·3	191·06	4	2	4	229·4	234·2	10·74
2	1	3	161·6	134·3	12·52	5	1	6	232·5	233·5	190·67
2	1	5	306·1	230·8	188·78	5	2	5	167·2	179·6	10·20
2	1	7	214·5	167·3	190·61	5	4	3	157·9	182·0	190·11
2	2	4	332·8	302·7	9·14	6	0	0	370·0	390·0	7·97
3	0	1	385·1	423·9	6·01	6	1	1	128·1	132·6	12·48
3	0	3	233·5	203·0	189·38	6	3	1	206·4	230·7	188·82
3	1	2	313·4	315·6	8·79	7	3	2	193·6	220·8	191·06

TABLE 5

Principal interatomic distances (Å) and selected angles (°) in the tetrahalides. The nomenclature of the dodecahedron edges and of θ_A and θ_B is that of ref. 27

(a) **Bond lengths/Å**

Compound	M − A [a]	M − B [a]	X − X*				M − A/ M − B
			a	*b*	*m*	*g*	
$ThCl_4$ [b]	2·903 (7)	2·718 (8)	3·17	3·93	3·19	3·61	1·07
$ThCl_4$	2·95 (6)	2·71 (5)	3·21 (7)	3·92 (8)	3·25 (7)	3·61 (8)	1·09 (3)
$PaCl_4$	2·95 (5)	2·64 (4)	3·24 (6)	3·83 (8)	3·21 (6)	3·57 (7)	1·12 (3)
UCl_4	2·95 (5)	2·60 (4)	3·23 (7)	3·78 (7)	3·19 (7)	3·54 (8)	1·13 (3)
$NpCl_4$	2·93 (6)	2·60 (4)	3·18 (7)	3·78 (7)	3·20 (7)	3·53 (8)	1·12 (3)
$ThBr_4$	3·12 (3)	2·85 (2)	3·38 (7)	4·12 (7)	3·42 (5)	3·81 (4)	1·09 (2)
$PaBr_4$ [c]	3·07 (2)	2·77 (2)	3·28 (3)	4·00 (3)	3·40 (3)	3·77 (3)	1·11 (2)

(b) Angles/°

Compound	X − M − X for dodecahedron edge:				θ_A	θ_B
	a	*b*	*m*	*g*		
$ThCl_4$ [b]	66·1	92·5	69·0	79·9	33·1	78·0
$ThCl_4$	65·9 (1·4)	92·8 (1·5)	69·9 (1·5)	79·3 (1·5)	33·0 (0·7)	77·2 (0·7)
$PaCl_4$	66·6 (1·2)	92·9 (1·4)	69·8 (1·3)	79·1 (1·3)	33·3 (0·6)	76·9 (0·7)
UCl_4	66·5 (1·3)	93·0 (1·5)	69·9 (1·4)	79·0 (1·4)	33·3 (0·6)	76·9 (0·7)
$NpCl_4$	65·8 (1·3)	93·0 (1·5)	70·3 (1·4)	78·9 (1·4)	32·9 (0·6)	76·8 (0·8)
$ThBr_4$	65·6 (1·0)	92·8 (1·0)	69·9 (1·0)	79·3 (1·0)	32·8 (0·5)	77·3 (0·5)
$PaBr_4$ [c]	67·3 (0·7)	92·4 (0·7)	68·1 (0·7)	80·2 (0·7)	33·7 (0·3)	78·2 (0·4)

[a] A and B refer to halogen atoms designated as in ref. 27. X–X are halogen contacts for the dodecahedron edges listed. [b] Calculated from the crystal data (ref. 2). [c] Data from ref. 4.

TABLE 6

X-Ray powder diffraction data for $ThBr_4$

h,k,l	sin $^2\theta_{obs}$	sin $^2\theta_{calc}$	I^*_{est}
1,0,1	0·0172	0·0170	S−
2,0,0	0·0302	0·0301	S−
1,1,2	0·0530	0·0527	M
2,0,2	0·0678	0·0677	M+
3,0,1	0·0771	0·0768	S−
1,0,3	0·0924	0·0922	S
3,2,1	0·1069	0·1066	S
3,1,2	0·1125	0·1124	S
4,0,0	0·1199	0·1196	W+
2,1,3	0·1221	0·1221	W
4,1,1	0·1367	0·1364	W−
4,2,0	0·1496	0·1494	VW−
3,0,3	0·1518	0·1518	W+
4,0,2	0·1571	0·1571	VW−
3,3,2	0·1721	0·1720	M+
2,0,4	0·1801	0·1802	M−
4,2,2	0·1868	0·1869	VW−
4,3,1	0·1961	0·1960	S−
5,0,1		0·1960	
2,2,4	0·2101	0·2100	M+
4,1,3	0·2115	0·2114	M+
3,1,4	0·2250	0·2249	M
5,2,1		0·2256	
5,1,2	0·2311	0·2315	VW−
4,4,0	0·2386	0·2387	VW−
6,0,0	0·2685	0·2685	W
2,1,5	0·2718	0·2720	M+
6,1,1	0·2856	0·2853	W
5,3,2	0·2913	0·2911	M−
4,2,4	0·2993	0·2993	M
3,2,5	0·3317	0·3315	M+
6,2,2	0·3355	0·3357	W
6,3,1	0·3448	0·3448	M
1,1,6	0·3526	0·3526	M+
6,1,3	0·3601	0·3602	M
7,0,1	0·3751	0·3746	W
6,4,0	0·3876	0·3875	W
5,4,3	0·3898	0·3899	M
5,3,4	0·4026	0·4033	W
7,1,2	0·4098	0·4101	M
5,5,2			
6,3,3	0·4197	0·4197	W
6,2,4	0·4478	0·4480	M
5,2,5	0·4503	0·4504	M
7,3,2	0·4698	0·4696	M+
7,4,1	0·4934	0·4935	W
8,1,1		0·4935	
2,1,7	0·4963	0·4966	M+
5,1,6	0·5309	0·5311	S−
6,5,3	0·5383	0·5386	W+
8,3,1	0·5530	0·5530	W
3,2,7	0·5555	0·5560	W+
4,1,7,	0·5854	0·5858	W+
5,3,6	0·5909	0·5905	W+
8,0,4	0·6261	0·6264	W−
7,2,5	0·6288	0·6288	M
7,6,1	0·6422	0·6422	M−
9,2,1		0·6422	
9,1,2	0·6480	0·6479	M−
8,2,4	0·6557	0·6562	M
2,2,8	0·6592	0·6592	M+
5,2,7	0·6745	0·6750	M+
3,1,8		0·6740	
9,3,2	0·7074	0·7074	W
5,5,6	0·7094	0·7094	M
7,1,6		0·7094	
7,4,5	0·7178	0·7180	M+
8,1,5		0·7180	
9,4,1	0·7315	0·7313	W
8,4,4	0·7449	0·7454	W+
10,0,0		0·7444	
8,6,0		0·7444	
4,2,8	0·7479	0·7484	M
10,2,0	0·7738	0·7740	W
8,3,5	0·7778	0·7775	M
2,1,9	0·7953	0·7959	M−
10,3,1	0·8205	0·8205	M−
3,0,9	0·8263	0·8258	W
9,5,2		0·8263	
10,1,3	0·8361	0·8359	M−
10,4,0	0·8629	0·8631	W+
9,2,5	0·8676	0·8668	M−
7,6,5		0·8668	
6,0,8		0·8673	
9,6,1	0·8802	0·8799	W+
10,0,4	0·8942	0·8939	W+
6,2,8	0·8979	0·8972	M−

* S, strong; M, medium; W, weak.

powder patterns of several different preparations of thorium tetrabromide complied strictly with the space group conditions for $D_{4h}^{19} - I4_1/amd$. A typical complete list of observed and calculated values of $\sin^2\theta$ for α_1 reflections is provided in Table 6. From these results it is apparent that we have not observed the three reflections found by Scaife[5] ($\sin^2\theta$ values 0·1270, 0·1310, and 0·2172, respectively) which break the space group conditions. We do, on the other hand, observe a few reflections extra to those listed by Scaife, all of which obey the space group conditions. The only other line observed by Scaife and apparently not present on our films is that which he recorded at a $\sin^2\theta$ value 0·1790 which may have been the α_2 reflection associated with the strong 2, 0, 4 line at $\sin^2\theta = 0{\cdot}1777$.

In view of these results we have refined the structure of $ThBr_4$ in $D_{4h}^{19} - I4_1/amd$. The positional parameters and bond lengths are compared with those for the tetrachlorides and for $PaBr_4$ in Tables 3 and 5, respectively.

Attempts to reproduce the $\beta \longrightarrow \alpha$ transition, observed by Scaife[5] for $ThBr_4$, by heating samples at 320 or 420 °C and by allowing products to crystallise at 400 °C on sublimation have all proved unsuccessful. In addition, in contrast to the slow $\beta \longrightarrow \alpha$ transformation stated to occur at room temperature ($t_{\frac{1}{2}} = ca.$ 12 weeks) we have observed no evidence for such a phase change in samples stored for 70 weeks in a nitrogen atmosphere.

The structures of the isostructural tetrahalides comprise infinite arrays of edge-sharing polyhedra. The dodecahedra about the metal atoms in the various compounds, which have strict $\bar{4}2m$ symmetry, are defined by the parameters θ_A, θ_B, and M–A/M–B listed in Table 5. The angle of intersection of the two trapezoids, which are each planar, is 90° in each case. The values for the above parameters may be compared with those given by Hoard and Silverton[27] for the ' most favourable ' dodecahedron, $\theta_A = 35{\cdot}2°$, $\theta_B = 73{\cdot}5°$, and M–A/M–B = 1·03, these values being calculated for ' neon shell ' ligands.

Covalent Radii.—Using the shorter (M–B) metal–halogen bond lengths and values for Cl and Br of 0·99 and 1·14 Å, respectively,[28] the following covalent radii are obtained: Th^{4+} 1·71 (1·71 and 1·72 from $ThBr_4$ and $ThCl_4$, respectively), Pa^{4+} 1·64 (1·63 and 1·65 from $PaBr_4$ and $PaCl_4$, respectively), U^{4+} 1·61, and Np^{4+} 1·61 Å. The fact that those for U^{4+} and Np^{4+} are identical perhaps illustrates the deficiencies inherent in the ' powder ' method although one must also consider the e.s.d's associated with these bond lengths and the fact that the difference between U^{4+} and Np^{4+} is expected to be only *ca.* 0·02 Å.[8]

[2/1834 *Received, 3rd August*, 1972]

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[27] J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, 1963, **2**, 235.

[28] L. Pauling, ' The Nature of the Chemical Bond,' 3rd edn., Ithaca, New York, 1960.