

Crystal Chemical Studies of the 5f-Series of Elements. XIX. The Crystal Structure of the Higher Thorium Hydride, Th₄H₁₅

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Using X-ray diffraction data, it is conclusively shown that the chemical formula for the higher thorium hydride is Th₄H₁₅. The unit cube contains four stoichiometric molecules and the unit cell constant is $a = 9.11 \pm 0.02$ Å. The space group is $I\bar{4}3d$ and the thorium atoms are in the sixteen-fold positions with parameter $x = 0.208 \pm 0.003$.

It is shown that the sixty hydrogen atoms are in positions 12(a) and 48(e). The parameter values $x = 0.400$, $y = 0.230$, $z = 0.372$ are suggested for the latter sites.

A thorium atom is bonded to twelve hydrogen atoms, three in positions 12(a) and nine in 48(e). A hydrogen atom (H_I) in 12(a) is bonded to four thorium atoms, a hydrogen atom (H_{II}) in 48(e) to three thorium atoms. The interatomic distances are Th-H_I = 2.46 Å, Th-H_{II} = 2.29 Å.

The structure is discussed in some detail.

Introduction

Thorium metal has long (Winkler, 1891; Matignon & Delepine, 1901; Sieverts & Roell, 1926) been known to react with hydrogen. However, the first X-ray study of such a reaction product was not made until 1944 (Zachariasen, 1944). The investigated sample, supplied by the late Prof. E. D. Eastman of the University of California, was reported to have a composition of about ThH₃. The X-ray diffraction patterns showed the presence in the sample of small amounts of ThO₂. The main constituent was found to be a cubic phase with $a = 9.09 \pm 0.02$ kX., space group symmetry $I\bar{4}3d$. The unit cell was found to contain 16 thorium atoms in positions 16(c) with $x = 0.214 \pm 0.010$. At the time no attempt was made to assign positions to the hydrogen atoms.

Shortly thereafter a careful study of the thorium-hydrogen system was carried out by Nottorf, Wilson, Rundle, Newton & Powell (1945). Vapor pressure and X-ray measurements showed the presence of two hydrides. The lower hydride was found to be tetragonal and to have the ideal composition ThH₂. The crystal structure of this hydride was recently described by Rundle, Shull & Wollan (1952). The higher hydride proved to be identical with the 'ThH₃' earlier described by this writer. However, the work of Nottorf *et al.* showed conclusively that the higher hydride was richer in hydrogen than indicated by the tentative formula 'ThH₃'. A sample of ThH_{3.12} was by X-ray patterns revealed as consisting of a mixture of ThH₂ and the higher hydride. Further samples were prepared with a hydrogen:thorium ratio as high as 3.62. As a consequence of the presence of impurities (particularly dioxide) the observed ratio of 3.62 represented a lower limit. Nottorf *et al.* accordingly suggested that the ideal formula for the higher hydride is ThH_{3.75} or ThH₄. The former of the two suggested formulas

was considered the more likely one since the impurities were known to be small.

It is the purpose of the present paper to report the 1944 results, and present conclusions with respect to the ideal chemical formula and the hydrogen positions.

Structure determination

Table 1 gives X-ray diffraction data for the higher hydride of thorium, as obtained with the original sample supplied by Prof. E. D. Eastman. Apart from traces of the thorium dioxide diffraction pattern, all observations correspond to a cubic body-centered translation lattice with a unit cell constant of

$$a = 9.11 \pm 0.02 \text{ Å.}$$

All reflections (H_1, H_1, H_3) are absent if $2H_1 + H_3 = 4n + 2$, showing that the thorium atoms are arranged according to the space-group symmetry $I\bar{4}3d$. Additional absences are reflections (H_1, H_2, H_3) with H_1, H_2, H_3 all even and $\Sigma H_i = 4n + 2$. These are the absences characteristic of the positions 16(c) of the space group $I\bar{4}3d$ involving only one degree of freedom.

In the 1944 report the parameter for the thorium positions was given as $x = 0.215 \pm 0.010$. This determination can be improved upon. Since I_{88} is observed as definitely stronger than I_{86} (subscript referring to values of ΣH_i^2) it can be concluded that $x < 0.211$. Similarly the observation $I_{62} \gg I_{56}$ requires $x > 0.205$. Hence, one may set

$$x = 0.208 \pm 0.003.$$

Table 2 gives the calculated values of the quantity $\Sigma p|F/f|^2$, where p is the multiplicity factor, F the structure factor and f the scattering power. This quantity can be directly compared with the observed intensity for neighboring reflections, and Table 2 shows that there is excellent agreement.

Table 1. X-ray diffraction data for Th_4H_{15} ; radiation: $\text{Cu } K\alpha$

Intensity	$\sin^2 \theta$	$H_1^2 + H_2^2 + H_3^2$	
		Th_4H_{15}	ThO_2
w	0.0442	6	—
s+	0.0589	8	3
m	0.0732	10	4
w	0.1021	14	—
vw-	0.1158	16	—
vvw	0.1548	—	8
m-	0.1602	22	—
w-	0.1741	24	—
m+	0.1885	26	—
vw-	0.2115	—	11
m	0.2168	30	—
vvw	0.2311	32	12
w-	0.2461	34	—
w-	0.2736	38	—
w+	0.3021	42	16
vw-	0.3318	46	—
vw-	0.3448	48	—
m	0.3622	50	19
m	0.3879	54	20
w-	0.4029	56	—
vw-	0.4177	58	—
m	0.4458	62	—
vvw	0.4569	64	24
w+	0.4733	66	—
vw-	0.5019	70	—
vw+	0.5147	73	27
m	0.5300	74	—
m-	0.6155	86	—
m	0.6311	88	—

Table 2. Calculated and observed intensities

$H_1^2 + H_2^2 + H_3^2$	$\Sigma p F ^2$	Observed intensity
6	24	w
8	108	s+
10	72	m
14	48	w
16	24	vw-
22	96	m-
24	72	w-
26	216	m+
30	192	m
32	12	vvw*
34	72	w-
38	72	w-
40	0	Nil
42	144	w+
46	48	vw-
48	56	vw-
50	216	m
54	264	m
56	144	w-
58	72	vw-
62	240	m
64	24	vvw*
66	192	w+
70	48	vw+
72	72	w+
74	288	m
78	48	Trace
80	24	Nil
82	72	Trace
86	264	m-
88	288	m

* Coincidence with ThO_2 line.

It should be emphasized that the thorium atoms are uniquely found to be arranged according to space group symmetry $I\bar{4}3d$. Unless one makes highly artificial assumptions, this is consequently the symmetry of the entire structure.

Sites available for hydrogen atoms in the space group $I\bar{4}3d$ are: 12(a) and 12(b) without degree of freedom, 16(c) and 24(d) with one degree of freedom, and 48(e) with three degrees of freedom. According to the chemical data cited above, the hydrogen:thorium ratio is definitely much larger than 3, 4 being the upper limit. Thus the number of hydrogen atoms per unit cell, on the basis of chemical evidence, may be given as $48 \leq n_{\text{H}} \leq 64$. If the sites 16(c) are occupied by hydrogen atoms, the largest attainable Th-H distance is 1.97 Å (namely for $x = 0.333$). Since the metallic radius of thorium is 1.79 Å, a Th-H distance of 1.97 Å is impossibly small, and it is, hence, to be concluded that the sites 16(c) are not occupied. The number of hydrogen sites per unit cell must as a consequence be a multiple of twelve. The value of only n_{H} which satisfies both this requirement and the chemical data is $n_{\text{H}} = 60$. The chemical formula for the higher hydride is thus Th_4H_{15} with four stoichiometric molecules per unit cell. The calculated density is $\rho = 8.29 \text{ g.cm.}^{-3}$.

The sites 24(d) can be occupied by at most one set of hydrogen atoms if impossibly small H-H and Th-H distances are to be avoided. In order to have $n_{\text{H}} = 60$ the sites 48(e) must accordingly be occupied. But since the sites 48(e) are occupied, the sites 24(d) cannot be, then otherwise there would be an excessive number of hydrogen atoms per unit cell. If the sites 12(b) are occupied, the shortest distance to a thorium atom would be 2.79 Å, which must be regarded as an unreasonably large separation.

The arguments presented in some detail above have eliminated all but the following possibility: 12 H_{I} atoms in 12(a) and 48 H_{II} atoms in 48(e).

The thorium atoms form a network of nearly regular tetrahedra sharing corners, but having no common edges. The tetrahedral edges range from 3.87 Å to 4.10 Å. There are twelve such tetrahedra per unit cell and the centers of these tetrahedra correspond to the sites 12(a). It is not possible to choose parameter values for the sites 48(e) such that an H_{II} atom is placed equidistant from four metal atoms with a reasonable Th- H_{II} separation. However, one finds that the thorium atoms form nearly equilateral triangles (the edges being 3.87, 3.95 and 4.01 Å) which are not faces of the previously mentioned tetrahedra. There are 48 of these triangles per unit cell, the centers of the circumscribed circles corresponding to positions 48(e) with $x = 0.400$, $y = 0.230$, $z = 0.372$. On the basis of an exhaustive search, it can be stated that these positions are the only reasonable sites for the H_{II} atoms.

The structure deduced for Th_4H_{15} is briefly summarized as follows:

Space group: $I\bar{4}3d$; $n = 4$.

16Th in 16(c) with $x = 0.208 \pm 0.003$.

12H_I in 12(a).

48H_{II} in 48(e) with $x = 0.400$, $y = 0.230$, $z = 0.372$.

Although the hydrogen positions have been deduced by indirect means, the conclusions seem to leave no reasonable doubt as to their correctness. The validity of the statement can, of course be tested by means of neutron-diffraction data for Th₄H₁₅ or preferably for Th₄D₁₅.

As to the chemical formula Th₄H₁₅, it is proper to say that this is the ideal composition of the phase. The chemical data show, however, that the homogeneity range is narrow. The homogeneity range may extend downwards to a hydrogen:thorium ratio of 3.4; but it is equally possible that the composition is sharply defined as Th₄H₁₅.

Discussion of the structure

The shortest interatomic distances in the structure are:

Th-3Th = 3.87 Å	H _I -4Th = 2.46 Å
-2Th = 3.95	-4H _{II} = 2.38
-3Th = 4.10	H _{II} -3Th = 2.29
-3H _I = 2.46	-2H _{II} = 2.02
-9H _{II} = 2.29	

The thorium-thorium separation is so much larger than the 3.59 Å observed in thorium metal that the main cohesive energy must be attributed to the thorium-hydrogen bonds. Since each thorium atom is bonded to twelve hydrogen atoms it is reasonable to assign the normal metallic radius of 1.79 Å to thorium. This gives a radius of 0.67 Å for H_I and a radius of 0.50 Å for H_{II}. Since H_I is in tetrahedral, H_{II} in triangular configuration, one would expect the effective radius of H_I to be somewhat larger than that of H_{II}. However, the expected radius difference is 0.04 Å, as against the observed value of 0.17 Å. It is possible that the H_{II} atoms as a result of H_{II}-H_{II} interaction are displaced from the ideal sites assigned to them. Thus one finds Th-9H_{II} = 2.37 Å and H_{II}-H_{II} = 2.29 Å if the parameter values for the H_{II} atoms are modified to $x = 0.441$, $y = 0.237$, $z = 0.320$. However, in the absence of direct evidence such arguments may be regarded as idle speculation.

It is of interest for comparison purposes to cite the results obtained for ThH₂ by Rundle, Shull & Wollan. These workers found Th-8 = 2.41 Å, hydrogen being in tetrahedral configuration. Since the metallic radius of thorium is 1.74 Å for coordination number eight, the effective hydrogen radius comes out to be 0.67 Å, in exact agreement with the value found for H_I above.

In UH₃ Rundle (1951) found U-12H = 2.32 Å with hydrogen in tetrahedral configuration. If one adopts 0.67 Å as the hydrogen radius, the uranium radius is 1.65 Å. This value for the uranium radius implies that the effective valence of uranium in UH₃

is about 4.6 (see the table of metallic radii of 5f elements as function of the number of valence electrons recently published by this writer (Zachariasen, 1952)). The isostructural compound PaH₃ has $a = 6.648 \pm 0.005$ Å as compared with $a = 6.645$ Å for UH₃. Using Rundle's parameter values for hydrogen, one finds Pa-12H = 2.32. This gives a protactinium radius of 1.65 Å, implying an effective valence of 4.8.

An obvious question to ask, and a simple one to answer, is why there exists no phase ThH₃ isostructural with UH₃ and PaH₃. The UH₃ type of structure may be regarded as unstable unless the metal-metal separation is greater than twice the metallic radius. A simple consideration shows that as a consequence of this requirement

$$R_{\text{H}}/R_{\text{M}} \geq \frac{5}{8}\sqrt{5} - 1 = 0.398,$$

where R_{H} and R_{M} are the radii of hydrogen and metal. Using the experimental value of $R_{\text{H}} = 0.67$ Å for the tetrahedral radius of hydrogen when bonded to a 5f metal atom, it follows that $R_{\text{M}} \leq 1.68$ Å. The fictitious ThH₃ structure is accordingly not stable.

Attempts to interpret observed interatomic distances in hydrides on the basis of a single value for the radius of hydrogen have not been successful. Thus Pauling's value of 0.27 Å for the single-bond radius of hydrogen would give Th-H_I = 2.25 Å, and Th-H_{II} = 2.21 Å as against the observed values of 2.46 Å and 2.29 Å. The discrepancy is, in the opinion of this writer, to be attributed to the failure of the basic assumption regarding the additivity of radii, and should not be regarded as evidence for unusual valence states of the metal atoms. In this connection it should be remarked that the distance Th-H_I = 2.46 Å is accurate to 0.01 Å since there is no degree of freedom for the hydrogen atoms in the sites 12(a). The value given above of Th-H_{II} = 2.29 Å is a minimum value, and this distance may actually be considerably larger.

The structure of Th₄H₁₅ will be dealt with again in a forthcoming paper on subnormal valence compounds.

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