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Crystal Structure of Terbium Trichloride¹

BY J. D. FORRESTER, ALLAN ZALKIN, DAVID H. TEMPLETON, AND J. C. WALLMANN

X-ray diffraction data from poor single crystals of TbCl_3 show that the crystals are orthorhombic, space group Cmcm , with $a = 3.86 \pm 0.02$, $b = 11.71 \pm 0.03$, $c = 8.48 \pm 0.03$ Å. The structure is the same as that of PuBr_3 . Each Tb has Cl neighbors at the corners of a trigonal prism (2 at 2.70 Å, 4 at 2.79 Å). Two more Cl neighbors (at 2.95 Å) are adjacent to 2 of the 3 lateral faces of the prism.

Introduction

Bommer and Hohmann² observed from x-ray powder photographs that the trichlorides of the rare-earth elements have three different crystal structures. The trichlorides of the elements lighter than terbium, as well as many bromides and hydroxides, have the UCl_3 -type structure.³ The trichlorides of the elements heavier than terbium have the YCl_3 -type structure.⁴ Terbium trichloride and a second form of DyCl_3 have a third structure which was determined in the present investigation. After the structure was known

it became obvious that it was the same as the structure determined by Zachariasen⁵ for PuBr_3 . Many other bromides and iodides have this structure also:^{3,6} NdBr_3 , SmBr_3 , EuBr_3 , $\beta\text{-NpBr}_3$, AmBr_3 , LaI_3 , CeI_3 , PrI_3 , NdI_3 , UI_3 , NpI_3 , PuI_3 , and AmI_3 .

Zachariasen determined the PuBr_3 structure from 17 lines on a powder diffraction pattern. Our work with single crystals gives essentially the same structure with greater precision for the atomic coordinates.

Experimental

It is much more difficult to prepare single crystals of TbCl_3 than of the other lanthanide chlorides, but after some failures we prepared the samples by the following method. Terbium oxide ($\text{Tb}_{1.07}\text{O}_7$) was dissolved in hydrochloric acid and evaporated to dryness. The oxychloride formed was broken up and treated with HCl at 400° for two hours to produce the trichloride. This trichloride was dumped in vacuum into a sidearm tube, sublimed into the sidearm (of vitreous silica), and sealed off. The trichloride in the silica tube was passed through a crystal-growing furnace at a temperature slightly above the melting point,⁷ $588 \pm 15^\circ$.

To prevent formation of the oxychloride, the silica tube was broken open in a dry box, and samples of TbCl_3 were loaded into Lindemann glass capillaries (0.2 mm. diameter and 0.01 mm. wall thickness). A diffraction pattern of a powder sample was in agreement with the powder diagram reported by Bommer and Hohmann² and confirmed the absence of the oxychloride.

Only poor single crystals were obtained. They were long thin plates of a fibrous nature. The x-ray patterns showed the best specimens to have various domains rotated by up to 15 or 20° about the fiber axis (a axis) with respect to each other. This rotation resulted in a corresponding

elongation of the diffraction spots which diminished our sensitivity for observation of weak reflections and made difficult the estimation of intensities. With one specimen we obtained Weissenberg photographs (layers 0 and 1) with rotation about a and with Cu radiation ($\lambda = 1.5418 \text{ \AA}$). This crystal then suffered a mishap. Further photography of a poorer crystal with Mo radiation ($\lambda = 0.7107 \text{ \AA}$) and the same setting gave Weissenberg diagrams (layers 0 through 2) and a precession photograph ($h0l$ reflections).

Intensities were estimated (by visual comparison with a scale prepared by exposing one reflection for various times) for 69 independent reflections on the zero-layer Weissenberg pattern (Cu radiation). Of these, 13 were recorded as zero. Intensities were recorded on a qualitative scale for the three Weissenberg photographs taken with Mo radiation.

No correction was made for absorption. The linear absorption coefficients are estimated as 53 cm.^{-1} (for $\text{CuK}\alpha$) and 8 cm.^{-1} (for $\text{MoK}\alpha$). The accuracy of the data is limited by neglect of absorption and by the difficulty of intensity estimation.

Calculations were made with the IBM-7090 computer using the Zalkin Fourier program and our version of the Gantzel-Sparks-Trueblood least-squares program (both unpublished). The function minimized in least-squares was $\sum (|F_o| - |F_c|)^2 / \sum F_o^2$. We used atomic scattering factors for Cl^- from Ibers⁸ and for Tb^{+++} from Thomas and Umeda⁹ with a dispersion correction¹⁰ of -11.

Results

Unit Cell and Space Group.—The crystals are orthorhombic. Mean values of the cell dimensions calculated from Weissenberg photographs (for b and c) and rotation photographs (for a) are:

$$a = 3.86 \pm 0.02, \quad b = 11.71 \pm 0.03, \quad c = 8.48 \pm 0.03 \text{ \AA}.$$

The systematic absences ($hk\ell$ absent if $h+k$ is odd, $h0\ell$ absent if ℓ is odd) are characteristic of space groups $Cmc2_1$, $C2cm$, and $Cmcm$. We find a satisfactory structure in the centric group $Cmcm$ (D_{2h}^{17}).

The symmetry permits only 16, 8, or 4-fold positions. A comparison of the molecular volumes of some trichloride structures (Table I) shows that 4 molecules per unit cell is the only reasonable number. With $Z = 4$, the calculated density is 4.60 g./cc.

TABLE I

MOLECULAR VOLUMES OF SOME TRICHLORIDES

Crystal	Unit cell volume	Molecules per cell	Molecular volume
$NdCl_3$ (UCl_3 -type)	199.6 \AA^3	2	99.8 \AA^3
$DyCl_3$ (YCl_3 -type)	493.5	4	123.4
$TbCl_3$	383.3	4	95.8

Determination of the Structure.—A study of the photographs showed that the distribution of intensities is similar for $h = 0$ and $h = 2$. Thus the atoms must all lie in (or near) planes with $x = 0$ or $1/2$. This fact and considerations of atomic size permitted an unambiguous interpretation to be made of a Patterson projection calculated with the $Ok\ell$ data. Atoms are located in special positions, Tb and Cl(1) in 4(c) and Cl(2) in 8(f),

$$4(c): \pm(0, y, \frac{1}{4}) + (0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0),$$

$$8(f): \pm(0, y, z; 0, y, \frac{1}{2} - z) + (0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0).$$

Atomic parameters were refined by least squares using the $Ok\ell$ data. With isotropic temperature factors of the form $\exp(-B\sin^2\theta/\lambda^2)$ and a scale factor there were 8 independent parameters. The function $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ was reduced to 0.18 for the 69 observations. This discrepancy is believed to be no more than the errors in the data. The final values of the observed and

TABLE II
OBSERVED AND CALCULATED STRUCTURE FACTORS

k	F_o	F_c	k	F_o	F_c	k	F_o	F_c	k	F_o	F_c
$h, \ell = 0,0$			8	54	-40	$h, \ell = 0,5$			$h, \ell = 0,8$		
2	71	-98	10	31	23	2	12	9	0	34	36
4	32	26	12	64	-57	4	19	-20	2	31	-35
6	88	-67	14	37	46	6	21	-33	4	60	65
8	104	73	$h, \ell = 0,3$			8	38	50	6	65	-76
10	88	-74	2	77	78	10	0	3	8	20	18
12	62	54	4	15	-13	12	0	-6	10	0	-4
14	0	-1	6	0	-12	$h, \ell = 0,6$			$h, \ell = 0,9$		
$h, \ell = 0,1$			8	0	-4	0	112	-110	2	44	-35
2	9	-8	10	15	15	2	61	61	4	0	4
4	12	-21	12	51	-47	4	33	-25	6	16	6
6	31	-29	14	36	34	6	43	49	8	0	5
8	66	46	$h, \ell = 0,4$			8	43	-54	$h, \ell = 0,10$		
10	0	-2	0	108	94	10	59	57	0	55	-63
12	0	7	2	66	-65	12	44	-45	2	47	36
14	30	-28	4	63	67	$h, \ell = 0,7$			4	16	-23
$h, \ell = 0,2$			6	71	-84	2	21	20	6	24	42
0	100	-86	8	42	43	4	0	4			
2	70	68	10	30	-34	6	0	8			
4	83	-98	12	52	52	8	20	-23			
6	102	108	14	14	-31	10	0	4			

calculated structure factors are listed in Table II and the final parameters in Table III. Because of the neglect of absorption, the thermal parameters are expected to be lower than the true values, as that of Cl(2) obviously is.

TABLE III

ATOMIC PARAMETERS AND STANDARD DEVIATIONS

Atom	\underline{x}	\underline{y}	\underline{z}	$\underline{B}, \text{\AA}^2$
Tb	0	$0.244 \pm .001$	$1/4$	0.4
Cl(1)	0	$.583 \pm .003$	$1/4$	$.4$
Cl(2)	0	$.145 \pm .002$	$0.569 \pm .002$	$.02$

As a check of the correctness of the structure we calculated intensities for the Weissenberg patterns which were taken with Mo radiation.¹¹ All were in satisfactory agreement with the observed intensities. A portion of the data for $h = 1$ are listed in Table IV.¹²

Interatomic distances are listed in Tables V and VI. Each Tb has 8 nearest Cl neighbors at an average distance of 2.81 Å. Each Cl has either 11 or 12 Cl neighbors closer than 4 Å.

DISCUSSION

The structure is closely similar to that determined for PuBr₃ by Zachariasen.⁵ The atomic coordinates, after interchange of \underline{a} and \underline{b} and a shift of origin, are compared with the PuBr₃ coordinates in Table VII. In this setting, the space group symbol is Comm. The agreement of these independent determinations is gratifying.

The structure can be described as consisting of triangular prisms with Tb at the centers and Cl at the corners. These prisms share triangular faces

TABLE IV
OBSERVED AND CALCULATED INTENSITIES

k	I_o	I_c	k	I_o	I_c	k	I_o	I_c
$h, \ell = 1, 0$			$h, \ell = 1, 2$			$h, \ell = 1, 4$		
5	vw ^a	3	3	vw	2	1	vw	1
7	vw	4	5	vw	5	3	0	0
9	0	0	7	vw	2	5	vw	2
11	w	6	9	vw	1	7	0	0
13	vw	1	11	0	0	9	0	0
$h, \ell = 1, 1$			$h, \ell = 1, 3$			$h, \ell = 1, 5$		
3	vs	100	1	vs	59	1	m	4
5	s	28	3	s	28	3	s	24
7	m	9	5	w	2	5	m	14
9	m	7	7	w	6	7	w	4
11	vw	2	9	m	18	9	vw	2
13	vw	2	11	w	4	11	0	0

^av = very, w = weak, m = medium, s = strong.

TABLE V
NEIGHBORS OF Tb ATOM

Neighbor	Number	Distance, Å
Cl(1)	2	2.70 ± .02
Cl(2)	4	2.79 ± .02
Cl(2)	2	2.95 ± .02
Cl(1)	1	3.97 ± .03

TABLE VI
Cl—Cl DISTANCES

Atom	Neighbor	Number	Distance, Å
Cl(1)	Cl(2)	4	3.40 ± .02
	Cl(2)	2	3.53 ± .04
	Cl(2)	4	3.63 ± .03
	Cl(1)	2	3.86 ± .02
Cl(2)	Cl(2)	1	3.07 ± .04
	Cl(2)	2	3.35 ± .03
	Cl(1)	2	3.40 ± .02
	Cl(1)	1	3.53 ± .04
	Cl(2)	1	3.58 ± .04
	Cl(1)	2	3.63 ± .03
	Cl(2)	2	3.86 ± .02

TABLE VII

ATOMIC COORDINATES OF $TbCl_3$ AND $PuBr_3$ ^a

Parameter	$TbCl_3$	$PuBr_3$ ^b
\underline{x} (Tb or Pu)	0.256	0.25
\underline{x} (Cl(1) or Br(1))	-.083	-.07
\underline{x} (Cl(2) or Br(2))	.355	.36
\underline{z} (Cl(2) or Br(2))	-.069	-.05

^aAlternate setting, space group Ccmm. ^bZachariasen, Ref. 5.

to form columns parallel with a. The UCl_3 -type structure can be described in terms of similar triangular columns, but the two structures differ in the way the columns are packed together (Fig. 1). In the UCl_3 -type structure there are three neighboring columns arranged so that each U atom has three Cl neighbors adjacent to the lateral faces of the prism. In $TbCl_3$ there are four neighboring columns, but only two of them provide a close Cl neighbor to the Tb atom. A ninth neighbor is in the direction of the third lateral face, but it is more than 1 Å further away than the others.

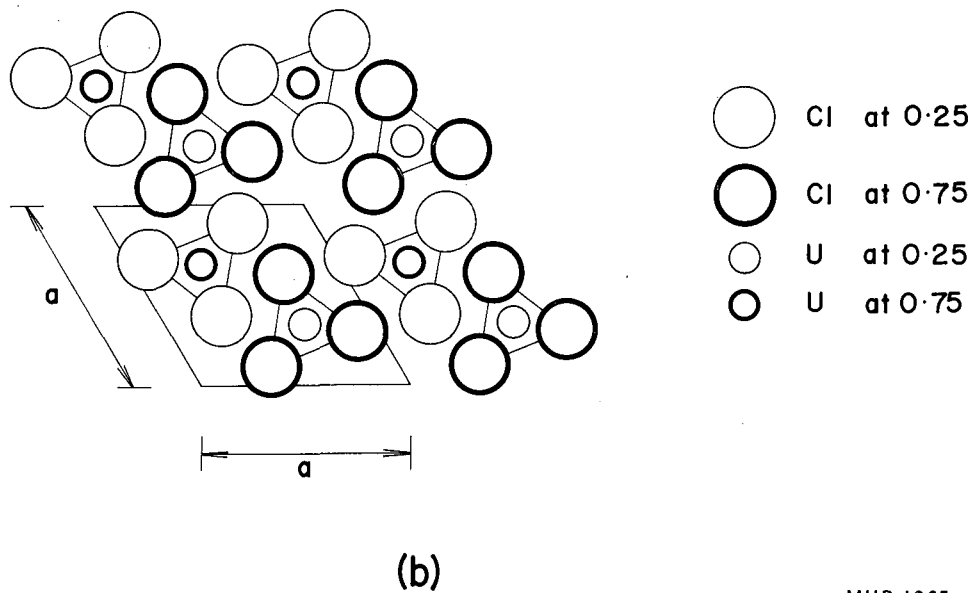
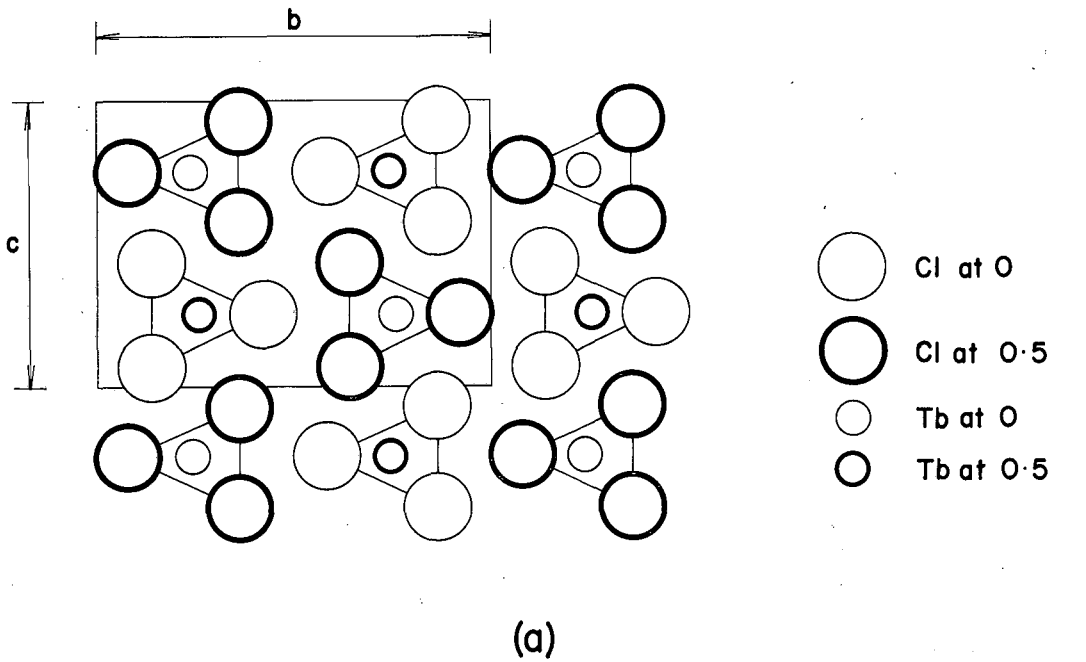
This arrangement of 8 nearest neighbors is similar to the environment of Y in YF_3 , though in YF_3 the 9th neighbor is relatively much closer.¹³

The direction of the triangular columns corresponds with the direction of the fibers into which the crystal breaks. From the structure one would predict cleavage on 010, since no strong bonds cross that plane. Apparently the forces holding one column to another in the c direction are also weaker than the forces within the column.

From the numerous bromides and iodides which have this structure, it is surprising that its occurrence in the rare-earth chloride series is limited to two examples. If it were stable over as wide a range of radius ratio as it is for the bromides and iodides, two or three other rare-earth chlorides would have this structure. Obviously some more delicate factor than radius ratio is involved in determining the structures of these substances.

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- (11) These intensities are based on a Tb form factor which contains the dispersion correction for Cu radiation, but this error is not serious for this qualitative comparison.
- (12) The complete data may be obtained from the authors on request.
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Fig. 1. Comparison of orthorhombic $TbCl_3$ structure and hexagonal UCl_3 structure. (a) Projection of $TbCl_3$ down \underline{a} axis. (b) Projection of UCl_3 down \underline{c} axis.

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