Discussion

The limits of stability of the rare earth polysulfide phase appear to be dependent on the sulfur vapor pressure and the atomic number (or ionic size) of the rare earth as well as the temperature. The stability zone becomes smaller with increasing atomic number. Whereas La, Pr, Gd, and Tb may be produced at 200 to 300° above their nominal decomposition temperature under vacuum by maintaining a small sulfur pressure in excess of the stoichiometry requirement, these same conditions become borderline for the preparation of Y and Ho polysulfides. The temperature has to be lowered to guarantee production of the latter. For Er, even the lower temperature and higher sulfur pressure conditions are borderline, and become inadequate to produce a polysulfide of Tm. A similar trend is revealed at very low sulfur pressures. The polysulfides of La and Pr require temperatures of the order of 100° higher than do those of Sm, Gd, or Tb to be reduced to the sesquisulfide stoichiometry.

The rare earth polysulfide compounds can be considered to exist as a single phase over a wide region of sulfur to metal atom ratios. The X-ray diffraction data reveal the polysulfide crystal structure for ratios as low as 1.7/1. The allowable sulfur content variation is especially large for the lighter rare earths. Here one may postulate that the larger size of the cations allows more space in the lattice for the incorporation of sulfur.

The failure of the previous investigators to observe the relatively large phase region may be explained by assuming that the condition of highest sulfur content is the most stable for the lighter rare earths. Their failure to produce the polysulfide of Er could have been due merely to the use of too low a sulfur pressure.

As a polysulfide, yttrium can be considered to have an ionic radius falling between Tb and Dy. Iandelli[5] places Y in the same position in the series of monosulfides, and Picon, *et al.*,[6] find it very close to Dy as a δ phase sesquisulfide.

Acknowledgments.—We wish to thank Dr. T. A. Henrie, of the Reno Station, United States Bureau of Mines, for the analysis of some of our samples. We also wish to thank Mr. John Robinson of this laboratory for preparing the X-ray diffraction spectra.

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Crystal Structure of Terbium Trichloride[1]

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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 (two at 2.70 Å., four at 2.79 Å.). Two more Cl neighbors (at 2.95 Å.) are adjacent to two of the three lateral faces of the prism.

Introduction

Bommer and Hohmann[2] 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 Zachariasen[5] for $PuBr_3$. Many other bromides and iodides have this structure also[3,6]: $NdBr_3$, $SmBr_3$, $EuBr_3$, β-$NpBr_3$, $AmBr_3$, 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 (Tb_4O_7) was dissolved in hydrochloric acid and evaporated to dryness. The oxychloride formed was broken up and treated with HCl at 400° for 2 hr. to produce the trichloride. This trichloride was dumped under vacuum into a side-arm tube, sublimed into the side arm (of vitreous silica), and sealed off. The trichloride in the silica tube was passed through a crystal-growing

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(1) Work done under the auspices of the U. S. Atomic Energy Commission.

(2) H. Bommer and E. Hohmann, *Z. anorg. allgem. Chem.*, **248**, 373 (1941).

(3) W. H. Zachariasen, *Acta Cryst.*, **1**, 265 (1948).

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(5) W. H. Zachariasen, *Nat. Nucl. Energy Ser., Div. IV*, **14B**, 1473 (1949).

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TABLE I
MOLECULAR VOLUMES OF SOME TRICHLORIDES

Crystal	Unit cell vol., Å.^{3}	Molecules per cell	Molecular vol., Å.^{3}
$NdCl_3$ (UCl_3-type)	199.6	2	99.8
$DyCl_3$ (YCl_3-type)	493.5	4	123.4
$TbCl_3$	383.3	4	95.8

furnace at a temperature slightly above the melting point,[7] 588 ± 15°.

To prevent formation of the oxychloride, the silica tube was broken open in a drybox, 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 Hohmann[2] 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 ($\lambda = 1.5418$ Å.). This crystal then suffered a mishap. Further photography of a poorer crystal with Mo radiation ($\lambda = 0.7107$ Å.) and the same setting gave Weissenberg diagrams (layers 0 through 2) and precession photographs (*h*0*l* and *h*1*l* 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 Cu Kα) and 8 cm.$^{-1}$ (for Mo Kα). 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 $\Sigma\,(|F_o| - |F_c|)^2/\Sigma F_o^2$. We used atomic scattering factors for Cl^- from Ibers[8] and for Tb^{+3} from Thomas and Umeda[9] with a dispersion correction[10] 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: $a = 3.86 \pm 0.02$, $b = 11.71 \pm 0.03$, $c = 8.48 \pm 0.03$ Å. The systematic absences (*hkl* absent if $h + k$ is odd, *h*0*l* 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.

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 0*kl* data. Atoms are located in special positions, Tb and Cl(1) in 4(c) and Cl(2) in 8(f): 4(c): $\pm(0, y, {}^1/_4) + (0, 0, 0;\ {}^1/_2, {}^1/_2, 0)$; 8(f): $\pm(0, y, z;\ 0, y, {}^1/_2 - z) + (0, 0, 0;\ {}^1/_2, {}^1/_2, 0)$. Atomic parameters were refined by least squares using the 0*kl* data. With isotropic temperature factors of the form $\exp(-B \sin^2 \theta/\lambda^2)$ and a scale factor there were eight independent parameters. The function $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ 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 calculated structure factors are listed in Table II and the final parameters in Table III. The thermal parameters, which are equal within the statistical precision, are expected to be lower than the true values because of neglect of absorption. A refinement with omission of 020 (the reflection at lowest angle) and of 029 (which is suspected of error in intensity estimation) gave thermal parameters 0.6, 0.9, and 0.4 Å.,^{2} respectively, but changed no coordinate as much as one standard deviation.

The standard deviations listed in Table III are those estimated by the method of least squares, assuming that the discrepancies represent random errors. We tried to estimate the accuracy of the coordinates by comparison of the photographs with lists of structure factors calculated for slightly different atomic locations. On this basis, the listed standard deviations seem to be optimistic by a factor of two or three. The chief uncertainty is the possibility of incorrect intensities because of the difficulty of resolving some of the elongated spots on the films.

The calculations are based on the assumption that the space group is Cmcm. The evidence for this assumption involves reflections which were not included in the least-squares calculations. If any atom is displaced from $x = 0$, the symmetry of mirror planes perpendicular to *a* is destroyed. Such displacements also destroy the equivalence of structure factors for reflections *hkl* and $(h + 2)kl$. From the precession photographs we have some reflections for *h* as large as 5, but can find no evidence for absence of the mirror plane. We estimate that displacements of as much as 0.25 Å. are unlikely. By a consideration of the sharpness of the peaks in the Patterson projection, we estimate a similar limit for deviations from the mirror symmetry perpendicular to the *c*-axis.

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.

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(8) J. A. Ibers, "International Tables for X-ray Crystallography," Kynoch Press, Birmingham, England, 1962, Vol. III, p. 202.

(9) L. H. Thomas and K. Umeda, *J. Chem. Phys.*, **26**, 293 (1957).

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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.

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS

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

TABLE III

ATOMIC PARAMETERS AND STANDARD DEVIATIONS[a]

Atom	x	y	z	B, Å.^{2}
Tb	0	0.244 ± 0.001	$^1/_4$	0.4 ± 0.2
Cl(1)	0	0.583 ± 0.003	$^1/_4$	0.4 ± 0.6
Cl(2)	0	0.145 ± 0.002	0.569 ± 0.002	0.0 ± 0.4

[a] Standard deviations are estimated by least squares and include no allowance for the systematic errors discussed in the text.

TABLE IV

OBSERVED AND CALCULATED INTENSITIES

k	I_o	I_c	k	I_o	I_c	k	I_o	I_c
	$h,l = 1,0$			$h,l = 1,2$			$h,l = 1,4$	
5	vw[a]	3	3	vvw	2	1	vvw	1
7	vw	4	5	vw	5	3	0	0
9	0	0	7	vvw	2	5	vw	2
11	w	6	9	vvw	1	7	0	0
13	vw	1	11	0	0	9	0	0
	$h,l = 1,1$			$h,l = 1,3$			$h,l = 1,5$	
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

[a] v, very; w, weak; m, medium; s, strong.

A portion of the data for $h = 1$ is 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. The only unreasonable distance is Cl(2)–Cl(2) = 3.07 Å., which is a function only of z for Cl(2). We can make this distance 3.22 Å. with $z = 0.560$ without much effect on other distances or on the agreement with the data, but 3.31 Å. ($z = 0.555$) seems to be in significant conflict with the data. Distances as short as 3.2 Å. are not uncommon for chlorine atoms shared by two cations.

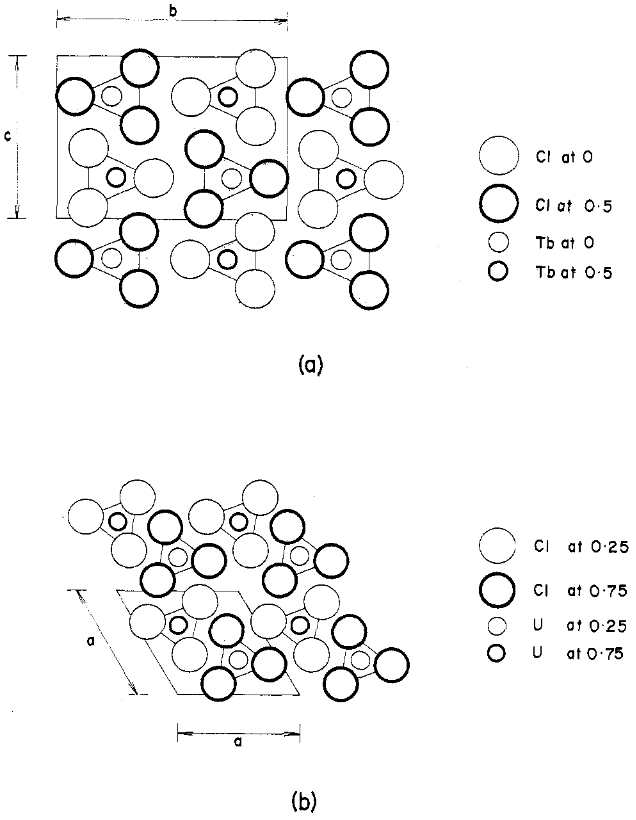

Fig. 1.—Comparison of orthorhombic $TbCl_3$ structure and hexagonal UCl_3 structure: (a) projection of $TbCl_3$ down a axis; (b) projection of UCl_3 down c axis.

TABLE V

NEIGHBORS OF Tb ATOM

Neighbor	Number	Distance, Å.
Cl(1)	2	2.70 ± 0.02[a]
Cl(2)	4	2.79 ± 0.02
Cl(2)	2	2.95 ± 0.02
Cl(1)	1	3.97 ± 0.03

[a] Standard deviations include no allowance for systematic errors.

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(12) The complete data may be obtained from the authors on request.

Table VI
Cl–Cl Distances

Atom	Neighbor	Number	Distance, Å.
Cl(1)	Cl(2)	4	3.40 ± 0.02[a]
	Cl(2)	2	3.53 ± 0.04
	Cl(2)	4	3.63 ± 0.03
	Cl(1)	2	3.86 ± 0.02
Cl(2)	Cl(2)	1	3.07 ± 0.04
	Cl(2)	2	3.35 ± 0.03
	Cl(1)	2	3.40 ± 0.02
	Cl(1)	1	3.53 ± 0.04
	Cl(2)	1	3.58 ± 0.04
	Cl(1)	2	3.63 ± 0.03
	Cl(2)	2	3.86 ± 0.02

[a] Standard deviations include no allowance for systematic errors.

Discussion

The structure is closely similar to that determined for $PuBr_3$ by Zachariasen.[5] The atomic coordinates, after interchange of *a* and *b* and a shift of origin, are compared with the $PuBr_3$ coordinates in Table VII. In this setting, the space group symbol is Ccmm. 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 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.

Table VII
Atomic Coordinates of $TbCl_3$ and $PuBr_3$[a]

Parameter	$TbCl_3$	$PbBr_3$[b]
x (Tb or Pu)	0.256	0.25
x (Cl(1) or Br(1))	−0.083	−0.07
x (Cl(2) or Br(2))	0.355	0.36
z (Cl(2) or Br(2))	−0.069	−0.05

[a] Alternate setting, space group Ccmm. [b] Zachariasen, ref. 5.

This arrangement of eight nearest neighbors is similar to the environment of Y in YF_3, though in YF_3 the ninth 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 occurence 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.

(13) A. Zalkin and D. H. Templeton, *J. Am. Chem. Soc.*, **75**, 2453 (1953).