tion of aminochlorophosphonitriles such as compound II, it is evident that the basic $-N(CH_3)_2$ substituents are important in directing arylation. The free electron pair on the nitrogen atom probably is the position to which the Lewis acid, $AlCl_3$, is attracted most strongly. Although the PN ring nitrogens also have electron pairs, these are involved in the π-bonding system of the ring[24] and are less influential in attracting the $AlCl_3$.

The arylations require stoichiometric rather than catalytic amounts of $AlCl_3$. This is an indication that II has the properties of an acyl halide where the $AlCl_3$ is believed to complex first with the oxygen atom rather than the halogen with subsequent rearrangement to give the carbonium ion and $AlCl_4^-$.[25] Although we have made no study of mechanism, we believe that a comparable situation exists in the arylation of II using $AlCl_3$, *i.e.*, the $AlCl_3$ complex forms first with the nitrogen atom of the $-N(CH_3)_2$ group and rearrangement gives the phosphonium ion and $AlCl_4^-$ so that the chlorine replaced by the aryl group is that attached to the same phosphorus carrying the $-N(CH_3)_2$.

Although it would be interesting and important to find that nucleophilic substitution of chlorine in $(NPCl_2)_3$ follows specific paths, and the work of Becke-Goehring and of Shaw indicates some general pattern with respect to aminolysis reactions, it is necessary to employ caution in the interpretation of experimental findings.

The work described above does substantiate that of Becke-Goehring and Shaw in confirming that aminolysis of $(NPCl_2)_3$ with strong nucleophiles such as $(CH_3)_2NH$ or NH_3 does not occur geminally. However, we do not find a specific direction with respect to preferential formation of a *cis* or *trans* isomer. Indeed, our results indicate that $P_3N_3Cl_4[N(CH_3)_2]_2$ is formed in a *cis* configuration, while $P_3N_3Cl_4(NH_2)_2$ is *trans*. Further, $P_3N_3Cl_3[N(CH_3)_2]_3$ has been obtained both as *cis* and *trans* depending on experimental conditions, and compounds IX and IXa, $P_3N_3Cl_2(C_6H_5)_2[N(CH_3)_2]_2$, not only are *trans* and *cis*, respectively, but came from the same reaction.

Finally, it should be noted that in most syntheses, the yields were considerably below 100%. It may be that the compounds obtained were not necessarily the only ones formed. Rather they may be those most readily isolated and purified. For this reason generalizations concerning positions of attack on the phosphonitrile ring should be approached with prudence and caution.

Acknowledgment.—This work was carried out for the Armstrong Cork Company, Lancaster, Pennsylvania, to whom we are indebted for long-term financial support.

[24] D. Craig, *Chem. Ind.* (London), 3 (1958); D. Craig and N. L. Paddock, *Nature*, **181**, 1052 (1958).

[25] M. H. Silke, *Trans. Faraday Soc.*, **46**, 761 (1950); G. Baddeley, *Quart. Rev.* (London), **8**, 368 (1954).

CONTRIBUTION FROM THE RESEARCH LABORATORIES,
LOCKHEED MISSILES AND SPACE COMPANY, PALO ALTO, CALIFORNIA

Rare Earth Compounds. I. Rare Earth Polysulfides[1a,1b]

BY S. A. RING AND MELVIN TECOTZKY[1c]

Received June 29, 1963

The polysulfides of Tb, Ho, and Er have been prepared for the first time. New information has been obtained for a number of rare earth polysulfides. A larger phase region with a more complex crystal structure has been shown to exist. Sulfur to metal atom ratios of 1.7 to 2.0 were found for the lightest rare earths and 1.7 to 1.8 for the heavier rare earths. As the atomic number of the metal component is increased, higher sulfur pressures at lower allowed temperatures are required to create the polysulfide phase.

Introduction

Flahaut, Picon, and co-workers have studied many of the rare earth polysulfides. They first prepared the sesquisulfides by reaction of the oxides with H_2S and then heated the sesquisulfides with excess sulfur to 600° to produce the polysulfides. In a summary article[2] the authors concluded that "polysulfides" are obtained, with the stoichiometry Ln_2S_4 and cubic crystal structure for the elements La through Nd and a stoichiometry close to $Ln_2S_{3.8}$, with a slight tetragonal distortion of the unit cell, for Eu, Gd, Dy, and Y. Sm exhibited both crystalline modifications. They could not prepare the polysulfide of Er (and do not report having worked on Ho or Tb). When syntheses of the polysulfides from the lighter rare earth sesquisulfides were performed employing insufficient sulfur, only starting product and cubic Ln_2S_4 forms were observed. These results led the investigators to conclude that the allowable range in sulfur content for the rare earth polysulfides must be very small.

In this work we continue to use the term "rare earth polysulfide" to describe this class of compounds

[1] (a) This work was done under the Lockheed Independent Research Program; (b) this work was presented in part before the Division of Inorganic Chemistry, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., Spring, 1963; (c) correspondence concerning this paper should be addressed to Melvin Tecotzky.

[2] J. Flahaut, M. Guittard, and M. Patrie, *Bull. Soc. Chim. France*, **26**, 1917 (1959).

TABLE I

PREPARATIVE CONDITIONS AND STOICHIOMETRY RANGES FOR RARE EARTH SULFIDES

Metal	Preparative procedure	Phase produced	Sulfur/metal (atom ratio)
La	103 hr. at 850°^{a}	Polysulfide	1.78 to 1.88
	Reheated with sulfur	Polysulfide	1.94 ± 0.03
	Vacuum heated at 560°	Polysulfide	1.75 to 1.80
Pr	16 hr. at 785°	Polysulfide	1.98 ± 0.03
	Vacuum heated at 560°	Polysulfide	1.70 ± 0.03
Sm	24 hr. at 825°	Polysulfide	Unknown
	Reheated with sulfur	Polysulfide	1.94 ± 0.03
Gd	30 hr. at 835°	Polysulfide	1.7 to 1.8
Tb	111 hr. at 850°	Polysulfide	1.74 to 1.80
Y	142 hr. at 820°	Variable mixture	. . .
	Reheated with sulfur	Polysulfide	1.72 to 1.78
Ho	140 hr. at 825°	Variable mixture	. . .
	Reheated with sulfur	Polysulfide	1.67 to 1.72
Er	134 hr. at 840°	Sesquisulfide	Unknown
	Reheated with sulfur	Variable mixture	1.7 (approx.)
Tm	170 hr. at 835°^{b}	Sesquisulfide	1.47 ± 0.03
	Reheated with sulfur^c	Sesquisulfide	Unknown

[a] Some unreacted metal always remains. [b] Sulfur:thulium preparative atom rato was 4.5. [c] Sulfur vapor density was 0.029 g./ml.

TABLE II

X-RAY DATA FOR LANTHANUM POLYSULFIDES[a]

Tetragonal $LaS_{1.75-1.80}$				Orthorhombic $LaS_{1.94}$			
hkl	P/P_0	Obsd. *d*	Calcd. *d*	*hkl*	P/P_0	Obsd. *d*	Calcd. *d*
200	40	4.07	4.08	020	40	4.15	4.14
113	10	4.00	4.00	200	25	4.06	4.09
210	30	3.65	3.65	113	vw	4.00	4.01
203	25	3.29	3.29	120	10	3.70	3.70
204	65	2.90	2.92	023	30	3.31	3.32
222	55	2.73	2.73	024	85	2.93	2.93
223	20	2.56	2.56	222	70	2.75	2.75
224	100	2.37	2.37	223	20	2.58	2.58
320	25	2.26	2.26	224	100	2.38	2.38
400	70	2.034	2.038	230	5	2.29	2.29
324	15	1.986	1.989	040	20	2.07	2.07
402			1.980	400	70	2.04	2.04
420	35	1.825	1.824	141	15	1.988	1.992
422	15	1.779	1.782	402			1.980
500	15	1.633	1.631	240	15	1.850	1.848
520	20	1.514	1.515	420	15	1.833	1.833
427	25	1.446	1.447	243	5	1.751	1.752
524	10	1.424	1.423	423	10	1.738	1.739
530	10	1.399	1.399	209	5	1.679	1.678
409	15	1.365	1.370	050	5	1.652	1.657
444			1.362	340			1.653
620	15	1.290	1.289	500	10	1.638	1.635
42, 10	15	1.230	1.229	430			1.642
550	15	1.155	1.153				
710			1.153				
702			1.155				

[a] Cell parameters (Å.) tetragonal $LaS_{1.75-1.80}$ $a = 8.16$, $c = 16.65$; orthorhombic $LaS_{1.94}$ $a = 8.17$, $b = 8.29$, $c = 16.58$.

containing sulfur in substantial excess of the +3 stoichiometry requirements.

Experimental

Bar-shaped pieces of rare earth metal, weighing a few tenths to two grams each, were cut from ingots of Lindsay nominal 99.9% pure metal using mineral oil as a protective coating and coolant. After rinsing in benzene and drying in a stream of nitrogen, the metal bars were placed in quartz containers with nominal 99.99% "flowers of sulfur" using a three-to-one atom ratio of sulfur to metal. The containers were then evacuated to 1 to 5 $\times 10^{-3}$ torr, sealed by fusion, and heated for the lengths of time shown in Table I.

After cooling, the bulk of the sulfur was removed by dissolution in carbon disulfide. The product was then ground to a powder in a mortar, soaked overnight in CS_2, then washed with liberal quantities of CS_2, and finally pumped dry under vacuum. (A sample of PrS_2 washed in the manner described gave no further weight loss on extraction with CS_2 for 3 days in a Soxhlet extractor.)

For those cases when the product was reheated with additional sulfur, the finely ground powders were sealed into evacuated quartz containers with an amount of sulfur calculated to give a vapor density of about 0.02 g./ml. and heated for 130 to 150 hr. at approximately 600°.

The products were chemically analyzed using a Leco induction apparatus for the sulfur and an EDTA titration method for the rare earths.[3]

The X-ray diffraction data were obtained with a diffractometer on powder samples using copper Kα radiation and a nickel filter.

Results

Typical reaction times and temperatures for complete conversion to a sulfide phase are listed in Table I. The lighter rare earth elements, with the exception of lanthanum, required milder conditions than the heavier rare earths for complete conversion to sulfide. Reaction conditions cannot be considered exactly reproducible because of variations in the thickness of the metal bars used.

On initial synthesis, only the polysulfides were produced for La through Tb, variable mixtures of the polysulfides and sesquisulfides for Ho and Y, and only the sesquisulfides for Er and Tm. By treating the as-produced sulfides of Ho and Y with additional sulfur, single phase polysulfide products were obtained free of the X-ray diffraction lines of the sesquisulfides. The polysulfide of Er was produced similarly, but the product usually still contained some of the sesquisulfide. A Tm polysulfide could not be produced even when a sulfur vapor density of 0.029 g./ml. was employed.

In the finely ground state, the polysulfides of Pr, Gd, Tb, Ho, and Er are all colored dark brown with a variable red tinge. The La polysulfides are a light, yellow-brown and the Sm compound a dark violet.

The variations in stoichiometry for the various sulfides were caused by uncertainties in the chemical analysis and possible nonhomogeneity within a sample as well as the variation in average sulfur to metal content among different preparations of the same compound. Confidence limits for compounds considered to have a single sulfur to metal ratio are indicated.

The X-ray spectra of the La polysulfides all contained too many lines to be indexed as simple cubic even at the highest sulfur to La ratio achieved. The position (*d*-value) and number of the diffraction lines varied

---

[3] G. Schwarzenbach, "Complexometric Titrations," Methuen and Company, Ltd., London, 1957, p. 73.

TABLE III

X-RAY POWDER DATA ON RARE EARTH POLYSULFIDES[a]

hkl	Cubic $PrS_{1.98}$			Tetragonal $PrS_{1.7}$			Tetragonal $GdS_{1.7-1.8}$			Tetragonal $TbS_{1.74-1.80}$			Tetragonal $HoS_{1.67-1.72}$			Tetragonal $YS_{1.72-1.78}$		
	P/P_0	Obs. d	Calc. d	P/P_0	Obs. d	Calc. d	P/P_0	Obs. d	Calc. d	P/P_0	Obs. d	Calc. d	P/P_0	Obs. d	Calc. d	P/P_0	Obs. d	Calc. d
002	40	4.03	4.03	30	4.01	4.04	35	3.96	3.96	45	3.965	3.952	50	3.92	3.92	W	3.97	3.95
201	70	3.60	3.61	100	3.57	3.58	100	3.50	3.50	100	3.488	3.480	100	3.44	3.44	S	3.50	3.47
220	65	2.85	2.85	60	2.82	2.82	60	2.75	2.75	70	2.743	2.741	80	2.71	2.71	S	2.74	2.73
003	65	2.68	2.69	–	–	–	25	2.64	2.64	25	2.638	2.636	25	2.62	2.61	M	2.64	2.64
221				40	2.66	2.66	25	2.60	2.60	20	2.595	2.590	20	2.56	2.56	M	2.59	2.58
310	–	–	–	–	–	–	–	–	–	5	2.450	2.452	–	–	–	W	2.45	2.44
222	100	2.32	2.33	85	2.31	2.31	85	2.26	2.26	95	2.258	2.253	90	2.23	2.23	S	2.25	2.25
203	55	2.23	2.24	50	2.23	2.23	60	2.18	2.19	70	2.178	2.178	65	2.16	2.16	S	2.18	2.18
004	50	2.01	2.01	–	–	–	–	–	–	5	1.974	1.976	20	1.958	1.960	W	1.975	1.976
400				50	1.998	1.994	50	1.95	1.95	40	1.938	1.938	35	1.911	1.916	M	1.933	1.932
223	20	1.955	1.954	50	1.945	1.946	–	–	–	10	1.901	1.900	10	1.883	1.882	W	1.896	1.896
204	25	1.801	1.803	–	–	–	–	–	–	5	1.757	1.760	10	1.747	1.746	–	–	–
402				25	1.789	1.790	20	1.75	1.75	15	1.740	1.740	25	1.717	1.722	–	–	–
420				–	–	–	–	–	–	–	–	–	–	–	–	W	1.733	1.728
421	30	1.761	1.759	45	1.744	1.744	45	1.70	1.70	40	1.692	1.695	35	1.671	1.675	M	1.686	1.067
403	20	1.612	1.612	15	1.601	1.603	–	–	–	10	1.560	1.561	15	1.543	1.547	W	1.557	1.557
205	45	1.498	1.497	–	–	–	20	1.47	1.47	5	1.463	1.463	15	1.451	1.451	W	1.463	1.463
423				50	1.487	1.487	30	1.46	1.45	30	1.447	1.449	35	1.432	1.434	M	1.443	1.445
440	20	1.426	1.425	20	1.412	1.410	20	1.38	1.38	15	1.369	1.370	25	1.353	1.354	W	1.363	1.365
225	15	1.404	1.406	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
424	15	1.345	1.343	–	–	–	–	–	–	–	–	–	15	1.287	1.290	–	–	–
442				–	–	–	–	–	–	5	1.294	1.295	–	–	–	–	–	–
600				–	–	–	–	–	–			1.292	–	–	–	W	1.288	1.288
601	–	–	–	10	1.315	1.311	–	–	–	–	–	–	5	1.263	1.261	–	–	–
610	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	W	1.269	1.270
206	20	1.274	1.275	–	–	–	–	–	–	–	–	–	10	1.238	1.237	W	1.244	1.247
602				15	1.265	1.263	–	–	–	–	–	–	–	–	–	–	–	–
620				–	–	–	–	–	–	5	1.225	1.226	15	1.212	1.212	W	1.219	1.222
443	20	1.260	1.259	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
226	15	1.214	1.215	–	–	–	–	–	–	–	–	–	10	1.177	1.178	W	1.184	1.186
622				15	1.206	1.204	–	–	–	–	–	–	–	–	–	W	1.165	1.167
425	15	1.202	1.201	15	1.196	1.197	25	1.18	1.18	15	1.168	1.169	20	1.156	1.156			1.166
623	10	1.152	1.152	–	–	–	–	–	–	–	–	–	–	–	–	W	1.106	1.108
641	5	1.108	1.107	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–

[a] Cell parameters (Å.): cubic $PrS_{1.98}$ $a = 8.06$; tetragonal $PrS_{1.7}$ $a = 7.98$, $c = 8.07$; tetragonal $GdS_{1.7-1.8}$ $a = 7.79$, $c = 7.92$; tetragonal $TbS_{1.74-1.80}$ $a = 7.76$, $c = 7.91$; tetragonal $HoS_{1.67-1.72}$ $a = 7.66$, $c = 7.84$; tetragonal $YS_{1.72-1.78}$ $a = 7.73$, $c = 7.90$.

with sulfur content. Two samples at each end of the sulfur content range gave the average diffraction spectra listed in Table II. Possible unit cells deduced from the data are indicated.

The polysulfide PrS_2 was the only compound produced in this investigation that could be considered to have a simple cubic crystal structure. A slight distortion to tetragonal is inferred from the X-ray spectrum of $PrS_{1.7}$.

Only a small amount of work was done on Sm sulfide. The X-ray diffraction spectrum of an as-initially-prepared polysulfide corresponded closely to the spectrum of the "disulfide" published by Houston.[4] After heating the same material with additional sulfur, a slight variation from a cubic structure was still observed.

Table III contains the X-ray data on cubic PrS_2 and those other polysulfides whose spectra appeared amenable to tetragonal indexing. Spectra were run on at least three separately prepared samples of each compound (except $PrS_{1.7}$ where only two were available). The *d*-values varied slightly from sample to sample because of differences in composition. The averaged observed *d*-values are listed. The columns headed P/P_0 list the normalized per cent peak height as measured from the diffractometer strip chart record. This is the first reported information for Tb, Ho, and Er polysulfides.

The X-ray data on the erbium polysulfide correspond closely to that of its neighbor holmium. The largest Er polysulfide cell size observed was the same as the average Ho polysulfide.

Relative data were obtained on the stability of the polysulfides at very low sulfur vapor pressures. When heated at 10^{-3} to 10^{-4} torr, the polysulfide of lanthanum lost sulfur rapidly, converting to a sesquisulfide in 4 hr. at 645°. Praseodymium polysulfide lost sulfur more slowly, requiring 16 hr. at 685°. The polysulfides of Sm, Gd, and Tb were converted to sesquisulfides at only 560°.

---

(4) M. D. Houston, *Ceram. Age*, **77** [9], 49 (1961).

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.

(5) A. Iandelli, "Rare Earth Research," E. V. Kleber, Ed., The Macmillan Co., New York, N. Y., 1961, p. 135.

(6) M. Picon, L. Domange, J. Flahaut, M. Guittard, and M. Patrie, *Bull. Soc. Chim. France*, **27**, 221 (1960).

CONTRIBUTION FROM THE LAWRENCE RADIATION LABORATORY AND DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA

Crystal Structure of Terbium Trichloride[1]

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

Received July 22, 1963

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$_4$O$_7$) 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

---

(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).

(4) D. H. Templeton and G. F. Carter, *J. Phys. Chem.*, **58**, 940 (1954).

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

(6) EuBr$_3$, NdI$_3$, PrI$_3$, and CeI$_3$ are said to have this structure by F. H. Spedding and A. H. Daane, Ames Laboratory Report IS-350, Sept., 1961 (unpublished).