$Na_2[(3)-1,2-B_9C_2H_{10}C_6H_5]$ (from 8.07 g of $(CH_3)_3NH[(3)-1,2-B_9C_2H_{11}C_6H_5]$) in 150 ml of THF was added 3.17 g (20.0 mmol) of $CrCl_3$. Precipitation with tetramethylammonium chloride and crystallization from ethanol–acetone gave dark violet microcrystalline $(CH_3)_4N[(\pi-(3)-1,2-B_9C_2H_{10}C_6H_5)_2Cr]$ (1.55 g, 2.85 mmol, 19%).

(e) **$Cs[(\pi-(3)-1,7-B_9C_2H_{11})_2Cr]$**.—To 29.0 mmol of $KLi[(3)-1,7-B_9C_2H_{11}]$ (from 5.0 g of $K[(3)-1,7-B_9C_2H_{12}]$) in 150 ml of THF was added 2.85 g (18.0 mmol) of $CrCl_3$. Precipitation with CsCl and crystallization from water gave brown plates of $Cs[(\pi-(3)-1,7-B_9C_2H_{11})_2Cr]$ (2.08 g, 4.63 mmol, 32%). The analytical data and infrared and electronic spectra for the bis(π-(3)-dicarbollyl)chromium derivatives are given in Tables I–III.

Preparation of the π-Cyclopentadienyl-π-dicarbollylchromium Derivatives. General Procedure.—A tetrahydrofuran solution of freshly prepared cyclopentadiene and the desired dicarbadodecahydroundecaborate(−1) ion salt was treated with a slight excess of sodium hydride at reflux temperature for 3 hr as recently described.[1] Solid chromium trichloride was then added under nitrogen at room temperature to the resultng filtered $C_5H_5^-$ and dicarbollide ion solution.

After heating for 3 hr, the green solution was cooled and the solvent was removed *in vacuo*. The residue was dissolved in benzene and repeatedly filtered through a 10-cm column of chromatographic polyamide to retain $(\pi-C_5H_5)_2Cr^+$ and other charged products. Crystals were obtained by adding hexane to the resulting dark red solution and letting it stand overnight. This procedure was used in the preparation of all $[\pi-C_5H_5]Cr[\pi-(3)-1,2-B_9C_2H_{11}]$ derivatives.

(a) **$[\pi-C_5H_5]Cr[\pi-(3)-1,2-B_9C_2H_{11}]$**.—Chromium trichloride (8.71 g, 55.0 mmol) was treated with the solution obtained by allowing 4.0 g (60.5 mmol) of C_5H_6 and 5.25 g (27.0 mmol) of $(CH_3)_3NH[(3)-1,2-B_9C_2H_{12}]$ to react with 3.9 g (162.5 mmol) of NaH (7.0 g of a 56% suspension in mineral oil) in 200 ml of THF. Dark red crystals of $[\pi-C_5H_5]Cr[\pi-(3)-1,2-B_9C_2H_{11}]$ (1.55 g, 6.21 mmol, 23%) were obtained.

(b) **$[\pi-C_5H_5]Cr[\pi-(3)-1,2-B_9C_2H_{10}CH_3]$**.—Chromium trichloride (5.55 g, 35.0 mmol) was treated with the solution obtained by allowing 2.64 g (40.0 mmol) of C_5H_6 and 5.19 g (25.0 mmol) of $(CH_3)_3NH[(3)-1,2-B_9C_2H_{11}CH_3]$ to react with 3.36 g (140.0 mmol) of NaH (6.0 g of a 56% suspension) in 200 ml of THF. Dark red crystals of $[\pi-C_5H_5]Cr[\pi-(3)-1,2-B_9C_2H_{10}CH_3]$ (2.11 g, 8.0 mmol, 32%) were obtained.

(c) **$[\pi-C_5H_5]Cr[\pi-(3)-1,2-B_9C_2H_9(CH_3)_2]$**.—Chromium trichloride (7.15 g, 45.0 mmol) was treated with the solution obtained by allowing 3.31 g (50.0 mmol) of C_5H_6 and 6.63 g (30. 0 mmol) of $(CH_3)_3NH[(3)-1,2-B_9C_2H_{10}(CH_3)_2]$ to react with 3.9 g (162.5 mmol) of NaH (7.0 g of 56% suspension) in 200 ml of THF. Dark red crystals of $[\pi-C_5H_5]Cr[(3)-1,2-B_9C_2H_9(CH_3)_2]$ (1.67 g, 6.0 mmol, 20%) were obtained.

(d) **$[\pi-C_5H_5]Cr[\pi-(3)-1,2-B_9C_2H_{10}C_6H_5]$**.—Chromium trichloride (6.35 g, 40.0 mmol) was added to the solution obtained by allowing 1.99 g (30.0 mmol) of C_5H_6 and 8.07 g (29.9 mmol) of $(CH_3)_3NH[(3-)1,2-B_9C_2H_{11}C_6H_5]$ to react with 3.36 g (140.0 mmol) of NaH (6.0 g of a 56% suspension) in 200 ml of THF. Dark red crystals of $[\pi-C_5H_5]Cr[\pi-(3)-1,2-B_9C_2H_{10}C_6H_5]$ (1.67 g, 5.13 mmol, 18%) were obtained.

(e) **$[\pi-C_5H_5]Cr[\pi-(3)-1,7-B_9C_2H_{11}]$**.—To a solution of 5.0 g (29.0 mmol) of $K[(3)-1,7-B_9C_2H_{12}]$ and 3.4 g (51.4 mmol) of C_5H_6 in 150 ml of THF was added 50.0 ml (80 mmol) of a 15.2% hexane solution of *n*-butyllithium. After stirring for 30 min at reflux temperature, 6.35 g (40.0 mmol) of $CrCl_3$ was added and the solution was stirred for 3 hr. The reaction product was isolated as described above. Dark red crystals of $[\pi-C_5H_5]Cr[\pi-(3)-1,7-B_9C_2H_{11}]$ (1.59 g, 6.37 mmol, 22%) were obtained. The analytical data and infrared and electronic spectra of the π-cyclopentadienyl-π-(3)-dicarbollylchromium derivatives are given in Tables IV–VI.

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Crystal Chemistry of the Rare Earth Sesquisulfides

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Rare earth sesquisulfides of La through Lu as well as Y have been prepared and characterized. The structures occurring for these compounds are now all known, and the cell dimensions are given, many for the first time. Three structure types are found. The A type exists from La through Dy, the D type from Dy through Tm, including Y, and the E type, for Yb and Lu. It is apparent that Pu_2S_3 may also have the A-type structure, and its cell dimensions have been refined by least squares. Although the Th_3P_4 structure (C type) may represent a fourth structure type, it is possible that sesquisulfides with this structure must be deficient in sulfur or impure. In order to help clarify the Th_3P_4 structure, a refinement of C-type Ce_2S_3 was undertaken using previously published data. Single crystals of most of the rare earth sesquisulfides have been prepared in a rare earth iodide melt. Electrical measurements on the single crystals generally showed semiconductor behavior as expected.

Introduction

The rare earth sesquisulfides have been investigated by Klemm, *et al.*,[1] and more recently by Flahaut and coworkers.[2,3] The characterization and structure determination of Sc_2S_3 have been reported by Dismukes and White.[4] Although some rare earth sesquiselenides and sesquitellurides have the Sc_2S_3 structure, no other sesquisulfides are known to have this structure. For the remaining rare earth sesquisulfides it has been proposed[2,3] that there are five commonly occurring structure types; however, until recently the structures

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[1] W. Klemm, K. Meisel, and H. U. v. Vogel, *Z. Anorg. Allgem. Chem.*, **190**, 123 (1930).

[2] M. Picon, L. Domange, J. Flahaut, M. Guittard, and M. Patrie, *Bull. Soc. Chim. France*, **2**, 221 (1960).

[3] J. Flahaut, M. Guittard, M. Patrie, M. Pardos, S. Golabi, and L. Domange, *Acta Cryst.*, **19**, 14 (1965).

[4] J. P. Dismukes and J. G. White, *Inorg. Chem.*, **3**, 1220 (1964).

of only two of these have been known: the defect Th_3P_4 type[5] and the corundum type.[6] Recently, the structures of two more types have been reported.[7,8]

The purpose of this investigation has been to prepare pure rare earth sesquisulfides in closed systems in order to maintain good control of stoichiometry and to determine their structure types. Crystals were grown where possible, and certain of their electrical properties were measured.

Experimental Section

Reactants.—The sulfur (99.999%) was obtained from the American Smelting Co. Iodine was reagent grade resublimed. An attempt was made to use the highest purity rare earth metals commercially available, and these were not further purified. Nuclear grade (99.9+%) metals of La, Pr, Nd, Sm, Gd, Dy, Ho, Er, and Y were obtained from the Lunex Co. Other metals (also 99.9+%) were obtained from the American Potash and Chemical Corp. The crystal sponge form was used for Gd, Dy, Ho, Er, and Y. The ingot form was used for the other metals, and the ingots were freshly filed in an argon-filled drybox before use.

Synthesis.—Appropriate amounts of reactants were sealed in evacuated silica tubes without mixing. For the more reactive rare earth metals (La through Sm) it was found necessary to coat the inside of the tube with carbon[9] or to use a graphite crucible inside the sealed tube. Alumina and boron nitride crucibles were found to be unsatisfactory.

The sealed ampoules (~20 cm long) were placed in two-zone tube furnaces. One zone was slowly raised to 400° while the other zone was held at 100°. Initially all reactants were in the hotter zone, but the sulfur (and iodine) quickly moved to the cooler zone before reacting significantly with the rare earth metal. In this manner the metal reacted slowly with vapors of sulfur (and iodine), and there was no detectable attack of the silica. After elemental sulfur (and/or iodine) was no longer present, the ampoule was transferred to a muffle furnace and heated at 600° or higher for 1–2 days.

When polycrystalline samples were prepared, the reactants were simply the rare earth metal and sulfur. However, when single crystals were to be grown, a 1:1:1 atomic mixture of metal, sulfur, and iodine was used. In this case it was necessary to use a sufficiently high temperature to decompose the rare earth sulfur iodides which are stable at lower temperatures. The rare earth iodide was washed from the crystals using alcohol and water. Although the odor of H_2S was present during washing, the crystals were only very slightly attacked by water.

X-Ray.—Powder diffraction patterns were obtained on all products at 25° using a Hägg–Guinier camera with strictly monochromatic Cu $K\alpha_1$ radiation. An internal standard of high-purity KCl (a = 6.2931 Å) was used, and all cell dimensions were refined by least squares. Qualitative relative intensities were measured with a densitometer.

Electrical Measurements.—When single crystals were available, the electrical resisitivity was determined from 4.2 to 298°K. The standard four-probe technique was used. The thermoelectric power (α) was determined at an average temperature of 45° with $\Delta T = 30°$.

Nomenclature

Flahaut[3] has assigned Greek letters to each of the five structure types he and his coworkers found for the rare earth sesquisulfides. However, we feel that the Greek letters should be reserved for a different structural modification of a given compound and should not be used to designate structure types. Therefore, we have replaced Flahaut's Greek letters as follows: α to A, β to B, γ to C, δ to D, and ϵ to E. White, *et al.*,[8] also made this change in nomenclature except that they replaced γ with A and gave no designations for Flahaut's α and β types. It is now known that the A type is orthorhombic, the C type is cubic, the D type is monoclinic, and the E type is rhombohedral (corundum type). However, the crystal class of the B type is still unknown.

Results

This investigation revealed only three structure types for the rare earth sesquisulfides. As we have previously indicated,[7] we find that the A type exists from La through Dy. This is in complete agreement with Klemm, *et al.*,[1] but Flahaut has only very recently[10] included La_2S_3 in this group. Qualitative comparisons of X-ray powder patterns were used to ascertain that the same structural modification was obtained in all three investigations. The D-type sesquisulfide structure was found for Dy through Tm and also for Y, and the E type (corundum type) was found only for the two smallest rare earths, Yb and Lu. The ranges of these latter two groups are in complete accord with the ranges Flahaut reports for the δ and ϵ types.

The cell dimensions for the A-, D-, and E-type rare earth sesquisulfides are given in Table I. The temperature ranges given are not the limits of stability but merely indicate the range over which these types were successfully prepared. An upper limit of 1250° could not be exceeded by our closed-system method. The indexed powder patterns are given in Table II. These patterns are actual examples and do not necessarily give exactly the cell dimensions of Table I. The dimensions and errors given in Table I are generally based on at least two different preparations. Only Dy_2S_3 was found to be dimorphic (Table I and Figure 1). Several attempts to prepare Eu_2S_3 were unsuccessful. The highest sulfur-to-metal ratio obtained was about Eu_3S_4, and the Th_3P_4 structure was found for this composition.

The analytical data for the rare earth sesquisulfides are summarized in Table III. It is felt that all of the experimental data agree with the calculated quantities within the errors of determination. No evidence for nonstoichiometry was obtained from either analytical or X-ray data. All samples were also analyzed for oxygen. The oxygen content was found to range from about 0.1% up to nearly 1%. However, since the sesquisulfides were not highly purified, this oxygen content could result from a very small quantity of a second phase such as a rare earth oxysulfide or sulfate. It is also possible that this oxygen content is the result of very slow hydrolysis since the rare earth sulfides were exposed to the air for some time before analysis. Those

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[5] W. Zacharaisen, *Acta Cryst.*, **2**, 57 (1949).

[6] J. Flahaut, L. Domange, and M. Pardo, *Compt. Rend.*, **258**, 594 (1964).

[7] C. T. Prewitt and A. W. Sleight, Winter Meeting of the American Crystallographic Association, Atlanta, Ga., 1967, Abstract No. J5; also C. T. Prewitt and A. W. Sleight, *ibid.*, **7**, 1090 (1968).

[8] J. White, P. Yocom, and S. Lerner, *ibid.*, **6**, 1872 (1967).

[9] The coating of carbon was obtained by the pyrolysis of benzene at 700°.

[10] P. Besancon, C. Adolphe, and J. Flahaut, *Compt. Rend.*, **266**, 111 (1968).

Table I

Cell Dimensions and Preparation Temperatures for Rare Earth Sesquisulfides[a]

Compd	a	b	c	V, Å³	Prepn temp, °C
La_2S_3 (A)	7.584 ± 2	15.860 ± 3	4.144 ± 2	498.4	600–1250
Ce_2S_3	7.513	15.715	4.091	483.0	600–1250
Pr_2S_3	7.472	15.604	4.058	473.1	600–1250
Nd_2S_3	7.442	15.519	4.029	465.3	600–1250
Sm_2S_3	7.382	15.378	3.974	451.1	600–1250
Gd_2S_3	7.338	15.273	3.932	440.7	600–1250
Tb_2S_3	7.303	15.200	3.901	433.1	600–1200
Dy_2S_3	7.279	15.136	3.878	427.2	600–1100
Dy_2S_3 (D)	17.496 ± 4	4.022 ± 2	10.183 ± 3	708.4	1250
Y_2S_3	17.520	4.019	10.170	708.0	900–1250
Ho_2S_3	17.452	4.001	10.128	699.1	900–1200
Er_2S_3	17.404	3.978	10.092	690.7	900–1100
Tm_2S_3	17.363	3.960	10.039	682.2	900–1000
Yb_2S_3 (E)	6.748 ± 2	...	18.191 ± 3	717.3	700–1250
Lu_2S_3	6.722	...	18.160	710.7	900–1100

[a] The β angles for the D-type phases in order of appearance in the table are: 98.67 ± 2, 98.64, 98.69, 98.67, and 98.78°.

Table II

Powder X-Ray Diffraction Patterns for the Rare Earth Sesquisulfides[a]

h k l	I/I_0	La	Ce	Pr	Nd	Sm	Gd	Tb	Dy
1 3 0	20	4.338	4.296	4.268	4.247	4.213	4.185	4.162	4.149
0 1 1	25	4.009	3.959	3.926	3.895	3.847	3.808	3.780	3.757
0 4 0	30	3.966	3.925	3.897	3.878		3.821	3.798	3.785
2 0 0	35	3.792	3.757	3.738	3.720	3.692	3.670	3.650	3.640
2 1 0	40	3.689	3.655	3.634	3.617	3.590	3.559	3.550	3.540
1 1 1	100	3.545	3.503	3.474	3.452	3.413	3.379	3.356	3.339
1 4 0	80	3.515	3.480	3.458	3.441		3.389	3.368	3.357
2 2 0	20	3.422	3.389	3.371	3.354	3.330	3.309	3.291	3.281
0 3 1	70	3.262	3.224	3.198	3.178	3.145	3.112	3.091	3.075
1 5 0	30	2.927	2.898	2.879	2.864	2.838	2.821	2.806	2.795
2 0 1	20	2.798	2.768	2.749	2.733	2.705	2.683	2.666	2.654
2 1 1	5	2.755	2.726	--	2.690	--	--	--	2.614
2 4 0	20	2.741	2.714	2.698	2.685	2.662	2.646	2.632	2.624
1 4 1	20	2.680	2.651	2.631	2.616	2.588	2.556	2.551	2.538
2 2 1	80	2.639	2.610	2.593	2.578	2.552	2.531	2.516	2.505
0 5 1	40	2.519	2.492	2.473	2.459	2.432	2.413	2.398	2.386
2 3 1	40	2.473	2.447	2.430	2.417	2.393	2.374	2.359	2.349
3 2 0	10	2.409	2.389	2.371	2.363	2.343	2.329	2.318	2.311
1 5 1	55	2.391	2.365	2.348	2.335	2.310	2.292	2.278	2.267
3 3 0	15	2.282	2.260	2.248	2.236	2.219	2.206	2.194	2.187

h k l	I/I_0	Dy	Ho	Er	Tm	Y
2 0 0	2	--	8.632	8.616	--	8.644
-1 0 1	10	8.175	8.128	8.120	--	8.203
2 0 1	10	7.122	7.081	7.064	--	7.092
-2 0 1	5	--	6.096	6.075	--	--
3 0 0	5	--	5.751	5.737	--	--
3 0 1	50	5.362	5.343	5.333	5.314	5.365
-3 0 1	2	--	--	4.680	--	4.711
2 0 2	70	4.664	4.643	4.626	4.597	4.660
-1 0 2	70	4.647	4.624	4.609		4.644
4 0 1	10	4.210	4.199	4.186	4.174	4.213
-4 0 1	100	3.771	3.759	3.750	3.739	3.775
0 1 1	40	3.736	3.713	3.694	3.676	3.731
1 1 1	40	3.692	3.672	3.655	3.639	3.690
2 1 0	2	--	3.627	3.611	--	--
-1 1 1	75	3.610	3.588	3.572	3.556	3.606
4 0 2	70	3.555	3.543	3.531	3.518	3.555
-3 0 2	10	3.536	3.521	3.510	3.499	3.538
2 1 1	50	3.500	3.481	3.466	3.450	3.498
5 0 0	10	3.460	3.451	3.443	3.434	3.461
5 0 1	10	3.435	3.423	3.416	3.406	3.440
0 0 3	65	3.358	3.339	3.325	3.310	3.351

h k l	I/I_0	Yb	Lu
0 1 2	80	4.915	4.899
1 0 4	90	3.592	3.580
1 1 0	95	3.375	3.362
0 0 6	50	3.030	3.024
1 1 3	80	2.947	2.937
2 0 2	40	2.781	2.771
0 2 4	95	2.458	2.450
1 1 6	100	2.255	2.248
2 1 1	5	2.192	2.184
1 2 2	55	2.146	2.138
0 1 8	40	2.119	2.113
2 1 4	95	1.987	1.980
3 0 0	95	1.948	1.940
1 2 5	5	1.838	1.882
2 0 8	10	1.795	1.789
1 0 10	90	1.737	1.733
1 1 9	35	1.734	1.729
2 2 0	70	1.687	1.681
3 0 6	65	1.639	1.633
2 2 3	35	1.625	1.619
1 2 8	25	1.584	1.579
0 2 10	70	1.544	1.540

[a] The reflections are generally given in order of decreasing d's. However, the crossovers in the A type for the h11 and h40 reflections should be noted.

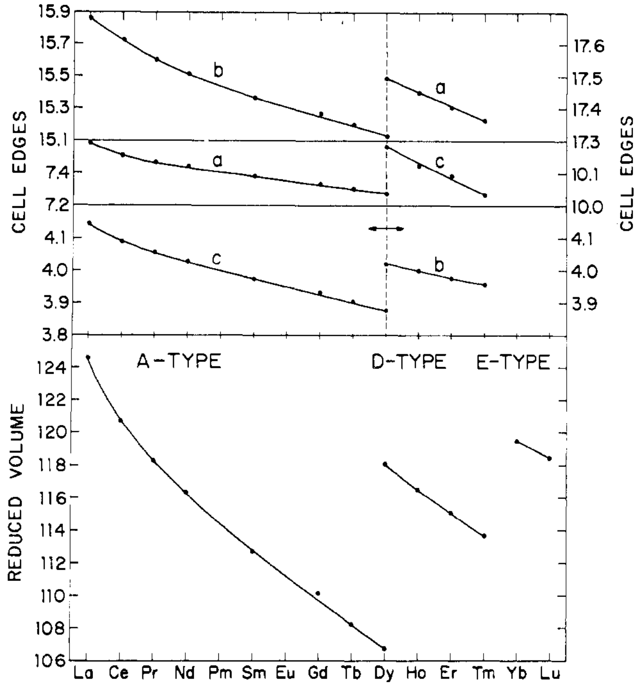

Figure 1.—Reduced volume and cell edges vs. atomic number for the rare earth sesquisulfides.

Table III

Analytical Data for the Rare Earth Sesquisulfides

Compd	% S		% metal		d, g/cm³	
	Calcd	Found	Calcd	Found	Calcd	Obsd
La_2S_3	25.72	25.3	74.28	74.3	4.98	4.93[a]
Ce_2S_3	25.56	25.4	74.44	74.2	5.18	5.15,[a] 4.95[b]
Pr_2S_3	25.45	25.4	74.55	74.6	5.31	5.35,[a] 5.19[b]
Nd_2S_3	25.01	24.9	74.99	74.8	5.49	5.36,[a] 5.26[b]
Sm_2S_3	24.24	24.3	75.76	75.8	5.84	5.87,[a] 5.69[b]
Gd_2S_3	23.42	22.2	76.58	76.4	6.19	6.16,[a] 5.97,[b] 6.14[c]
Tb_2S_3	23.23	23.1	76.77	76.6	6.35	
Dy_2S_3 (A)	22.84	22.3	77.16	77.2	6.55	6.50[a]
Dy_2S_3 (D)	22.84	22.1	77.16	77.3	5.92	5.75,[b] 5.84[c]
Ho_2S_3	22.58	21.7	77.42	77.2	6.07	
Er_2S_3	22.33	21.9	77.67	77.6	6.21	6.09,[a] 6.07[b]
Tm_2S_3	22.16	21.2	77.84	77.9	6.34	
Yb_2S_3	21.75	21.2	78.25	78.4	6.14	6.08,[a] 6.02[b]
Lu_2S_3	21.56	20.6	78.44	78.6	6.25	
Y_2S_3	35.11	33.8	64.89	65.1	3.86	3.87,[a] 3.87[b]

[a] Highest density reported by Klemm, et al.[1] [b] Highest density reported by Flahaut and coworkers.[2,3] [c] This work.

sulfides prepared in an iodide melt were analyzed for iodine, but iodine was never detectable.

The properties of the rare earth sesquisulfide single crystals are summarized in Table IV. All crystals of the A and D structure types grew as needles (up to ~1 cm in length) where the needle axis was the short (~4 Å) crystallographic axis. Crystals of the E structure type grew as hexagonal plates which were generally twinned. Attempts to obtain La_2S_3 crystals in a LaI_3 melt at 1250° yielded only LaSI which has been reported by Dagron, *et al.*[11] Similar attempts to prepare crystals of Er_2S_3, Tm_2S_3, and Y_2S_3 at 1250° also yielded only sulfur iodides.

Marcon and Pascard have reported[12] indexing powder patterns of A-type Ce_2S_3 and Pu_2S_3. The authors gave their *d* values for A-type Pu_2S_3 but unfortunately did not do so for A-type Ce_2S_3. We have indexed their powder pattern of Pu_2S_3, and in Table V we compare our indexing and cell with their indexing and cell. Our indexing accounts for all but three very weak lines of their pattern. The new *d*'s are generally in better agreement with their observed *d*'s than are their own calculated *d*'s. Their indexing bears no direct relationship to the correct indexing which is not surprising since Marcon and Pascard did not have the benefit of single-crystal data. We can only assume that their powder pattern of A-type Ce_2S_3 was similarly incorrectly indexed.

In 1949, Zachariasen[5] published the structure of C-type Ce_2S_3 based on X-ray powder data and noted that

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(11) C. Dagron, J. Etienne, and P. Laruelle, Second International Conference or Solid Compounds of Transition Elements, Enschede, Holland, 1967, Abstract No. 9.2.

(12) J. P. Marcon and R. Pascard, *J. Inorg. Nucl. Chem.*, **28**, 2551 (1966).

TABLE IV

CRYSTAL DATA FOR SOME RARE EARTH SESQUISULFIDES

Compd	Growth, temp, °C	Color	E_a,[a] eV	$\rho_{25°}$, ohm-cm	$\alpha_{45°}$,[b] μV/deg
Nd_2S_3 (A)	600	Black	0.0	2.7×10^{-2}	
Sm_2S_3 (A)	1250	Red	0.001	1.6×10^{-1}	−230
Gd_2S_3 (A)	1100	Red	0.007	4.0×10^{-2}	−360
Tb_2S_3 (A)	1100	Red	0.0	3.0×10^{-2}	−180
Dy_2S_3 (D)	1100	Green	0.34	2.0×10^{-3}	+4000
Ho_2S_3 (D)	1275	Yellow-orange	0.5	7.0×10^{6}	
Yb_2S_3 (E)	1275	Yellow	0.29	2.7×10^{4}	
Lu_2S_3 (E)	1250	Black	0.0	2.3×10^{-3}	−6

[a] Derived from the slope of log ρ *vs.* $1/T$. [b] Thermoelectric power (α) is referred to lead ($\alpha_{Pb} = -2.76\ \mu$V/deg).

TABLE V

INDEXING OF Pu_2S_3 POWDER PATTERN

I[a]	*hkl*[a]	*d* Calcd[a]	*d* Obsd[a]	*d* Calcd[b]	*hkl*[b]
ww	103	4.221	4.230	...	...
w	020	4.203	4.203	4.206	130
mw	200	3.847	3.837	3.861	011
				3.842	040
ms	120	3.688	3.685	3.685	200
s	121	3.584	3.581	3.583	210
ss	211	3.409	3.409	3.420	111
				3.407	140
w	122	3.316	3.319	3.322	220
ms	114	3.150	3.146	3.147	031
mw	220	3.836	2.837	2.837	150
w	204	2.699	2.705	2.707	201
mw	222	2.657	2.658	2.659	240
ww	130	2.631	2.634	...	...
mw	131	2.592	2.592	2.590	141
s	300	2.564	2.554	2.553	221
ww	223	2.475	2.473	...	...
mw	302	2.430	2.432	2.435	051
m	106	2.399	2.394	2.393	231
w	125	2.341	2.341	2.340	320
ms	116	2.307	2.310	2.312	151
mw	313	2.207	2.214	2.215	330
w	322	2.103	2.105	2.104	170
m	225	2.071	2.073	2.073	311
w	140	2.027	2.033	2.031	251

[a] Data under these columns are taken from ref 12 and are based on an orthorhomic cell: a = 7.69 Å, b = 8.41 Å, and c = 15.15 Å. [b] Correct indexing based on a = 7.369 (2) Å, b = 15.367 (6), Å, and c = 3.989 (3) Å.

the structure was similar to that of Th_3P_4. In Th_3P_4, Th occupies equipoint 12a and S occupies equipoint 16c of space group Ia3d. In order to fit Ce_2S_3 into this structure, Zachariasen proposed that Z = 5.4 so that there would be 16 S per cell and $10^2/_3$ Ce would be distributed randomly over the 12a equipoint. The x parameter for S was assumed to be $^1/_{12}$ and structure factors were calculated. Zachariasen's R [$R = \Sigma(I_o - I_c)/\Sigma I_o$] is 0.194.

We decided to refine the Ce_2S_3 structure by least squares using Zachariasen's powder data in order to establish how reasonable the model is and if the multiplicity factor for Ce and the refined interatomic distances could be of value in understanding the structure. Taking Zachariasen's diffractometer data, we assigned *hkl*'s and refined the scale factor, the over-all temperature factor, the multiplicity factor for Ce, and the positional parameter for S. A program for refining powder data was used which minimizes $\Sigma w \cdot (I_o - I_c)^2$. Neutral scattering factors were taken from Cromer and Waber.[13] Real and imaginary anomalous dispersion factors[14] were used, and unit weights were assigned for each reflection. The final R, as defined above, for all 17 observations was 0.072. Table VI gives the observed and calculated intensities. In this table the intensities were calculated using

TABLE VI

OBSERVED AND CALCULATED INTENSITIES AND LEAST-SQUARES REFINEMENT RESULTS FOR C-TYPE Ce_2S_3[a]

h	k	l	I_o	I_c	A_c	B_c	M
2	1	1		71	73	-81	12
-2	-1	-1		80	27	112	12
			148	151			
2	2	0	13	12	-50	-15	12
3	1	0	178	180	-26	160	24
3	2	1		60	-106	-39	24
-3	-2	-1		55	-108	3	24
			113	114			
4	2	0	75	66	-145	-34	24
3	3	2		21	-56	-112	12
-3	-3	-2		22	-103	77	12
			46	43			
4	2	2		6	64	-33	12
-4	-2	-2		9	58	66	12
			19	15			
5	1	0		9	22	-61	24
4	3	1		22	-57	82	24
-4	-3	-1		16	-11	-86	24
			56	47			
5	2	1		7	58	22	24
-5	-2	-1		6	59	11	24
			12	13			
4	4	0	4	3	-56	-16	12
5	3	2		16	-64	90	24
-5	-3	-2		19	-14	-120	24
6	1	1		13	-44	-133	12
-6	-1	-1		12	-95	99	12
			62	61			
6	2	0	19	13	-100	-19	24
5	4	1		14	-54	95	24
-5	-4	-1		11	-5	-99	24
			28	25			
6	3	1		5	-51	-43	24
-6	-3	-1		3	-54	10	24
			6	8			
4	4	4		7	-175	-105	4
-4	-4	-4		6	-183	4	4
			10	12			
6	4	0	13	13	115	34	24
7	2	1		10	-39	-102	24
-7	-2	-1		11	-87	68	24
6	3	3		5	79	-71	12
-6	-3	-3		5	31	105	12
5	5	2		4	61	81	12
-5	-5	-2		6	105	-43	12
			30	41			

[a] The refined parameters were: s = (0.26 ± 0.02) × 10^{-4}, T_o = 0.33 ± 0.28 Å^2, p(Ce) = 0.887 ± 0.032, and x(S) = 0.0767 ± 0.0031.

$$I_c = s(A_c^2 + B_c^2)M \text{ Lp} \exp[-2T_0 ((\sin \theta)/\lambda)^2]$$

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(13) D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965).

(14) D. T. Cromer, *ibid.*, **18**, 17 (1965).

where

$$A_c = \sum_i p_i[(f_i + \Delta f_i') \cos \varphi_i - \Delta f_i'' \sin \varphi_i]$$

$$B_c = \sum_i p_i[(f_i + f_i') \sin \varphi_i + \Delta f_i'' \cos \varphi_i]$$

$$\phi_i = 2\pi(hx_i + ky_i + lz_i)$$

and s is a scale factor, M is the multiplicity, Lp is the Lorentz-polarization factor, T_0 is the over-all temperature factor, and p_i is an equipoint occupation factor. Coordinates for Ce were $^1/_4$, $^3/_8$, 0, and for S were x, x, x. Overlapping reflections which include equivalent pairs affected differently by anomalous dispersion are grouped together as single observations. Table VII lists the interatomic distances for C-type Ce_2S_3.

Table VII

Interatomic Distances (Å) in the CeS_8 Dodecahedron[a]

$Ce(^1/_4, ^3/_8, 0)–S(x, x, x)$	3.05	(×4)
$–S(^1/_4 + x, ^1/_4 + x, ^1/_4 + x)$	2.93	(×4)
$S(x, x, x)–S(^1/_2 - x, x, \bar{x})$	3.27	(×2)
$–S(^1/_4 + x, ^1/_4 + x, ^1/_4 + x)$	3.74	(×4)
$–S(^1/_4 - x, ^1/_4 + x, ^1/_4 - x)$	4.18	(×4)
$–S(^1/_2 + x, ^1/_2 - x, \bar{x})$	5.42	(×4)
$S(^1/_4 + x, ^1/_4 + x, ^1/_4 + x)–S(^1/_2 - x, x, \bar{x})$	4.18	(×4)

[a] Errors calculated using the refinement results are ±0.03 Å for Ce–S and ±0.04 Å for S–S.

Discussion

The A structure type is found for the larger rare earths, and the structure of one member of this group, Gd_2S_3, was recently solved and refined by Prewitt and Sleight.[6] There are two kinds of nonequivalent cations in this structure. One cation is seven-coordinated and the other is eight-coordinated. Two members of the D structure type have been examined. A structure determination for Ho_2S_3 by White, *et al.*,[8] reveals that the D structure type has six nonequivalent cations with half in six- and half in seven-coordination. The structure of Dy_2S_3 (D type) has been refined by Prewitt and Sleight[15] and confirms the general arrangement reported for Ho_2S_3. The coordination of the cations in the E structure type (corundum type) is six. Thus, the average coordination numbers of the cations are 7.5, 6.5, and 6.0 for the A, D, and E types, respectively, which is the order expected from the relative sizes of the rare earth cations. Examples of formulas which represent the coordination numbers are $La^{VIII}La^{VII}S^{V}_3$, $Ho^{VII}Ho^{VI}S^{V}S^{IV}_2$, and $Yb^{VI}_2S^{IV}_3$. Figure 1 shows the regular variation of cell dimensions with atomic number for the A and D structure types. However, volumes change very abruptly when structure types change as shown in Figure 1 where the reduced cell volumes (volumes per formula unit) are plotted against atomic numbers and in Figure 2 where the volumes are plotted against cubed effective ionic radii. Also plotted in Figure 2 are volumes taken from the work of others.[2,6,8,10] Although the coordinations of the rare earths vary between the different structure types, only six-coordinated radii taken from Shannon and Prewitt[16] are used in the plots.

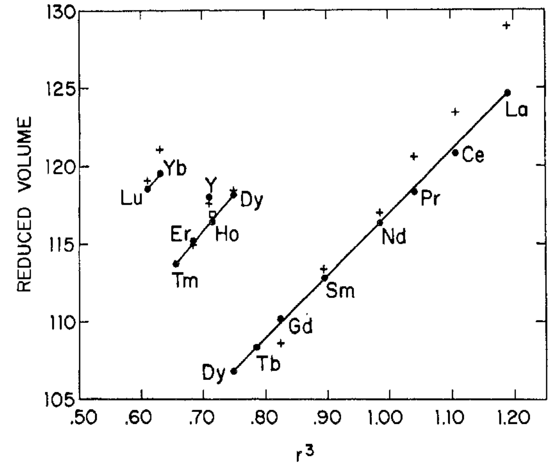

Figure 2.—Reduced volume *vs.* radii cubed. Volumes indicated by dots are taken from Table I, by crosses from Flahaut and coworkers,[2,3,6] and by the square (Ho_2S_3) from ref 8.

There are several interesting aspects of Figure 2. First, the volume–radii relationships for the A and D structures taken from the present work are nearly linear, except for that of Y_2S_3. This linearity is significant because the Shannon and Prewitt radii were determined from oxide and fluoride structures and were not necessarily intended to be used with sulfides or other compounds with anions larger than oxygen or fluorine. For whatever the reason, it does appear that average interatomic distances in at least the lanthanide sesquisulfides can be predicted using these cation radii and fixed for four- and five-coordinated sulfur. Our cell volumes agree very closely with the previous data for the D form but differ greatly for the A and E forms. Since these other papers do not include detailed chemical and X-ray data, it is difficult to ascertain what might cause such differences. Careful rechecking of our chemical data and comparison of single-crystal and powder X-ray photographs do not reveal significant inconsistencies.

Flahaut[2,3] has reported a β- or B-type structure as also occurring for certain rare earth sesquisulfides. The occurrence of this type has been confirmed by others,[12,17] but it was not observed in this work. Apparently this type has been prepared only in open systems, and therefore the exact stoichiometry is in question. Marcon and Pascard,[18] as well as Fitzpatrick and Munir,[17] have, in fact, indicated that this type must be sulfur deficient. Besancon, *et al.*,[10] have also given support to this conclusion by reporting that the presence of sulfur greatly enhances the B to A transformation. A structure determination of the B-type structure would be of great help in completely resolving this problem. Unfortunately, crystals of phases with the B-type structure have apparently not been prepared.

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(15) C. T. Prewitt and A. W. Sleight, to be submitted for publication.

(16) R. D. Shannon and C. T. Prewitt, to be submitted for publication.

(17) R. L. Fitzpatrick and Z. A. Munir, *Mater. Res. Bull.*, **2**, 939 (1967).

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Very little resistivity data have been reported for rare earth sesquisulfide crystals. For the Sc_2S_3 it has been shown[4] that stoichiometric samples are semiconductors whereas sulfur-deficient samples are metallic. Measurements on Ce_2S_3 and Dy_2S_3 crystals (both C type and sulfur deficient) indicated metallic or highly degenerate semiconducting behavior with the resistivity increasing with temperature.[19,20] Although the same type of behavior was observed for some crystals grown in this work (Table IV), most crystals were well-behaved, but not intrinsic, semiconductors. Most of these crystals are impure by semiconductor standards, and more work is obviously needed. The sample container is crucial, and graphite seems to be best. However, it is also crucial to control carefully the metal-to-sulfur ratio in the rare earth sulfides either by using a closed system or by possibly controlling the sulfur vapor pressure above the sample.

Occurrence of the Th_3P_4 Structure.—The cubic form (C type) of the eare earth sesquisulfides is generally regarded as one of the common forms, and Zachariasen[5] has proposed that this form has a defect Th_3P_4 structure. Zachariasen's work was based solely on powder patterns, and apparently the space group and structure of this form have never been confirmed for crystals of any rare earth sesquisulfide. In Zachariasen's study of Ce_2S_3, he proposed that Ce must occupy $10^2/_3$ of the possible 12 sites in the Th_3P_4 structure. This is equal to a fractional occupation factor of 0.889. Although the calculated error is large, the most striking result of our structure refinement is the final value of the occupation parameter which is 0.887 ± 0.032. One must conclude from this that Zachariasen was correct and that this site is not completely filled. Perhaps the formula $Ce_{2.67}S_4$ with $Z = 4$ describes the situation better than Ce_2S_3 with $Z = 5.33$.

The x parameter for S shifted from the value of 0.083 assigned by Zachariasen to 0.0767, resulting in two different Ce–S distances, 3.05 and 2.93 Å, with the average being the same as Zachariasen's (2.99 Å). This is in good agreement with the calculated Ce^{3+}–S distance of 2.98 Å using the Shannon and Prewitt[16] Ce^{3+} radius and Pauling's radius for S^{2-}. The sulfur atoms form a triangular dodecahedron around Ce with S–S distances ranging from 3.27 to 5.42 Å. The over-all temperature factor of 0.33 Å^2 is smaller than one would expect, but, considering the conditions of the refinement, this is not particularly disturbing.

Rare earth sesquisulfides have generally been prepared in open systems, and in such cases the stoichiometry of the product sulfide is not well controlled. The tendency of Ce_2S_3 samples to lose sulfur when sintered at high temperatures has been mentioned by Cutler and Leavy.[21] The Th_3P_4 phase is well known to exist over a wide range of compositions;[2,3] thus, very heavy reliance must be placed on chemical analyses. Such analyses have indicated that certain C-type rare earth sesquisulfides have been stoichiometric within the limits of the analyses. However, much better control of stoichiometry can be obtained in a closed system, and preparations in closed systems have never given the Th_3P_4 structure for the sesquisulfide composition even at the same temperature for which open system preparations have reportedly given the Th_3P_4 structure. Unfortunately, there is a temperature limit above which a closed system is not technically possible. Silica may be used up to a temperature of about 1250° if carbon coatings or crucibles are used; however, higher temperatures necessitate the use of an alternate container. Alumina and boron nitride are unsatisfactory, and metals which might be used react with sulfur. Although some workers[21,22] have used sealed molybdenum vessels at temperatures above the limit of silica, this is not a closed system in the true sense because sulfur readily reacts with molybdenum. In fact, Henderson, *et al.*,[20] have noted that molybdenum as well as other metals react significantly with rare earth sesquisulfides at high temperatures. Consequently, samples sintered at high temperatures in sealed molybdenum vessels could easily be deficient in sulfur.

The plausibility of the Th_3P_4 structure for any phase would of course increase as the cation-to-anion ratio approached 3:4. There are two intimately related routes by which this can be accomplished for the rare earth sulfides. Solid solutions of the type $A^{II}{}_xR_{8/3-2/3x}S_4$ are known[3] up to $x = 1$, *e.g.*, $SrNd_2S_4$, where the cation-to-anion ratio would then be 3:4 as ideally required for the Th_3P_4 structure. It has, in fact, been shown by several workers[17,23] that small amounts of large divalent cations stabilize the Th_3P_4 structure under conditions which would otherwise give the A-type structure. It has also been shown[17] that large tetravalent cations do not stabilize the Th_3P_4 structure, but of course these cations would result in an even further departure from the ideal 3:4 stoichiometry. The alternate, but only formally distinguishable, route for obtaining cation-to-anion ratios deviating from 2:3 in the direction of 3:4 is to have sulfur deficiencies. This would presumably result in more cation sites being occupied and thus might more appropriately be termed cation excess.

Besancon, *et al.*,[10] have reported that the addition of sulfur greatly enhances the C-type to A-type transformation. This is most readily explained by assuming that sulfur is in fact taken up in order to achieve a 2:3 cation-to-anion ratio. The fact that the transition can also occur without additional sulfur does not indicate that the Th_3P_4 phase is stoichiometric because disproportionation could readily occur with an undetected second phase.

Crystals of C type Dy_2S_3 have been extensively studied,[20] and there is overhwelming evidence that the crystals contain an excess of Dy. The metal analyses

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are consistently high, the measured density is high, the magnetic susceptibility is high, and the electrical resistivity indicates metallic behavior instead of the expected semiconducting behavior which is found for monoclinic (D type) Dy_2S_3. Of course, this does not preclude the possibility that more stoichiometric cubic Dy_2S_3 might be prepared under other conditions.

The unit cell dimensions of the Th_3P_4 type rare earth sulfides[2] are nearly invariant over the composition range $R_{2.677}S_4$ (R_2S_3) to R_3S_4 for R = La, Ce, Pr, and Nd. This means that the average cation-to-sulfur distance is nearly invariant over this range because the *average* distance changes very little with changes in the one positional parameter. The average cation size might be expected to increase since formally some cations are being reduced from R^{3+} to R^{2+}. The filling of some cation vacancies would not be expected to compensate for such an increase; consequently, the best rationalization appears to be that the cations do not increase in size when they are formally reduced because the additional electrons are not localized at the cations. The expected increase in unit cell dimensions does occur on going from Sm_2S_3 to Sm_3S_4 indicating that Sm^{2+} is really present and the additional electron has not been delocalized. This conclusion is supported by magnetic and electrical data[24] in that CeS is metallic with a magnetic moment corresponding to Ce^{3+}, whereas SmS is a semiconductor with a magnetic moment corresponding to Sm^{2+}. Of course, Sm^{2+} is well known in other compounds, whereas Ce^{2+} is not.

At this time it is not possible to state with certainty whether or not the Th_3P_4 phase can exist at *exactly* the sesquisulfide stoichiometry for the rare earth sulfides. It is possible that this C-type structure is a valid high-temperature form, but it is likewise possible that in the high-temperature preparations of this form at least some sulfur is always lost. Clarification of this point will have to await more sophisticated preparative or analytical techniques.

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The Crystal Structure of a Brominated Carborane-Metal Sandwich Compound, $N(CH_3)_4[(B_9C_2H_8Br_3)_2Co]$[1]

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The crystal structure of the tetramethylammonium salt of bis-π-(5,9,10-tribromo-(1)-2,3-dicarbollyl)cobalt(III), $N(CH_3)_4[(B_9C_2H_8Br_3)_2Co]$, has been determined by an X-ray diffraction study of a single-crystal specimen. The monoclinic unit cell, space group $P2_1/c$, with $a = 19.893 \pm 0.010$ Å, $b = 19.487 \pm 0.010$ Å, $c = 15.058 \pm 0.010$ Å, and $\beta = 93.15 \pm 0.05°$, contains eight formula units and four crystallographically independent anions. The calculated density is 1.967 g/cm^3, in agreement with the measured value of 1.98 ± 0.01 g/cm^3. The structure was solved by statistical methods and refined by a least-squares procedure to a conventional *R* of 8.7% on 3002 data collected by counter methods. All four independent anions have the same shape to within the accuracy of this determination. The anion, the product of a bromination during which the bis(dicarbollyl)cobalt "sandwich" is believed to remain intact, consists of two substituted icosahedra with the cobalt as their common vertex. In each icosahedron, the carbons are adjacent to each other and to the cobalt, while the three borons bonded to bromine form the corners of a triangular face. Two corners of this face are as far as possible from the carbons, and the third is adjacent to the cobalt. These bromination sites are consistent with a charge distribution in the reactant which is analogous to that in o-$B_{10}C_2H_{12}$ but modified slightly by the presence of the Co(III).

Introduction

Hawthorne and coworkers[3-8] have recently synthesized a number of π-dicarbollylmetal compounds analogous to the π-cyclopentadienyl "sandwich" compounds. They found[8,9] that one of these substances, $Co(B_9C_2H_{11})_2^-$, could be electrophilically brominated by treatment with neat bromine or bromine in glacial acetic acid to give $Co(B_9C_2H_8Br_3)_2^-$. This is thought[9] to be the first example of a substitution upon the intact bis(dicarbollyl)metal "sandwich" compound.

This determination of the crystal structure of the tetramethylammonium salt of the product ion once again establishes the bis(dicarbollyl)metal structure as two icosahedra with the metal atom as their common vertex. This work was undertaken in order to ascer-

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

(2) National Science Foundation graduate fellow.

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