configuration. This would imply that for the *S* ligand, Co-A and Cr-A have the same configuration and also Co-B and Cr-B have identical configurations. An analogous relationship exists between Co-A′ and Cr-A′ and between Co-B′ and Cr-B′, where the ligand has the *R* configuration.

Although the ligand field absorption band of the chromium(III) complex is ~1500 cm^{-1} toward higher energy than that of the cobalt(III) complex, isomers B and B′ for both metals have larger ϵ_M values than isomers A and A′. Co-A and Cr-A both show positive CD's at the low-energy end of the absorption; Co-B and Cr-B both show stronger, negative CD's at this energy. Similarly, Co-A′ and Cr-A′ both have negative CD's whereas Co-B′ and Cr-B′ show stronger, positive CD's. Other pairs of tris cobalt(III) and chromium(III) complexes for which isomers believed to have the same absolute configuration show similar CD curves (the transition for chromium(III) occurring at higher energy in each case) include those of ethylenediamine, 1,2-propanediamine,[6] and acetylcamphor.[7] An exception to this behavior has been found for the tris-biguanide complexes.[8]

The above arguments strongly suggest but do not prove that the chromium(III) and cobalt(III) diastereomers showing parallel chromatographic behavior have identical absolute configurations. The B and B′ isomers were shown[1] to be thermodynamically more stable than A and A′ for cobalt(III). However the chromium(III) isomers for a given ligand are formed in essentially the statistical 1:1 ratio, and no isomerization can be detected by tlc after refluxing chloroform solutions of the isomers for 24 hr in the presence of charcoal.

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The Crystal Structure of High-Pressure Synthesized Holmium Diantimonide

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The synthesis of the rare earth diantimonides, with the exception of EuSb$_2$, has been previously reported.[1-3] Up to and including SmSb$_2$, the synthesis is conventional; the structure is of the LaSb$_2$ type.[1] For Gd and Tb, this structure type, along with a new structure type, is synthesized *via* high pressure.[2] This second type, which has been found for Gd through Lu with the exception of Yb, has been reported to be orthorhombic with two molecules per unit cell.[2,3]

TABLE I

OBSERVED AND CALCULATED POWDER PATTERN OF HoSb$_2$

Pseudo-hexag-onal indices	Ortho-rhombic indices	*d*, Å		*I*	
		Calcd	Obsd	Calcd	Obsd
001	001	7.840	. . .	1	. . .
002	002	3.920	. . .	1	. . .
100	110 020	2.895	2.89	15	w
101	111 021	2.716	2.709	100	vs
003	003	2.613	2.608	35	m
102	112 022	2.329	2.327	81	s
004	004	1.960	. . .	0	. . .
103	113 023	1.940	1.939	17	w
110	200 130	1.671	1.669	7	vw
111	201 131	1.635	1.634	48	m
104	114 024	1.623	1.624	48	m
005	005	1.568	. . .	1	. . .
112	202 132	1.538	1.539	42	m
200	220 040	1.448	1.447	43	m
201	221 041	1.423	. . .	1	. . .
113	203 133	1.408	1.405	10	vw
105	115 025	1.378	1.378	34	m
202	222 042	1.358	. . .	2	. . .
006	006	1.307	1.307	12	w
114	204 134	1.272	1.270	30	m
203	223 043	1.266	1.266	65	m+

In an attempt to determine, by single-crystal methods, the structure of this apparently new type, we have prepared HoSb$_2$ using high-pressure techniques.

Experimental Section

Holmium, filed in an inert atmosphere, was mixed with antimony in a 1:2 gram-atom ratio. This mixture was then subjected to 65 kbars and 1000° for 5 hr in a girdle–anvil device. Powder patterns were compared with the published LuSb$_2$ pattern to establish whether the synthesis was successful. Not all of the lines of LuSb$_2$ were present in patterns for several preparations of HoSb$_2$. Debye–Scherrer techniques (λ(Cu Kα_1) 1.54050 Å) were used throughout this investigation because the expected single crystals did not materialize.

Results and Discussion

The orthorhombic indexing of Eatough and Hall was suspected to be incorrect. As one piece of evidence, the d_o–d_c comparison is unsatisfactory. Secondly, it was noted that the published cell parameter *a* could not be obtained from the reported pattern and indexing. It is in error by 0.1 Å. Finally, while some of our patterns exhibited the line corresponding to the first line of the LuSb$_2$ pattern, it was missing in others. Suspecting the LuSb$_2$ pattern to be a two-phase pattern, we have worked with patterns which did not show this line. A satisfactory hand indexing was accomplished for a hexagonal cell with a = 3.33 Å and c = 7.83 Å. Since this volume is sufficient for only one molecule of

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$HoSb_2$, it is an easy matter exhaustively to check all possible structures. No ordered structure which gave reasonable intensity agreement was found for this cell. A disordered model which gave good agreement led to an ordered structure in a larger pseudoorthohexagonal cell. The unit cell parameters are $a = 3.343 \pm 0.001$ Å, $b = \sqrt{3}a = 5.790 \pm 0.001$ Å, and $c = 7.840 \pm 0.002$ Å with $Z = 2$ and a density of 8.94 g/cm^3. Atomic positions, using space group $C222$, are as follows: Ho, 2a (0, 0, 0); Sb, 4k ($^1/_4$, $^1/_4$, 0.34). The value of z for Sb was chosen to make $d_{Ho-Sb}/(r_{Ho} + r_{Sb}) = d_{Sb-Sb}/2r_{Sb}$ using the radii of Teatum, Gschneidner, and Waber.[4]

The calculated powder pattern, using a cylindrical absorption correction ($\mu r = 19.2$), temperature factors of $B = 1.0$ Å^2, and the program of Smith,[5] is listed together with the observed pattern in Table I. The structure of $HoSb_2$ is shown in Figure 1; distances are given in Table II.

TABLE II

DISTANCES IN $HoSb_2$ (Å)

Ho	4 Sb	3.15	Sb	2 Sb	3.02
	6 Ho	3.34		2 Ho	3.15
				6 Sb	3.34

We are well aware of the fact that the structure presented may indeed be only a subcell of the true structure. As stated earlier, single crystals were not obtained; thus we must infer, in view of the excellent intensity fit, that this structure is at least qualitatively correct and definitely represents an improvement over the earlier work. Unit cell constants for Gd–$TmSb_2$ cannot be determined by us because no data for these have been published. Cell constants have been determined for $LuSb_2$ using the published pattern, this structure, and a least-squares program. The values are $a = 3.3211 \pm 0.0005$ Å, $b = 5.7521 \pm 0.0009$ Å, and $c = 7.782 \pm 0.001$ Å. The calculated density is 9.35 g/cm^3. It is noted that these cell constants are in disagreement with those of Eatough and Hall by less than 3%. These differences are, however, from 12 to 19 times the standard errors given by them.

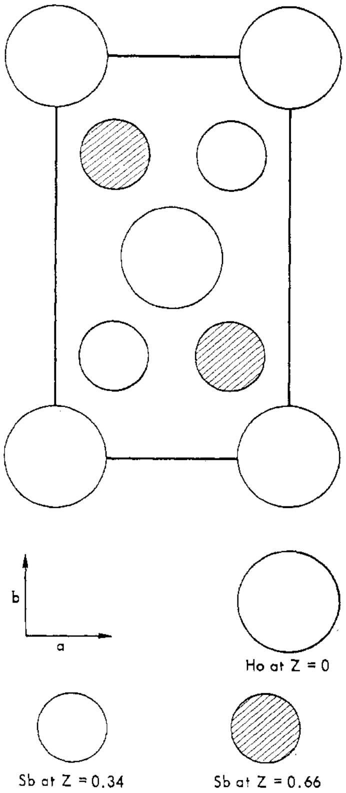

Figure 1.—Crystal structure of $HoSb_2$.

This structure accurately accounts for the published pattern of $LuSb_2$ in regard to intensities as well as d spacings. Two lines are, however, not accounted for by this structure; they are at $d_1 = 3.09$ and $d_2 = 1.551$. We have not established what these lines come from but note that they probably belong to the same impurity since $d_1 = 2^*d_2$.

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