

numerical results which are of the right order of magnitude, as previously observed for other ionic equilibria,³ and we confirm that the pressure chromism of blue CoCl_2 solutions arises from the shift in equilibrium 1 toward increased octahedral species favored by the free energy of ion solvation.

The thermodynamic analysis in alcoholic solutions is considerably more difficult. Ewald and Hamann,¹⁵ who first studied this equilibrium in isopropyl alcohol under pressure, were unable to relate the decrease in absorbance at 6600 Å to the variation of K with pressure. More recently, Kitamura¹⁶ measured this equilibrium in several alcohols to 10 kbars, but his data analysis led him to suspiciously high volume changes ($\Delta V \approx 150$ – $500 \text{ cm}^3/\text{mol}$) for primary alcohols ($n = 2$ in eq 1). The principal difficulty in obtaining accurate ΔV values appears to arise from the uncertainty in the variation of K with pressure, because nearly half of Co(II) possesses a tetrahedral coordination sphere in $\sim 10^{-3} m$ CoCl_2 solutions and the absorption due to (o) is not observed at any pressure. We measured ΔV from the initial slope of $\ln K$ vs. P plots in ethanol to be 45 (25°), 40 (40°), and 30 cm^3/mol (60°). The substantial volume change can be explained by the Born formula to give $\Delta V = 54 \text{ cm}^3/\text{mol}$ at 25° , assuming $n = 2$ ¹¹ and $R = 3.7 \text{ \AA}$ for $\text{Co}(\text{CH}_3\text{CH}_2\text{OH})_6^{2+}$.¹⁶ The values are larger than in water because the factor $\epsilon^{-2}d\epsilon/dP$ (eq 2) is nearly 5 times greater for ethanol. However the temperature dependence of ΔV is opposite to what is predicted from $\epsilon(T)$. This discrepancy cannot be resolved with the available information, and the agreement at room temperature may be fortuitous. Kitamura¹⁶ observed the pressure effect to be strongly dependent on the molecular structure of the alcohols, which also implies that absorbance measurements are insufficient to obtain ΔV by eq 2 for one particular equilibrium and that it is futile to speculate about the microscopic behavior of solvated ions in nonaqueous solutions under pressure.

(15) A. H. Ewald and S. D. Hamann, *Aust. J. Chem.*, **9**, 54 (1956).

(16) Y. Kitamura, *Rev. Phys. Chem. Jap.*, **39**, 1 (1969).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY OF KANSAS, LAWRENCE, KANSAS 66044

The Diastereomers of Tris[*N*-(*R* or *S*)- α -benzylethyl- 5-nitrosalicylaldiminato]chromium(III)

BY JUDY E. GRAY AND G. W. EVERETT, JR.*

Received January 25, 1971

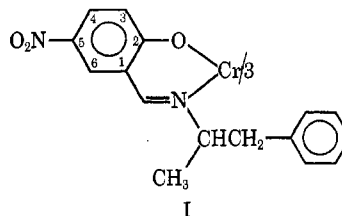
A recent publication from this laboratory described the preparation and diastereomer separation of tris[*N*- α -benzylethyl-5-nitrosalicylaldiminato]cobalt(III), where the α -benzylethyl substituent may have either the *R* or the *S* configuration.¹ For ligands of a given chirality, four diastereomeric complexes are possible, namely, Δ -trans, Λ -trans, Δ -cis, and Λ -cis.² However,

(1) K. S. Finney and G. W. Everett, Jr., *Inorg. Chem.*, **9**, 2540 (1970).

(2) Δ and Λ refer to right- and left-hand helicity about the C_3 or pseudo- C_3 axis as recommended by IUPAC, *ibid.*, **9**, 1 (1970).

only the trans isomers were found in each case; these showed CD curves of opposite sign in the ligand field region.

In this note are presented the results of our stereochemical investigation of the analogous chromium(III) complexes, tris[*N*- α -benzylethyl-5-nitrosalicylaldiminato]chromium(III), I, where the α -benzylethyl group is *R* or *S*.



Experimental Section

The complexes were prepared by Yamada's general method³ using either (*R*)- α -benzylethylamine ($[\alpha]_D^{25} -32.8^\circ$) or (*S*)- α -benzylethylamine ($[\alpha]_D^{25} +33.0^\circ$). 5-Nitrosalicylaldehyde was prepared according to the procedure given by Miller.⁴ Products from the complexation reactions were chromatographed on $20 \times 20 \text{ cm}$ preparative thin layer plates having a 2-mm layer of silica gel. Diastereomer separation was achieved using the solvents and techniques employed earlier for the corresponding cobalt(III) complexes.¹ An initial elution with chloroform was followed by several elutions using a 1:4 (by volume) toluene-chloroform mixture. The separated isomers were removed from the silica gel with chloroform and then recrystallized at least once from chloroform by dropwise addition of heptane. Results of elemental analyses, obtained from an F & M Model 185 C, H, and N analyzer, are given in Table I.

ORD and CD spectra were recorded at $\sim 25^\circ$ on a Cary 60 spectropolarimeter. Absorption spectra were obtained using a Cary 14 spectrophotometer, and optical rotations at 589 m μ were measured on a Perkin-Elmer 141 automatic polarimeter.

Results

Tris[*N*-(*S*)- α -benzylethyl-5-nitrosalicylaldiminato]chromium(III).—Three tlc bands resulted from chromatography of the product from the chelation reaction. The most slowly moving band is yellow and was proven by nmr to consist of free ligand. The other bands are brown, and samples isolated from these bands are designated hereafter as isomers A and B in order of increasing rate of elution. The visible absorption and CD spectra of both isomers are shown in Figure 1; the corresponding ORD curves are presented in Figure 2. The CD spectra of A and B are dominated by positive and negative Cotton effects, respectively, at the low-energy portion of the absorption, $\sim 17,400 \text{ cm}^{-1}$. These molecules and their cobalt(III) analogs have four chiral centers, one on each ligand and one at the metal atom. The CD spectra demonstrate that A and B differ in configuration about the metal atom. Since they contain ligands of identical chirality, A and B are diastereomers (epimers). Their CD curves are expected to be of opposite sign in the visible region, but these curves are not expected to be enantiomeric.

Tris[*N*-(*R*)- α -benzylethyl-5-nitrosalicylaldiminato]chromium(III).—Chromatographic behavior of this complex is the same as for the complex having the *S* ligand. The isomers are designated A' and B' in order of increasing rate of elution. A' and B' show negative and positive Cotton effects, respectively, at $\sim 17,400 \text{ cm}^{-1}$. Therefore they differ in helicity and are dia-

(3) S. Yamada and K. Iwasaki, *Bull. Chem. Soc. Jap.*, **41**, 1972 (1968).

(4) W. v. Miller, *Ber.*, **20**, 1927 (1887).

TABLE I
 CHARACTERIZATION OF THE INDIVIDUAL DIASTEREOMERS

Tlc band	Complex	% calcd			% found			Visible CD max, cm ⁻¹ ($\Delta\epsilon$)
		C	H	N	C	H	N	
A	Cr((<i>S</i>)-BzEt-5-NO ₂ sal) ₃	63.92	5.03	9.32	63.28	5.32	9.07	17,390 (2.42)
B	Cr((<i>S</i>)-BzEt-5-NO ₂ sal) ₃				63.24	5.10	9.01	17,240 (-4.36)
A'	Cr((<i>R</i>)-BzEt-5-NO ₂ sal) ₃				63.32	5.06	9.42	17,390 (-2.82)
B'	Cr((<i>R</i>)-BzEt-5-NO ₂ sal) ₃				63.44	5.04	9.03	17,390 (4.18)

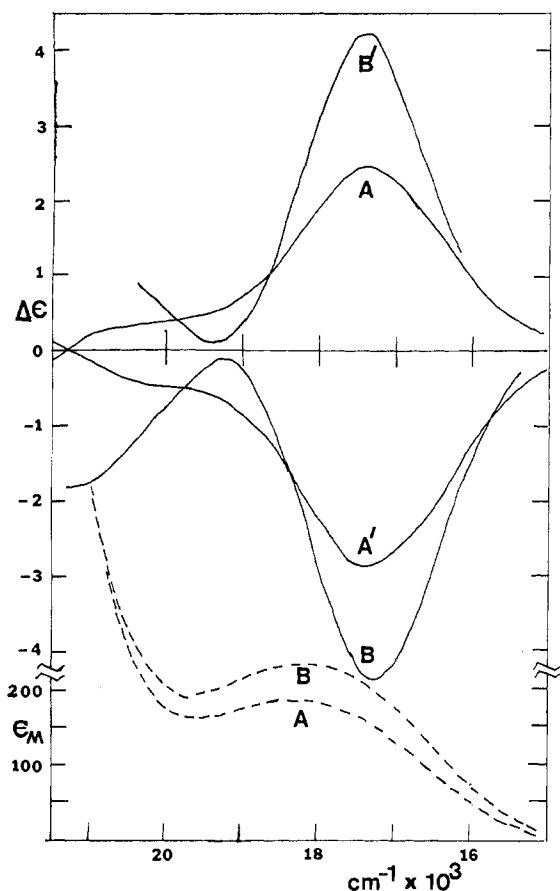


Figure 1.—Circular dichroism and absorption spectra of chromium(III) diastereomers in dichloromethane solution. See text for explanation of labels.

stereomers analogous to A and B. Absorption spectra of A' and B' are identical with those of A and B, respectively.

The CD spectra show that A and A' have opposite configurations about the metal atom. A and A' differ also in ligand chirality and thus are enantiomers. The same is true also of isomers B and B'. This is clearly evident in the mirror image character of the ORD and CD curves of A and A' and of B and B'.

Discussion

The symbols A, B, A', and B' used here parallel those used for the analogous cobalt(III) complexes earlier;¹ *i.e.*, the more rapidly eluted cobalt(III) isomer having the *S* ligand was designated as isomer B. No attempt was made to assign absolute configurations to the cobalt complexes A, B, A', and B', since no information is presently available relating CD spectra and absolute configurations of chiral cobalt(III)-salicylaldimine complexes. For similar reasons, no attempt is made here to assign absolute configurations to the chromium(III) isomers. However we feel that several lines of evidence indicate that the chromium(III) complexes A,

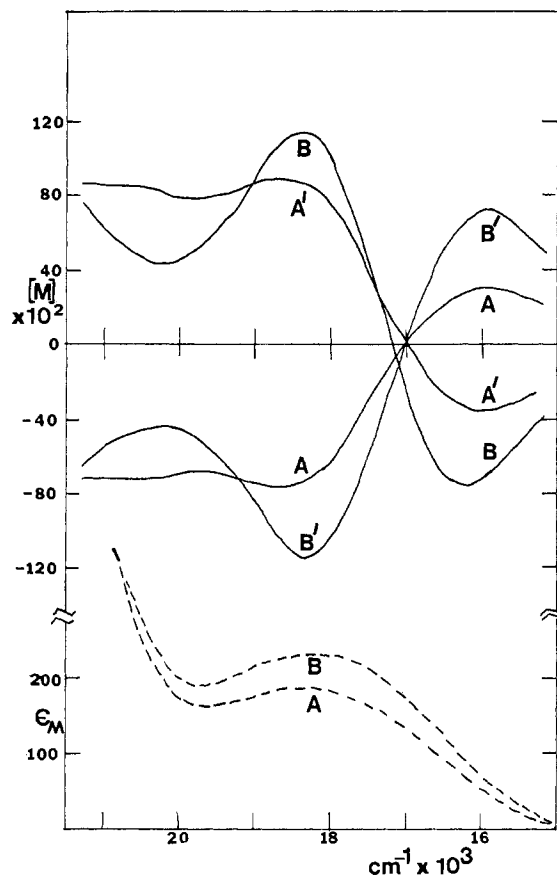


Figure 2.—Optical rotatory dispersion and absorption spectra of chromium(III) diastereomers in dichloromethane solution. See text for explanation of labels.

B, A', and B' have the *same* configurations as the cobalt(III) complexes A, B, A', and B', respectively.

Pmr spectra of the cobalt(III) isomers demonstrated they all have *trans* geometry. The apparent absence of *cis* isomers may be explained by steric considerations; a molecule with three bulky nitrogen substituents on the same octahedral face would be highly strained.^{1,5} The same argument holds for the chromium(III) complexes, and although distinction between *cis* and *trans* isomers is not possible by pmr for chromium(III), it is entirely reasonable to assume the isomers reported here all have *trans* geometry (*C*₁ point group).

Dia stereomers of the chromium(III) and cobalt(III) complexes were separated using the same solvents and adsorbent. The polarities of cobalt(III) and chromium(III) complexes of identical ligands are expected to be very similar if the complexes have the same absolute configuration. Under identical chromatographic conditions the relative rates of elution of the chromium(III) diastereomers should parallel those of the cobalt(III) diastereomers having the same absolute

(5) B. O. West, *J. Chem. Soc.*, 4944 (1960).

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 $\sim 1500\text{ cm}^{-1}$ 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 shown¹ 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.

Acknowledgment.—Support for this research has been provided by the University of Kansas General Research Fund and by the National Science Foundation under Grant GP-19877.

(6) (a) A. J. McCaffery, S. F. Mason, and R. E. Ballard, *J. Chem. Soc. A*, 2883 (1965); (b) A. J. McCaffery, S. F. Mason, and B. J. Norman, *Chem. Commun.*, 49 (1965).

(7) (a) R. M. King and G. W. Everett, Jr., *Inorg. Chem.*, **10**, 1237 (1971); (b) W. DeW. Horrocks, Jr., D. L. Johnston, and D. MacInnes, *J. Amer. Chem. Soc.*, **92**, 7820 (1970).

(8) G. R. Brubaker and L. E. Webb, *ibid.*, **91**, 7199 (1969).

CONTRIBUTION FROM THE LAWRENCE RADIATION LABORATORY,
UNIVERSITY OF CALIFORNIA, LIVERMORE, CALIFORNIA 94550

The Crystal Structure of High-Pressure Synthesized Holmium Diantimonide

BY QUINTIN JOHNSON

Received February 5, 1971

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

(1) R. Wang and H. Steinfink, *Inorg. Chem.*, **6**, 1685 (1967).

(2) N. L. Eatough and H. T. Hall, *ibid.*, **8**, 1439 (1969).

(3) N. L. Eatough and H. T. Hall, *ibid.*, **9**, 416 (1970).

TABLE I
OBSERVED AND CALCULATED POWDER PATTERN OF HoSb_2

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

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}

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 ($\lambda(\text{Cu K}\alpha_1)$ 1.54050 \AA) 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_e 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 \AA . 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 $a = 3.33 \text{\AA}$ and $c = 7.83 \text{\AA}$. Since this volume is sufficient for only one molecule of