tained small peaks attributable to BiF_2O^+, BiF_3O^+, and $Bi_2F_8O^+$ (~0.1% of BiF_4^+ peak) and a variable amount of unidentified organic material which appeared to arise from reaction with residuals in the instrument since some of these peaks also resulted when other reactive solids such as NO_2ClO_4 were being analyzed. A series of spectra on one BiF_5 sample at nominal ionizing voltages of 15, 20, 25, and 30 eV and the use of CO_2^+ and SiF_3^+ peaks[20] as internal standards indicated that the BiF_4^+ and $Bi_2F_9^+$ ions both have appearance potentials of 14.5–15 eV while that of the BiF_3^+ ion was about 12 eV.

Antimony Pentafluoride.—A sample of SbF_5 was examined at 30, 80, 90, and 110°. The initial spectra were surprisingly complex and indicated the presence of mono- and diantimony species in which one or more F atoms were substituted by Cl or OH, such as SbF_3Cl^+ and $Sb_2F_5ClOH^+$. The diisotopic nature of both Sb and Cl and the overlap of mass peaks of different species prevented complete identification. These impurity peaks decreased substantially upon pumping and warming. The spectrum of SbF_5 as recorded at 90–110° and 70 eV is shown in Table I.

Acknowledgment.—The assistance of Dr. Robert Rowatt and Mr. Yukio Mizumoto in preparing the samples and of Mr. George Vaughn in obtaining the spectra is gratefully acknowledged.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA,
SANTA BARBARA, CALIFORNIA 93106

Pressure Effects on the Absorbance of Cobaltous Chloride Solutions[1a]

BY SILVIO RODRIGUEZ[1b] AND HENRY OFFEN*

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In 1923 Wick[2a] observed a marked pressure-induced change in the color of aqueous solutions of $CoCl_2$. Lüdemann and Franck[2b] made a detailed study of the pressure chromism of these aqueous solutions, with and without added salt, in the ranges 25–500° and 1–6000 atm. The color change was attributed to modification of the equilibrium between Co(II) species in octahedral (o) and tetrahedral (t) coordination[3]

$$CoS_6^{2+} + nCl^- \rightleftarrows CoS_{4-n}Cl_n^{2-n} + (2 + n)S \qquad (1)$$

where S is the solvent and $0 \leq n \leq 4$, depending on the chloride ion concentration. Since the number of ions changes in this complex equilibrium, a strong pressure dependence of the equilibrium constant is anticipated due to ion–solvent interactions. The pressure parameter yields the volume change $\Delta V = -RT\text{d} \ln K/\text{d}P$ for the reaction. The objective of the present high-pressure spectrophotometric study is to ascertain the extent to which ion solvation and electrostriction are responsible for the observed pressure chromism of Co(II) solutions.

The high-pressure optical cell used for solid samples[4] was modified to accept liquids in plastic capsules. The cell and press fit into the sample compartment of a Cary Model 14 spectrophotometer. The pressure was calibrated by means of reversible phase transitions in chlorobenzene (4.6 kbars)[5] and bromobenzene (3.3 kbars)[6] and by comparison of the L_a absorption shift of anthracene in pentane (to 6 kbars) with the shift measured by Robertson, *et al.*[7] The advantage of this apparatus is its simplicity, although the error in absorbance measurements is greater than for conventional optical bombs designed for fluids.

The $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition of $Co(H_2O)_6^{2+}$, which is responsible for the pink color (λ 5120 Å) of aqueous solutions, is largely insensitive to pressure and temperature.[2b] The blue color (λ ~6600 Å) of aqueous solutions with excess halide is assigned to $^4A_2(F) \rightarrow {}^4T_1(P)$ of the tetrahedrally coordinated Co(II). While the extinction coefficient ϵ of tetrahedral species in crystalline Cs_2CoCl_4 decreases sharply at very high pressures,[8] the best guess for solutions at relatively low pressures is that the transition probability of $CoCl_3H_2O^-$ and $CoCl_2(H_2O)_2$ is independent of pressure.[2b] With this assumption the observed pressure decrease of the absorbance near 6600 Å can be related directly to the shift in equilibrium 1. Since $\epsilon_{6600} \approx 100\epsilon_{5120}$, experimental conditions can be easily achieved in which (o) > (t) and $\ln A_{6600} \approx \ln K$.[9,10] This approximation leads to $\Delta H = 10$ kcal/mol which is in essential agreement with earlier measurements.[9,10] The initial slope of the linear plot of $\ln A_{6600}$ *vs.* P gives reasonable ΔV values of 8 (0°), 16 (25°), and 24 cm³/mol (50°) for 0.5 *m* $CoCl_2$ and 4 *m* LiCl. The observed decrease in ΔV at higher pressures is greater than normally observed for chemical equilibria,[3] so that the results must be viewed with caution. Multiple equilibria and changes in ϵ with pressure can invalidate the equality $K(P) \approx A_{6600}(P)$. Until these effects are determined independently, the $\Delta V(P)$ behavior cannot be ascribed to an unusually high compressibility of the ions.

Effects of electrostriction make the largest contribution to the volume change of ionic equilibria[3]

$$\Delta V = -\sum_i (Q_i^2/2R_i)(\epsilon^{-2}\text{d}\epsilon/\text{d}P) \qquad (2)$$

where ϵ is the dielectric constant, Q is the total charge of the ion of radius R, and the summation refers to all ionic products and reactants (opposite sign). It is clear that the application of the Born formula depends critically on the value of n in eq 1. If we choose $n = 3$ in aqueous, concentrated salt solutions,[2b,11–13] eq 2 yields ΔV values of 10 (0°), 15 (25°), and 19 cm³/mol (50°), assuming the temperature dependence is entirely due to $\epsilon(T)$ and estimating R to be 2.2 Å for the octahedral species, 1.8 Å for Cl^-, and 2.3 Å for the tetrahedral species.[14] Thus the Born formula gives

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[1] (a) This work was supported by the Cancer Research Coordinating Committee (University of California) and the U. S. Office of Naval Research. (b) University of Chile-University of California Cooperative Program Fellow.

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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, Kitamura[16] 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 cm^3/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 $\Delta V = 54$ cm^3/mol at 25°, assuming $n = 2^{11}$ and $R = 3.7$ Å for $Co(CH_3CH_2OH)_6{}^{2+}$.[16] The values are larger than in water because the factor $\epsilon^{-2}\mathrm{d}\epsilon/\mathrm{d}P$ (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. Kitamura[16] 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.

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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.*

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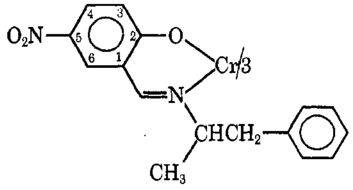
A recent publication from this laboratory described the preparation and diastereomer separation of tris(*N*-α-benzylethyl-5-nitrosalicylaldiminato)cobalt(III), where the α-benzylethyl substituent may have either the *R* or the *S* configuration.[1] For ligands of a given chirality, four diastereomeric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



I

Experimental Section

The complexes were prepared by Yamada's general method[3] using either (*R*)-α-benzylethylamine ($[\alpha]^{25}\mathrm{D}$ $-32.8°$) or (*S*)-α-benzylethylamine ($[\alpha]^{22}\mathrm{D}$ $+33.0°$). 5-Nitrosalicylaldehyde was prepared according to the procedure given by Miller.[4] Products from the complexation reactions were chromatographed on 20 × 20 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 ~25° on a Cary 60 spectropolarimeter. Absorption spectra were obtained using a Cary 14 spectrophotometer, and optical rotations at 589 mμ 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, ~17,400 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 ~17,400 cm^{-1}. Therefore they differ in helicity and are dia-

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