

since the effect was absent with such samples equilibrated below 721° and then cooled or with samples not containing excess metal. The additional 652° point was properly detected over a range of compositions and appears to be the result of a phase transformation in DyCl₂. The high-temperature form could not be quenched to room temperature.

The freezing point depression of DyCl₃ for dilute solutions of metal is quite consistent with the presence of an oxidation-reduction reaction on metal "solution" which produces monomeric Dy²⁺ ions. In fact, the solutions appear nearly ideal, and the entropy of fusion of DyCl₃ which would make the data up to even 10 mole % Dy (30% Dy²⁺) consistent with this model is close (6.4–6.7 eu) to the 6.8 eu extrapolated from known values for the neighboring HoCl₃ and ErCl₃.¹¹

The two stable lower chloride phases are both black, electrically insulating, and highly susceptible to attack by air. The stoichiometry DyCl_{2.11±0.02} for the higher one was estimated on the basis of X-ray powder patterns of equilibrated mixtures plus the liquidus composition at its melting point as an upper limit. Patterns at DyCl_{2.12} and DyCl_{2.09} were those of this phase, DyCl_{2.08}, a mixture, and DyCl_{2.02}, that of DyCl₂. The two phases give somewhat similar patterns and are presumably related by a 3Dy²⁺ = 2Dy³⁺ substitution. The low-temperature form of DyCl₂ is isostructural with YbCl₂ as reported by Döll and Klemm,¹² with lattice constants derived for the same orthorhombic symmetry of *a*₀ = 6.69 Å, *b*₀ = 6.76 Å, *c*₀ = 7.06 Å, 0.08 to 0.15 Å larger than given for YbCl₂.

The saltlike character of DyCl₂, its relationship to the known YbCl₂, and the cryoscopic evidence given above leave little doubt that the compound is properly considered as a simple dysprosium(II) salt. It is unfortunate that magnetic data cannot be expected to confirm the presence of Dy²⁺ because of the near coincidence of the theoretical moments for Dy³⁺ and Dy²⁺ (Ho³⁺), 10.63 and 10.60 BM, respectively.¹³

The relatively substantial reduction demonstrated for dysprosium(III) is followed by a lesser amount reported for holmium (18.5% or HoCl_{2.44}),⁹ a more limited reaction of Er with ErCl₃ (5%),⁸ and then by a greatly enhanced stability of thulium(II) (at least as TmI₂⁷) and ytterbium(II). Consequently, there is little resemblance of reduction tendencies of the heavy half of the lanthanides to the simple regularity found in the first half. Nonetheless, it appears that the extent of reduction of all of these elements can be rather simply interpreted in terms of the prime importance of the enthalpy of sublimation of the metals themselves, with small variation in the known ionization energies being of secondary importance.⁸ Thus, in the present case it is the relatively low Δ*H*_{sub}^o of dysprosium metal which appears principally responsible for the relatively ready reduction.

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Proton Magnetic Resonance Spectra of Aqueated Bis(ethylenediamine)cobalt(III) Ions

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Although the bis(ethylenediamine)cobalt(III) complex ions have been of considerable interest in the study of reaction mechanisms and bonding of octahedral complexes, they have been examined only briefly with nuclear magnetic resonance techniques.^{1–3}

The amino proton peaks of bis(ethylenediamine)cobalt(III) complexes appear in the same spectral range as the water peak and hence are difficult to observe. Clifton and Pratt¹ used deuterium oxide as solvent and noted the gradual disappearance of the amino peaks as the attached protons are replaced by deuterium. Recently Jolly, Harris, and Briggs⁴ reported nmr examination of some of the ammine complexes of cobalt(III) in concentrated sulfuric acid. This was attempted with bis(ethylenediamine) complexes, but it was found that rapid oxidation of the ligands ensued. However, it was discovered that a given amino peak could be made visible by a judicious increase of the acidity to shift the water peak downfield; solutions up to 8 *M* in sulfuric acid were successfully used although it was found that use of perchloric acid resulted in better resolution. Deuterium oxide was also employed when desirable although again the HDO peak tended to obscure one or more of the amino proton peaks in acidic solution. In neutral or basic solutions, the amino peaks disappear completely because of rapid exchange of the amino and water protons.⁵

The nmr spectrum of the highly symmetrical *trans*-diaquobis(ethylenediamine)cobalt(III) ion in acidic solution consists of two broad singlets at 1.88 and 4.58 ppm downfield from *t*-butyl alcohol used as an internal standard, with the former assigned to the eight methylene and the latter to the eight amino protons (Figure 1A). The observed broadening of the amino peaks is anticipated because of nuclear quadrupole relaxation effects⁶ while broadening of the methylene proton peaks is due to a slight degree of coupling with the amino protons. The broadening is gradually eliminated in deuterium oxide solution, and the amino peak disappears as the amino protons are replaced by deuterium.

The position of the methylene proton peak is pH-dependent, varying from 1.88 ppm at pH 4 or below to 1.58 ppm at pH 9 or above. The change in the chemical shift corresponds to the ionization of the diaquobis-

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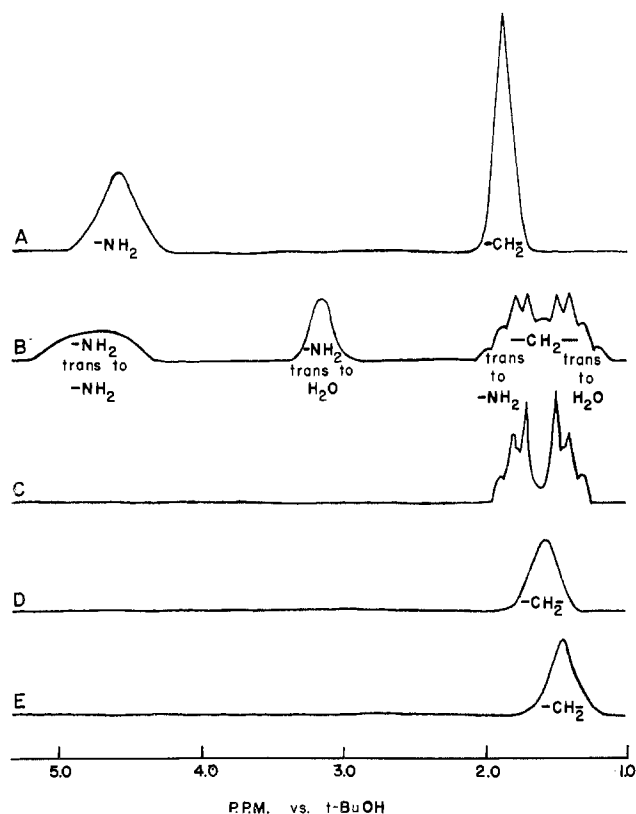


Figure 1.—Pmr spectra of $0.8 M$ $[\text{Co}(\text{en})_2(\text{H}_2\text{O})(\text{OH})](\text{ClO}_4)_2$ with *t*-butyl alcohol as reference standard: A, *trans* in $2 M$ HClO_4 ; B, *cis* in $2 M$ HClO_4 ; C, *cis* in $2 M$ D_2SO_4 ; D, *trans* in $1 M$ KOH ; E, *cis* in $1 M$ KOH . The H_2O peak is omitted for simplicity.

(ethylenediamine)cobalt(III) ion to produce the aquo-hydroxo and dihydroxo species, a process for which the ionization constants have been reported to be $10^{-4.45}$ and $10^{-7.94}$, respectively.⁷ It is not known whether to ascribe the pH dependency of the chemical shift to the increase in electron density associated with deprotonation or to a change in magnetic anisotropy or both. Increase in pH also causes a slight further broadening of the methylene peak due to exchange of the amino protons (Figure 1D). In deuterium oxide, the methylene peak becomes sharp.

Attempts to determine the two ionization constants of the diaquobis(ethylenediamine)cobalt(III) ion by correlating the chemical shift of the methylene protons with pH were unsuccessful. Difficulties were encountered due to low solubility of the aquo-hydroxo species, rapid isomerization in the intermediate pH range,⁷ smearing of peaks due to mixtures of species and exchange broadening, and insufficient change in chemical shift in relation to the reproducibility of the determination.

The spectrum of the *cis* ion is somewhat more complicated since neither the amino nor the methylene protons are equivalent. Two of the four nitrogen atoms are situated *trans* to oxygen atoms while the other two are *trans* to each other. The resulting nonequivalence is transmitted to the adjacent methylene protons which

are represented, in acidic solution, by two identical overlapping quintets with centers at 1.42 and 1.82 ppm (Figure 1B). By analogy with the *trans* compound, the downfield peak is assigned to the methylene protons *cis* to both oxygen atoms. The five lines of each quintet are caused by coupling with the two protons which are on the adjacent carbon and the two which are on the nitrogen atom, with both coupling constants about 5.6 cps. This is in agreement with the findings of Anderson and Silverstein for amine salts.⁸

If deuterium oxide is used as solvent with a deuterated acid, two of the lines of each quintet disappear in a few days as a result of slow replacement of the amino protons by deuterium (Figure 1C). The process can be followed quantitatively by observing the areas under the amino proton peaks. The replacement by deuterium can be expedited by making the solution momentarily basic with sodium deuterioxide and then reacidifying.

In basic solution, the peak at low field shifts upfield, as does the single peak of the *trans* species, and coalesces with the second peak. The simultaneous increase in the rate of exchange of the amino protons with solvent water eliminates all spin-spin splitting, and only a broad singlet, at 1.46 ppm, is observed (Figure 1E).

Two broad amino peaks appear downfield. The first, at 3.17 ppm, has an intensity corresponding to four protons and is assigned to the amino groups located *trans* to the oxygen atoms. A broader peak, at 4.7 ppm, has equal intensity and by comparison with the *trans* compound is assigned to the amino groups located *cis* to both oxygen atoms (*trans* to each other). The excessive broadness suggests a possible further differentiation of the four protons due to differences in stereochemical position.

Experimental Section

trans- $[\text{Co}(\text{en})_2(\text{H}_2\text{O})(\text{OH})](\text{ClO}_4)_2$ was prepared by the method of Kruse and Taube;⁹ however, a modification using $[\text{Co}(\text{en})_2(\text{H}_2\text{O})(\text{OH})]\text{Br}_2$ ¹⁰ as starting material was more reliable. Either *cis*, *trans*, or a *cis-trans* mixture of $[\text{Co}(\text{en})_2(\text{H}_2\text{O})(\text{OH})]\text{Br}_2$ may be used as the starting material.

To 10 g of $[\text{Co}(\text{en})_2(\text{H}_2\text{O})(\text{OH})]\text{Br}_2$ dissolved in 15 ml of $2 M$ perchloric acid, an equivalent amount of silver perchlorate was added. After digestion for several minutes, the precipitated silver bromide was filtered off and the pH of the solution was adjusted and maintained between *ca.* 4 and 5 by the dropwise addition of concentrated sodium hydroxide. Fine crystals of the less soluble *trans*- $[\text{Co}(\text{en})_2(\text{H}_2\text{O})(\text{OH})](\text{ClO}_4)_2$ begin to precipitate immediately. The product was collected by filtration, washed with alcohol and ether, then dried at 80° . The compound was further purified by reprecipitation from cold $2 M$ perchloric acid by the addition of concentrated sodium hydroxide; yield 70%.

Solutions of *cis*- $[\text{Co}(\text{en})_2(\text{H}_2\text{O})(\text{OH})](\text{ClO}_4)_2$ were prepared by dissolving the *trans* compound in $2 M$ perchloric acid and by letting the solution stand for 3 days to ensure nearly complete isomerization to the *cis* compound.⁷

Proton magnetic resonance spectra were recorded using a Varian A-60 spectrometer at a temperature of *ca.* 32° , the normal temperature of the probe.

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Solvent Effect on Association in Molten Nitrates. Cadmium(II) and Bromide in Equimolar Lithium Nitrate–Sodium Nitrate¹

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The association constant of cadmium(II) with bromide has been reported from potentiometric measurements in the molten salt solvents sodium nitrate,² potassium nitrate,² and equimolar potassium nitrate–sodium nitrate,³ and in mixtures of lithium nitrate with potassium nitrate.⁴ Measurements have not been possible in lithium nitrate because of the instability and apparent irreversibility of the emf in cells with silver or silver–silver halide electrodes in the solvent lithium nitrate. However, the Helmholtz free energy of association, calculated from the association constants with an equation of the quasi-lattice model of molten salt solutions, $K = Z[\exp(-\Delta A/RT) - 1]$,⁵ has been found to vary linearly with the composition of the solvent in mixed solvents.^{4,6} Hence, an estimate of the Helmholtz free energy of association in lithium nitrate may be obtained by extrapolation of the results obtained in solvent mixtures containing lithium nitrate.

In this note we report measurements of the association constant of cadmium ion with bromide ion in molten equimolar lithium nitrate–sodium nitrate at 240°. The Helmholtz free energy of association, ΔA_1 , is calculated from the association constant, and ΔA_1 in lithium nitrate is obtained by graphical extrapolation and by a least-squares fit of the values of ΔA_1 in sodium nitrate, potassium nitrate, and the mixtures of lithium nitrate with sodium nitrate or potassium nitrate. The estimate is in agreement with the one obtained previously from mixtures of lithium nitrate with potassium nitrate and is discussed in terms of the apparent "radius" of the nitrate ion in molten alkali nitrates.

The association constant for the formation of CdBr^+ in LiNO_3 – NaNO_3 was calculated from measurements of the electromotive force of concentration cells with silver–silver bromide electrodes by methods which have

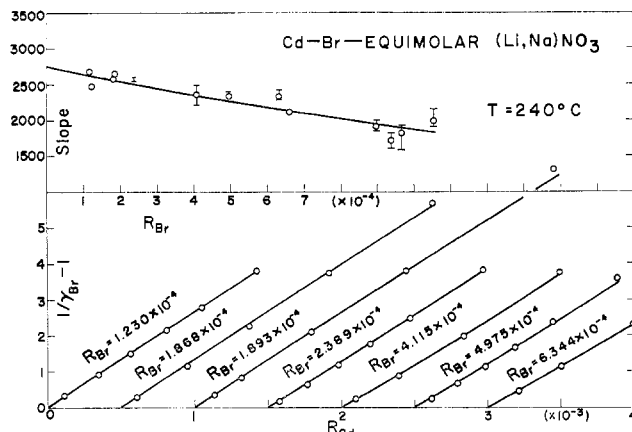


Figure 1.—Lower: $(1/\gamma_{\text{Br}}) - 1$ vs. the mole ratio of $\text{Cd}(\text{NO}_3)_2$ at various fixed mole ratios of $(\text{Li,Na})\text{Br}$ in equimolar LiNO_3 – NaNO_3 at 240°. Upper: Extrapolation of the limiting slopes, $[(\partial \ln (1/\gamma_{\text{Br}})/\partial R_{\text{Cd}(\text{NO}_3)_2})]_{R_{\text{Cd}(\text{NO}_3)_2} \rightarrow 0}$, to infinite dilution of $(\text{Li,Na})\text{Br}$ to obtain the association constant.

been described previously.^{3,4} The electromotive force data are available from the ADI Auxiliary Publications Project.⁷ Representative plots of the function $(1/\gamma_{\text{Br}} - 1)$, calculated from the electromotive force measurements, are shown in the lower half of Figure 1 at various bromide concentrations. γ_{Br} is the stoichiometric activity coefficient of the solute $(\text{Li,Na})\text{Br}$ in the presence of cadmium nitrate.^{3,4} The concentrations are expressed as the mole ratios $R_{\text{Cd}} = n_{\text{Cd}(\text{NO}_3)_2}/n_{(\text{Li,Na})\text{NO}_3}$ and $R_{\text{Br}} = n_{(\text{Li,Na})\text{Br}}/n_{(\text{Li,Na})\text{NO}_3}$, where the n values are the numbers of moles of the components. The upper half of Figure 1 is a plot of the limiting slopes, $\lim_{R_{\text{Cd}} \rightarrow 0} (\partial(1/\gamma_{\text{Br}})/\partial R_{\text{Cd}})_{R_{\text{Br}}}$ vs. R_{Br} , the concentration of bromide. The extrapolated value of this slope is the thermodynamic association constant for the association of cadmium(II) with bromide ion and was found to be $K_1 = 2700 \pm 200$ (moles of nitrate/mole). The Helmholtz free energy of association is $-\Delta A_1 = 6.23$ kcal/mole, calculated from the equation $K_1 = Z[\exp(-\Delta A/RT) - 1]$ with the value of the quasi-lattice coordination number $Z = 6$.

The association constant and Helmholtz free energy of CdBr^+ in equimolar LiNO_3 – NaNO_3 are compared in Table I with previously reported results in the solvents sodium nitrate,² potassium nitrate,² and equimolar sodium nitrate–potassium nitrate,^{2,3} and in mixtures of lithium nitrate and potassium nitrate.⁴ The Helmholtz free energies are plotted, as the circles in Figure 2, as functions of the composition of the mixed solvents. The equations of the three lines were obtained by simultaneously fitting the ΔA values for all of the solvents by the method of least squares, assuming a linear dependence on composition and assigning equal weight to each of the points. The least-squares values and standard deviations of $-\Delta A$ in KNO_3 , NaNO_3 , and LiNO_3

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