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Solute–Solvent Interactions in Some Concentrated Cobalt(II) Bromide Solutions

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The predominant solute species in concentrated aqueous and methanolic $CoBr_2$ solutions differ considerably. In water, the solute is described as $Co(H_2O)_6^{2+}$ with the average Co–O distance being *ca.* 2.1 Å. This solute species has been previously identified for aqueous $CoCl_2$ solutions at comparable concentrations. The predominant solute species in the methanol solution is $CoBr_2(CH_3OH)_2$ with cobalt(II) having approximately tetrahedral nearest neighbor geometry. The Co–Br distance is 2.45 Å, and the Co–O distance is *ca.* 2.0 Å. The highly associated solute species present in $CoCl_2$–alcohol solutions at comparable concentrations is not noted in the $CoBr_2$–CH_3OH solution. The solutions were examined by X-ray diffraction.

Introduction

That the coordination of cobalt(II) is significantly influenced by both solvent and ligand has been shown for both dilute[1-3] and concentrated[4] cobalt(II) chloride solutions. The cation environment is completely different in concentrated aqueous solution when $CoCl_2$ is dissolved in water, in hydrochloric acid, or in alcohols. In water, cobalt(II) is coordinated as $Co(H_2O)_6^{2+}$ with the cobalt(II)–oxygen distance being *ca.* 2.1 Å,[4] and no primary cobalt(II)–chloride bonding occurs. In solutions with excess chloride, $CoCl_4^{2-}$ is the predominant species.[5] In concentrated alcoholic cobalt(II) chloride solutions which contain no excess chloride, cobalt(II) achieves four-chloride, pseudotetrahedral coordination through solute association.[4,6]

In the solid state and in nitromethane solutions,[7] the existence of $CoBr_4^{2-}$ as a slightly distorted tetrahedral species has been substantiated in anhydrous systems which contain $CoBr_2$ plus excess bromide. However, cobalt(II)–bromide bond distances for tetrahedrally or octahedrally coordinated complexes are not readily available in the literature.

Concentrated aqueous and methanol solutions of cobalt(II) bromide were prepared such that the mole fractions of cobalt(II) and bromide are similar in these two solutions and are also similar to the mole fractions of cobalt(II) and chloride in a previous paper.[4] These solutions were examined by X-ray diffraction in an attempt to determine the coordination geometry of the ligand environment of Co(II) as well as to determine appropriate cobalt(II)–ligand bond distances.

Experimental Section

Solutions were prepared from anhydrous $CoBr_2$ and solvent, anhydrous methanol or deionized water, by weight. Densities were measured with a Westphal balance.

X-Ray Techniques.—X-Ray scattering data were obtained with a θ–θ diffractometer[8] and were obtained as count rate *vs.* scattering angle from $s \simeq 0$ to $s = 12.6$ Å^{-1} ($s = 4\pi\lambda^{-1} \sin \theta$). Several runs over this angular range were made. Each run consisted of counting for a preset time at angular increments of 0.6° in 2θ.

The count data were corrected for background (<2 cpm), polarization,[9] and X-ray absorption[10] and were visually scaled to the independent atom scattering factor for the solution. Several scalings were performed for each solution; the validity of each scaling was judged in part by a sensitive integral test.[11] The independent atom scattering curve was constructed by $\Sigma x_i f_i(s)^2 + \Sigma x_i I(s)_{\text{inc}}$ for each solution; f_i's are the atomic scattering factors[12a] corrected for anomalous dispersion,[12b] and the incoherent scattering values[13a] have been corrected by the Breit–Dirac factor.[13b]

The difference between the "corrected" intensity data, $I(s)$, and the independent atom scattering factor was tabulated as a function of s at increments of 0.05 Å^{-1}. This difference is termed $i(s)$[14] where $i(s) = I(s) - [\Sigma x_i f_i(s)^2 + \Sigma x_i I_{\text{inc}}(s)]$. The scaled intensity functions are shown in Figure 1.

Radial-distribution functions (RDF's) were obtained from $i(s)$, or in fact from $si(s)$, but the Fourier transform[14] is

$$4\pi r^2\rho(r) = 4\pi r^2\rho_0 + 2r\pi^{-1}\int si(s)^* \exp(-0.01s^2) \sin sr \, dr$$

where $si(s)^* = si(s)[\Sigma x_i f_i(0)]^2/[\Sigma x_i f_i(s)]^2$; the integral is consistent with that proposed by Waser and Pings.[15] The above integral was evaluated in increments of 0.05 Å^{-1} from $s = 0$ to $s = 12.6$ Å^{-1}. The RDF's obtained are shown in Figures 2 and 3.

Interpretation of X-Ray Diffraction Information.—The area under a peak in the RDF may be correlated with the average number of atoms of type j around atom i in solution[14,16] by $A_{ij} \simeq x_i \sigma n Z_i Z_j$, with the average interaction distance being denoted by the position of the peak, r_{ij}. A_{ij} denotes experimental area under the peak, x_i is the mole fraction of i, Z_i and Z_j are the atomic numbers of atoms i and j, σ is a counting factor, and n represents the average number of atom-pair interactions at the distance r_{ij}.

In these solutions, where the coordination of cobalt(II) is being investigated, the areas indicative of cobalt(II)–ligand bonding may be compared in the two solutions in terms of the "area per cobalt," where the area per cobalt = A_{ij}/x_{Co}.

For interactions between unlike atoms, $\sigma = 2$; thus, each

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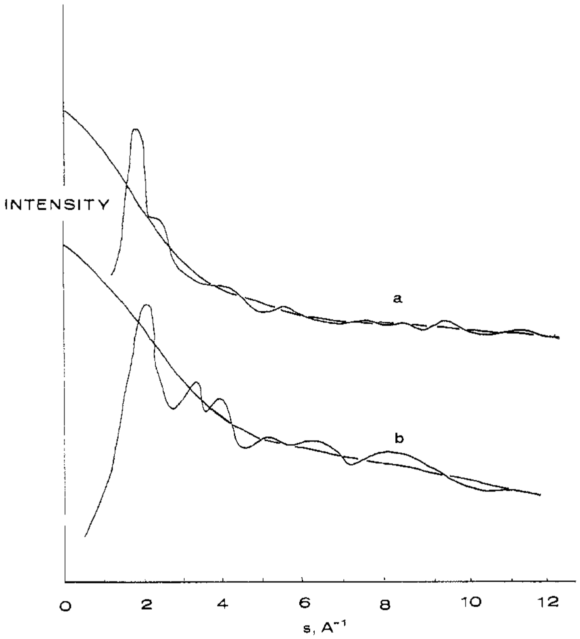

Figure 1.—Scaled intensity functions for the cobalt(II) bromide solutions: (a) $CoBr_2$ in H_2O; (b) $CoBr_2$ in CH_3OH.

Co–Br and each Co–O contact per cobalt contributes *ca.* 1900 and 435 $(e^-)^2$ respectively, to the area per cobalt.[14]

Molecular Weight Measurements.—Solute molecular weights were obtained from examining cobalt(II) bromide–methanol solutions at various concentrations with a Mechrolab vapor pressure osmometer which has been "standardized" with benzil–methanol solutions.

Results and Discussion

Diffraction Measurements.—The RDF's of the aqueous solution and the methanol solution are significantly different.

Aqueous Cobalt(II) Bromide Solution.—This solution is magenta, and its RDF shows a broad maximum centered at *ca.* 2.1 Å (Figure 2). This cobalt(II)–ligand distance is near the cobalt(II)–oxygen distance reported for complexes where cobalt(II) is octahedrally coordinated both in the crystalline state[17–19] and in solution.[4]

The absence of a peak in the RDF at 2.4–2.6 Å[20] indicates that no extensive bonding between cobalt(II) and bromide occurs.

The experimental area per cobalt in this solution is about 2560 (e^-).^{2} Since each primary Co–O contact per cobalt(II) contributes *ca.* 435 $(e^-)^2$ to this area and since no extensive cobalt(II)–bromide bonding occurs, the cation solute species may be represented as $Co(H_2O)_6^{2+}$. Furthermore, the area per cobalt and the primary cobalt(II)–ligand bond distance in this solution and in the aqueous cobalt(II) chloride solution[4] compare quite favorably, indicating that the primary coordination of Co(II) is similar in both aqueous solutions.

The peak in the RDF at about 3.25 Å is attributed to Br–O contacts in solution and has been previously reported.[21] The corresponding Cl–O peak in the aqueous cobalt(II) chloride solution is found at 3.1 Å.[4]

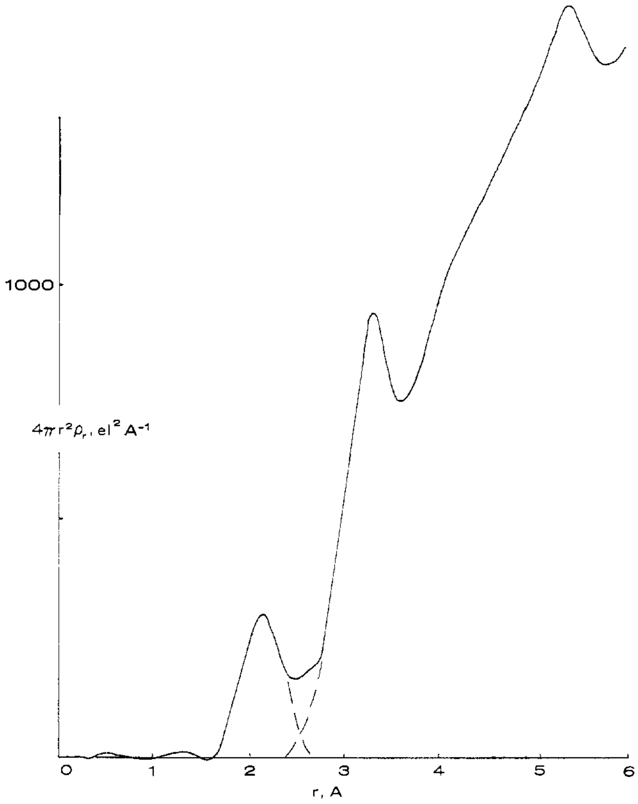

Figure 2.—RDF of the aqueous $CoBr_2$ solution. Dashed lines indicate graphical resolution. Peak area is $\simeq$138 $(e^-)^2$. Mole fractions: $x_{Co} = 0.050$; $x_{Br} = 0.100$; $x_O = 0.850$.

Alcoholic Cobalt(II) Bromide Solution.—This solution is blue, and its RDF is vastly different from the RDF of the aqueous solution.

The small peak at 1.5 Å is correlated with intramolecular bonding characteristic of the solvent.[16]

The first major peak in the RDF (Figure 3) indicative of cobalt–ligand bonding is found at 2.45 Å. Accompanying this peak is a shoulder at *ca.* 2.0 Å. After area corrections due to solvent–solvent contacts at 2.7 Å[16], the area per cobalt was determined to be 4730 $(e^-)^2$.

The area per cobalt may be interpreted in terms of either tetrahedral or octahedral geometry for the nearest neighbor ligand environment of Co(II). Corresponding to the observed area per cobalt, consideration is restricted to $CoBr_2(CH_2OH)_2$ and $CoBr_{1.5}(CH_3OH)_{4.5}$ as possible average solute species.

The mean solute species consistent with octahedral geometry, $CoBr_{1.5}(CH_3OH)_{4.5}$, is indicative of more than one solute species in solution and must be interpreted in light of an average over time and space. This species would exhibit approximately equal contributions from Co–O (4.5×435 $(e^-)^2$ and from Co–Br (1.5×1900 $(e^-)^2$) contacts per cobalt in the RDF. A peak in the RDF indicative of Co–O bonding would be expected to occur at *ca.* 2.1 Å consistent with octahedral geometry. The RDF obtained for this solution

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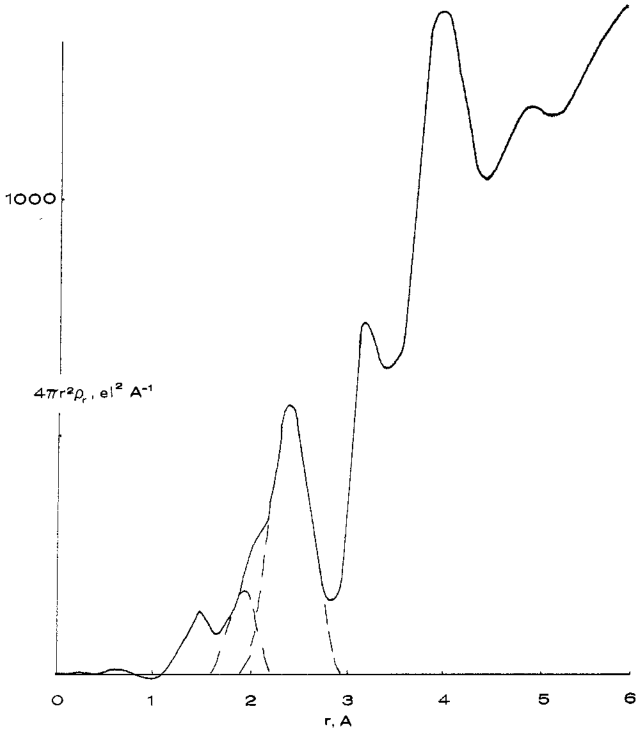

Figure 3.—RDF of the $CoBr_2$–CH_3OH solution. Dashed lines indicate peak resolution. Total peak area is $\simeq 251$ $(e^-)^2$; constituent peak areas are $\simeq 44$ (e^{-2}) (2.0 Å) and $\simeq 207$ $(e^-)^2$ (2.45 Å). Mole fractions: $x_{Co} = 0.053$; $x_{Br} = 0.106$; $x_O = 0.420$; $x_C = 0.420$.

exhibits a shoulder at *ca.* 2.0 Å and a sharply defined major peak at 2.45 Å; both are inconsistent with an RDF representing the octahedral model. The peak at 2.45 Å cannot be correlated with Co–Br bonding in terms of octahedral coordination. For octahedral geometry, Co–Cl distances are ≥ 2.45 Å,[17–19] and Co–Br bond distances for octahedral geometry would exceed this. Additional evidence of the inadequacy of the octahedral model is provided by molecular weight measurements (see below) which indicate that each cobalt(II) is strongly coordinated to a minimum of two bromides.

On the basis of these two points, the octahedral model, $CoBr_{1.5}(CH_3OH)_{4.5}$, may be eliminated as a predominant solute species in this solution.

The tetrahedrally coordinated model, $CoBr_2(CH_3OH)_2$, is consistent with the molecular weight measurements. The first major peak may be graphically resolved to show a small peak at *ca.* 2.0 Å and a sharply defined, symmetrical peak at 2.45 Å. The former is assigned to Co–O bonding and the latter to Co–Br bonding; resolved areas per cobalt are 830 and 3900 $(e^-)^2$, respectively. Thus area analysis of the resultant peaks as well as the unresolved peak is consistent with the species $CoBr_2(CH_3OH)_2$. The Co–Br distance at 2.45 Å for tetrahedral geometry is quite reasonable since Co–Cl bond distances for tetrahedral geometry are reported from 2.30 to 2.35 Å.[22–24]

The major peak at 4.0 Å in the RDF lends credence to the assignment of tetrahedral coordination for cobalt(II) in this solution; this peak occurs at $(^8/_3)^{1/2} \times 2.45$ Å and is attributed to Br–Br contacts from bromides coordinated to cobalt(II). It is unreasonable to expect on the basis of energetics that this peak may be assigned to contacts between randomly distributed bromides in solution. (In the aqueous solution where "free" bromides are postulated, no peak at 4.0 Å is observed.) The peak at 3.25 Å in this RDF is observed and is correlated with Br–O contacts in the solution.[21,25]

The RDF of a $CoBr_2$–C_2H_5OH solution was obtained, but it cannot be resolved, at present, in an unambiguous manner. This RDF is similar in general appearance to the RDF of the methanol solution with maxima at *ca.* 2.5, 3.2, and 4.0 Å.

Molecular Weight Measurements.—Solute molecular weights as a function of concentration are shown in Table I.

TABLE I

SOLUTE MOLECULAR WEIGHTS OF $CoBr_2$ IN CH_3OH

Concn, *M*	Apparant solute mol wt[a]	Concn, *M*	Apparent solute mol wt[a]
0.072	228	0.428	223
0.126	217	0.711	228
0.163	219	0.746	213
0.381	223	0.833	221

[a] Based on a molecular weight of 210.2 for benzil.

Over the concentration range examined, the solute molecular weight may be correlated with $CoBr_2$, indicating two strong cobalt–bromide bonds per cobalt(II). If dissociation does not occur in the region of 0.7 *m*, it may be eliminated as a reasonable possibility at the much higher concentrations examined in the diffraction experiment. Furthermore, the molecular weight studies indicate that solute association is not a predominant factor in these solutions at these concentrations.

Conclusions

In the concentrated aqueous solution, cobalt(II) is, on the average, coordinated by six waters with the Co–O distance being near 2.1 Å. In this concentration range, water is a better coordinating ligand toward cobalt(II) than bromide. The RDF of this solution is quite similar to the RDF of the corresponding aqueous cobalt(II) chloride solution, and $Co(H_2O)_6^{2+}$ is presented as a reasonable description for the cation solute species.

Unlike the $CoCl_2$–alcohol solutions previously reported, the $CoBr_2$–CH_3OH solution does not contain a highly associated solute species. Colligative measurements indicate two cobalt–bromide bonds per cobalt(II), and diffraction measurements indicate that tetrahedrally coordinated $Co(CH_3OH)_2Br_2$ is a realistic solute species in this solution. The primary Co–Br and Co–O distances are 2.45 and 2.0 Å, respectively.

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The relative coordinating ability of bromide may now be included in the series of potential ligands toward cobalt(II) in concentrated solutions.[4] This series is $H_2O > Cl^- > Br^- \sim CH_3OH \sim C_2H_5OH$.

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The Extraction of Scandium from Aqueous Sulfate Solutions by Bis(3,5,5-trimethylhexyl)ammonium Sulfate

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The complex formed in the extraction of scandium from aqueous sulfate solutions by bis(3,5,5-trimethylhexyl)ammonium sulfate dissolved in chloroform has been isolated from the organic phase and has been found to have the stoichiometric formula $(R_2NH_2)_4ScOH(SO_4)_3$ where R is 3,5,5-trimethylhexyl. This complex has been shown to be monomeric whereas the amine sulfate salt conforms to a monomer–dimer equilibrium over the concentration ranges studied. Equilibrium studies have been carried out and are in agreement with the suggested stoichiometry for the complex providing that the monomer–dimer equilibrium of the amine sulfate in chloroform is taken into account.

Introduction

Bis(3,5,5-trimethylhexyl)amine and mono(3,5,5-trimethylhexyl)amine have been used in studies of the extraction of iron(III) from aqueous sulfate solutions.[1–3] The complexes isolated from the organic phase were found to have the stoichiometries $(R_2NH_2)_2FeOH(SO_4)_2$ and $(R_3NH)_2FeOH(SO_4)_2$, respectively, where R is 3,5,5-trimethylhexyl. These complexes are considered to be formed by the reaction of the amine sulfate with the species $FeOHSO_4$ and $(FeOHSO_4)_2$ from the aqueous phase.

Since scandium(III) also tends to form partially hydrolyzed species[4] in aqueous solutions it was considered that the extraction of scandium by bis(3,5,5-trimethylhexyl)amine from aqueous sulfate solutions might occur by a process similar to that of iron(III) by reaction of the amine sulfate with species such as $ScOHSO_4$ and $(ScOHSO_4)_2$ from the aqueous phase. This has, in fact, been found to be the case, except that the stoichiometric formula of the scandium complex contains two amine sulfate molecules for each scandium ion and not one as found for iron(III).

Experimental Section

Preparations.—Bis(3,5,5-trimethylhexyl)ammonium sulfate was prepared as described previously[5] and was recrystallized from acetone as white needles. On standing in air the compound absorbed 0.5 mol of water; mp 200–201°. *Anal.* Calcd for $C_{36}H_{80}N_2SO_4 \cdot 0.5H_2O$: C, 66.9; H, 12.6; N, 4.36; S, 4.96; O, 11.1. Found: C, 66.8; H, 12.4; N, 4.39; S, 4.87; O, 11.4.

The scandium complex with bis(3,5,5-trimethylhexyl)ammonium sulfate was prepared by shaking a 0.05 *M* solution of the amine sulfate in chloroform with successive, equal volumes of a 1.0 *M* aqueous scandium(III) sulfate solution at pH 2.3 until no more scandium could be extracted. The organic phase was separated and filtered and the solvent was evaporated under reduced pressure. A white waxy solid was obtained. *Anal.* Calcd for $[(C_9H_{19})_2NH_2]_4ScOH(SO_4)_3$: C, 60.4; H, 11.4; N, 3.9; S, 6.7; Sc, 3.1. Found: C, 59.9; H, 11.0; N, 3.6; S, 7.0; Sc, 3.1. This compound absorbed 1 mol of water on exposure to air.

Using the above procedure extract residues were prepared for aqueous scandium solutions with pH values in the range 0.85–2.7. The optimum pH value (2.3) for preparing the pure scandium complex was obtained by this means. The solids isolated from the organic phase in each case were analyzed for scandium, amine, and sulfate content.

Analyses.—Scandium was determined colorimetrically using a standard technique with chrome Azurol S[6] or by atomic absorption spectrophotometry[7] (error ±1%).

The amine content was determined as described previously,[1] and sulfate was calculated from the microanalytical figures for sulfur.

Scandium sulfate was prepared using scandium oxide obtained from the South Australian Department of Mines (spectroscopic analysis showed a Sc_2O_3 purity of 99.5%).

Molecular weight measurements were obtained in chloroform solution using a Hewlett-Packard vapor pressure osmometer, Model 302.

Equilibrium Studies.—Equilibrium studies were carried out at 25.0° using equal volumes of aqueous and organic solutions and an equilibration time of 30 min. After separation and filtration the aqueous phases were analyzed for scandium as above and the scandium concentrations in the organic phases were determined by difference. Stock amine sulfate solutions in chloroform were prepared either by using the pure salt or by using the amine and equilibrating the solution with an equivalent amount of aqueous sulfuric acid. These solutions were diluted to give concentrations with respect to the total amine content of 0.02–1.00 *M*. These organic solutions were then preequilibrated with aqueous solutions of the same composition as those used in the

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