other, the ammonia photoaquated from *cis*- and *trans*-$Rh(NH_3)_4(^{15}NH_3)Cl^{2+}$ in aqueous chloride solution is expected to have the same ^{15}N enrichment as that photoaquated in a perchlorate medium. If, on the other hand, a complete scrambling of the five ammonia ligands in *cis*- and *trans*-$Rh(NH_3)_4(^{15}NH_3)Cl^{2+}$ is occurring during the chloride photoaquation/photoanation cycle depicted in Figure 3, then the ^{15}N enrichment of the photoaquated ammonia $Z(^{15}NH_3)$ can be calculated from the following equations for the respective isomers:

cis-$Rh(NH_3)_4(^{15}NH_3)Cl^{2+}$

$$Z(^{15}NH_3) = \frac{\Phi_{NH_3}}{\Phi_{Cl^-} + \Phi_{NH_3}}(\alpha_{eq}^{NH_3}N_{cis} + (1 - \alpha_{eq}^{NH_3}) \times 0.36) + \frac{\Phi_{Cl^-}}{\Phi_{Cl^-} + \Phi_{NH_3}}A \quad (4)$$

trans-$Rh(NH_3)_4(^{15}NH_3)Cl^{2+}$

$$Z(^{15}NH_3) = \frac{\Phi_{NH_3}}{\Phi_{Cl^-} + \Phi_{NH_3}}(\alpha_{eq}^{NH_3} \times 0.36 + (1 - \alpha_{eq}^{NH_3})N_{trans}) + \frac{\Phi_{Cl^-}}{\Phi_{Cl^-} + \Phi_{NH_3}}A \quad (5)$$

The values for $Z(^{15}NH_3)$ calculated for each experiment (the almost temperature-independent ratio $\Phi_{NH_3}/\Phi_{Cl^-} = 0.11$, taken from ref 13; and $\alpha_{eq}^{NH_3} = 0.49$, taken from Table I) are compared in Table II with the experimental values. The conclusion from these experiments is clear, viz. that during the photoaquation/photoanation cycle, the five ammonia ligands in $Rh(NH_3)_5Cl^{2+}$ are scrambled. Triplet $Rh(NH_3)_5{}^{3+}$ is, according to the dissociative model, an intermediate in both the photoaquation[13] and in the photoanation step,[14] and a complete scrambling or at least an almost complete scrambling is thus taking place during each step. This result suggests the generality of thermal equilibrium, at ambient temperature, between the pentacoordinated excited-state isomers of rhodium(III) amine complexes, independent of the strength of the five ligands.

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Spectrophotometric Investigations of the Octahedral–Tetrahedral Equilibria in Cobalt(II)–Thiocyanate Systems in Aqueous Methanol

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Spectrophotometric investigations of the complex formation equilibrium constants at constant ionic strength were carried out for Co(II)–SCN^- systems between 15 and 37 °C in aqueous methanol at water mole fractions between 0.03 and 1.00. At 25 °C, the logarithms of the stability constants in water are $\beta_1 = 1.077 \pm 0.022$, $\beta_2 = 1.735 \pm 0.028$, $\beta_3 = 1.988 \pm 0.051$, and $\beta_4 = -0.0794 \pm 0.0116$. As methanol is added to these systems, the equilibrium constants increase. In methanol (water mole fraction 0.03), the logarithms of the stability constants are $\beta_1 = 2.504 \pm 0.0095$, $\beta_2 = 5.720 \pm 0.017$, $\beta_3 = 7.021 \pm 0.134$, and $\beta_4 = 7.797 \pm 0.050$. At each solvent composition the enthalpy and entropy of complexation were determined for each successive complexation step. The first three complexes exist in the octahedral form, and the tetrakis complex exists in the tetrahedral form.

Introduction

Geometry changes involving a metal ion center can be important in simple inorganic systems as well as the more complex biochemical enzyme systems. We have been characterizing geometry changes in lanthanide salt systems as a function of solvent composition in aqueous methanol,[1] aqueous dimethyl sulfoxide (Me_2SO)[1] and aqueous *N,N*-dimethylformamide (DMF)[2] using the ultrasonic relaxation technique. Recently, we have demonstrated that significant chemical differences can be detected in aqueous methanol with ultrasonics between the high coordination number lanthanide(III) ions, which undergo coordination number changes in solution, and the chemically similar octahedral d-block transition-metal ion, scandium(III), which does not.[3] In aqueous Me_2SO, differences in behavior have been detected with the same cation, zinc(II), and two different ligands, chloride and nitrate.[4] An octahedral to tetrahedral change occurs at high water mole fractions at the zinc center as the third chloride adds to the bis complex, and this change is absent under similar concentrations in the zinc nitrate system, where only the one to one complex is detected by using ultrasonics.[4] No evidence for this structural change is apparent from the potentiometric investigations at constant ionic strength of the complex formation equilibrium constants in aqueous Me_2SO and aqueous DMF, where no abnormalities in behavior are detected in the region where the coordination number and geometry changes occur.[5,6] These observations led to this current investigation of the cobalt(II)–thiocyanate system where a kinetic study postulates the existence of an octahedral–tetrahedral geometry change, but where no equilibrium data exist as a function of solvent composition to determine if the effect can be detected by equilibrium measurements.

Swift utilized the temperature-jump relaxation technique in the study of the kinetics of the complexation reactions between Co(II) and Zn(II) with NO_3^- and SCN^- in water.[7] In the cobalt(II) nitrate system, Swift found that there was a relatively

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long relaxation time, which was independent of the sums of the free-metal and -ligand concentrations. The addition of SCN^- did not effect this relaxation but did cause a very rapid absorbance change, faster than 20 μs. The reaction that was postulated in the presence of either nitrate or thiocyanate is

$$Co(H_2O)_4^{2+} + 2H_2O = Co(H_2O)_6^{2+} \qquad (1)$$

A similar reaction was postulated for the zinc system. Activation parameters for Co(II) were determined to be $\Delta H^* = 6$ kcal/mol and $\Delta S^* = 36$ cal/(mol deg). Co(II) solvent exchange rates determined at 25 °C by using NMR line broadening techniques are $1.1 \times 10^6\ s^{-1}$ in water,[8] $1.8 \times 10^4\ s^{-1}$ in methanol,[9] and 2.3×10^3 and $3.9 \times 10^3\ s^{-1}$ in DMF.[10,11] The aqueous solvent exchange rate is more rapid than the predicted octahedral–tetrahedral conversion, a feature not observed during the zinc geometry change.[4] In addition, in the concentration range used in the temperature-jump study, if the Co(II)–thiocyanate association constants are large, it would be unlikely that there would be significant concentrations of hydrated Co(II) ions present of either geometry.

The conjugate acid of SCN^- is isothiocyanic acid, HNCS, where the association constant has recently been remeasured at 25 °C and ionic strengths of 2 and 4 to be 0.135 ± 0.007 and 0.168 ± 0.007, respectively.[12] At the lower ionic strengths used in this study, no detectable HNCS should be present above pH 2–3. At constant ionic strength an IR study demonstrated that association between Na^+ and SCN^- is absent, while several first-row transition-metal ions formed stable complexes with SCN^-.[13] The IR peak corresponding to the mono complex between Co(II) and SCN^- is at 2112 cm^{-1}, with an extinction coefficient of 696 $M^{-1}\ cm^{-1}$, and β_1 is 8.9, which is somewhat lower than the value of 32 reported by earlier investigators.[14] Tribalat and co-workers have examined the complexation reaction using solvent extraction,[15] polarography,[16] and spectroscopy.[17] The absorption maximum for the one to one complex is at 520 nm with an extinction coefficient of about 30, and β_1 is 7.5 ± 0.5 at $I = 1.5$ and 20 °C.[17] Using the UV absorption, Tribalat obtained $\beta_1 = 9.9 \pm 1$ at the same ionic strength.[18] Using solvent extraction with methyl isobutyl ketone, they were able to measure aqueous complexation constants for up to four complexes, obtaining $\beta_1 = 9 \pm 1.5$, $\beta_2 = 40 \pm 15$, $\beta_3 = 60 \pm 20$, and $\beta_4 = 0.5 \pm 0.3$,[16] which corresponds to the following values for the successive stability constants at $I = 1.5$: $K_1 = 9$; $K_2 = 4.4$; $K_3 = 2$; $K_4 = 0.008$. Using kinetic polarographic waves for Ti(IV)–SCN^- in competition with Co(II)–SCN^- yielded $\beta_1 = 9.6 \pm 0.4$ at the same ionic strength.[19] Similar results for the formation of the mono and bis complexes have been obtained, with the results varying between 9.5 and 18.6 for β_1 and 20.9 for β_2.[20,21]

Cobalt has two possible binding sites to thiocyanate at either the nitrogen or sulfur end. In the study of isothiocyanic acid the assumption was made that the hydrogen binds to the harder nitrogen end of the molecule.[12] Calculations have been made on the electron distribution within the SCN^- ion by Jones[22] and by di Sipio.[23] Folkesson and Larsson carried out ESCA investigations on the solid potassium salts of transition-metal complexes with SCN^- and on $K_2Co(NCS)_4$. They determined that the cobalt is bound to the nitrogen end of the molecule, whereas the analogous platinum compound is bound to sulfur.[24] Emission Mössbauer spectroscopic studies at 78 K on solid tetraalkylammonium salts of $[Co(NCS)_4]^{2-}$ indicated the existence of a single Co–ligand bond, assumed to be through the nitrogen atom.[25] After irradiation of the $[^{57}Co(NCS)_4]^{2-}$ species, two kinds of Fe(II) species were detected, the predominant one bound through nitrogen, with a small buildup of sulfur-bonded compounds caused by the irradiation.[26] Fronaeus and Larsson's IR measurements in water and in methyl ethyl ketone were interpreted in terms of an octahedral aqueous complex and a tetrahedral complex in the organic solvent.[27] The octahedral species is characterized as one with little electron exchange between the metal and the ligand, whereas the tetrahedral one is predicted to have electron donation from the nitrogen atom to the Co(II).[27] Thus, at least the tetrahedral $Co(NCS)_4^{2-}$ species is consistent with the solid-state results.

In methyl ethyl ketone the tetrahedral species was made by dissolving NaSCN and $Co(ClO_4)_2$ in the ratio of 5:1 in at least 20% organic solvent, and the tetrahedral complex is bright blue.[27] Katzin and Gebert have investigated cobalt(II) nitrates and perchlorates in alcohol and acetone, obtaining red-pink octahedral solvated species in water and observing a tendency for ligand coordination in the organic solvents leading to blue solutions.[28] Brubaker and Johnson studied cobalt(II)–thiocyanate complexes in 4-methyl-2-pentanone, obtaining primarily three to four thiocyanate groups bound per cobalt, and they attributed the blue color to tetrahedral geometry.[29] However, in the presence of a less coordinating anion, perchlorate, no significant spectral shift was observed for Co(II) as acetone or ethanol are added to water,[30] which may be interpreted to mean that in order to change the coordination from octahedral to tetrahedral a strongly coordinating ligand other than the solvent is required.

Preliminary measurements in our laboratory were made by mixing various amounts of thiocyanate and cobalt in water and in aqueous methanol. Prior to dilution, when only relatively high concentrations of metal and ligand stock solutions were present, the solution was blue when high ratios of SCN^- to Co(II) were used. Upon the addition of inert electrolyte, $NaClO_4$, and dilution to an ionic strength of 0.5, the blue color disappeared and pink to rose-colored solutions were stable. Thus, we decided to carry out a detailed spectroscopic investigation of the association behavior of cobalt(II)–thiocyanate systems as a function of solvent composition in aqueous methanol to determine if geometry changes could be characterized in these solutions. By carrying out these equilibrium measurements as a function of temperature, we anticipated that thermodynamic differences between the different geometric forms might also be established.

Experimental Section

Reagents. The cobaltous nitrate $[Co(NO_3)_2{\cdot}6H_2O]$, obtained from Fisher was ACS Certified. Certified ACS grade KSCN and NaSCN were also obtained from Fisher. The water contents of the salts were checked by using Dowex 50W-XB cation-exchange resin.[31] The ionic medium was maintained by using purified grade $NaClO_4$, obtained from either Fisher or MCB Manufacturing Chemists. All of the water used in these experiments was deionized water, and the methanol, obtained from MCB and Fisher, was used without further preparation. Stock solutions of the cobaltous nitrate and of sodium perchlorate were made up at various solvent compositions and were stored until needed. Because of the possibility of decomposition, the NaSCN and KSCN solutions

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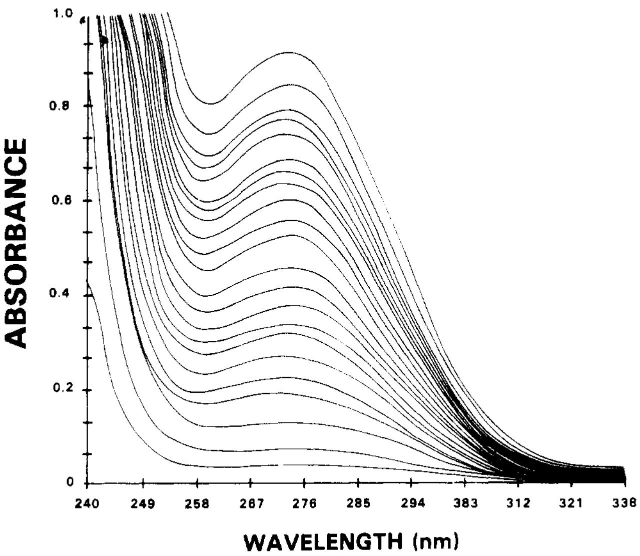

Figure 1. Absorption data at 15 °C for the calculation of the first three complexes at $X_w = 0.89$. The data for these systems correspond to those in Table I, plus the Co(II) reference.

were not made until just before their use. All experimental solutions for the spectroscopic experiments were made by volume, using burets to add reagents to either 25- or 50-mL volumetric flasks. The solutions were discarded daily. The water content in the methanol solutions was determined by Karl Fischer titrations using a Metrohm Karl Fischer automatic titrator with an electronic buret.

Equipment. The preliminary spectrophotometric measurements were made on a Pye-Unicam UV-vis spectrometer without thermostating. All of the final experimental results reported here were made by using a Gilford Model 2600 microprocessor-controlled UV-vis single-beam spectrometer. The temperature was maintained by using a Gilford Thermoset temperature controller, which both reproduces and measures the temperature to within 0.1 °C. As an aid in controlling the temperature, a Forma temperature bath was used in conjunction with the Thermoset temperature controller. The output of the Gilford apparatus was directly connected to an Apple III microcomputer, where it was stored in digital form on disk, and a graphical display was also obtained. Figure 1 is a representative series of outputs obtained on this manner. The hard copy of the digital and graphical data was obtained by using an IDS Prism 132 printer connected to the Apple III computer with a Pkaso printer interface, made by Interactive Structures of Bala Cynwyd, PA.

The cell compartment of the Gilford apparatus holds up to four quartz cuvettes, allowing three test solutions and one reference solution to be run at any given time. The Gilford apparatus was programmed in the difference spectral mode to subtract out the value of the reference solution from each test solution, although the direct reference values could also be saved by the computer. Each series consisted of the same concentration of Co(II) at constant ionic strength with perchlorate, with the reference solution containing no KSCN and the test solutions containing various quantities of KSCN. Each solution was investigated at four temperatures: 15, 20, 25 and 37 °C. Thermal equilibrium was reached at each temperature within minutes with the Thermoset temperature controller. In order to test for sample stability, after the conclusion of the four temperature runs, the initial temperature data were repeated. The wavelength of 280 nm was chosen as the best wavelength for the determination of the first three complexes, whereas the tetrakis complex was studied at 620 nm.

Spectroscopic Measurements. In the absence of SCN^-, cobaltous nitrate obeys Beer's law at its absorption wavelengths, either in the presence or absence of inert electrolyte, thereby indicating the absence of any measurable complex between Co(II) and either nitrate or perchlorate. Since the tetrakis complex has such a low K_4 compared to the first three complexes and is a different color, in the presence of the inert electrolyte used in the first portions of the study, $Co(NCS)_4^{2-}$ could be eliminated from the solutions by the choice of reactant concentrations. Using the modified Benesi-Hildebrand method described by Jaffe and Orchin,[32] it is possible to experimentally determine the extinction coefficients and complexation constants independently for the mono and tris complexes by using concentration ranges where only one type of complex predominates.

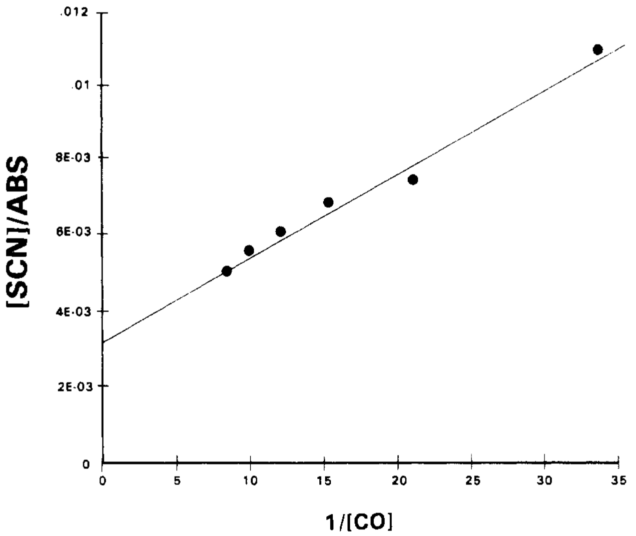

Figure 2. Estimation of K_1 at 25 °C and $X_w = 0.36$ using eq 4.

Under the conditions where $[Co^{2+}] >> [SCN^-]$, the formation of the mono complex is described by K_1:

$$K_1 = [CoNCS^+]/[Co^{2+}][SCN^-] \tag{2}$$

If C_M and C_L represent the total concentration of cobalt and thiocyanate respectively, then K_1 can be written as

$$K_1 = [CoNCS^+]/C_M(C_L - [CoNCS^+]) \tag{3}$$

where it is assumed that the concentration of complex is present to a much lesser extent than the total metal ion concentration. By applying Beer's law for the complex, $A = \epsilon_1 b[CoNCS^+]$, with b as the path length and ϵ_1 as the extinction coefficient of the complex, and then rearranging, one obtains

$$bC_L/A = 1/(K_1\epsilon_1)C_M + 1/\epsilon_1 \tag{4}$$

A plot of bC_L/A as a function of $1/C_M$ yields both the extinction coefficient and the value of K_1. Figure 2 is a representative plot at one temperature and solvent composition. Similar results were obtained for the other solutions.

In a similar fashion, when $C_L >> C_M$, one can obtain an equation for the tris complex:

$$bC_M/A = 1/(K_3\epsilon_3)C_L + 1/\epsilon_3 \tag{5}$$

ϵ_3 is the extinction coefficient for the tris complex. This expression assumes that the predominant species present is the bis complex and that only some tris complex is formed. Plots according to eq 5 were linear. It is not possible to develop a similar equation for the bis complex, since there are no distinct experimental conditions where it is the predominant species. Thus, K_2 must be determined by using computer methods. K_4 can be determined by either graphical or computer methods by using a wavelength where the first three complexes do not absorb.

Computer Evaluation of Stability Constants. Although several alternate computer calculations to determine the stability constants of complexes exist, we have chosen the one by Gaizer, which was developed for use on minicomputers.[33,34] This program can calculate up to nine different species, including pH-dependent ones, and the program calculates both the extinction coefficients and the β values for each complex, defined in the standard manner:

$$\beta_{qp} = [M_qL_p]/[M]^q[L]^p \tag{6}$$

If Beer's law is obeyed by each of the complexes in a 1-cm path length, then the absorbance of the system containing j complex species, is given by

$$A_m = \epsilon_M[M] + \epsilon_L[L] + \sum(\beta_j\epsilon_j[M]^q[L]^p)_j \tag{7}$$

The data required by the program for pH-independent complexes are the total concentrations of metal (C_M) and of ligand (C_L) and the measured

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Table I. Absorption Data Corresponding to Figure 1 (Computer Output)

water mole fraction 0.89 wavelength 280 nm
temp 15 °C ionic strength 0.5

q	p	r	log β	mol absorb
1	1	0	1.2405	243
1	2	0	1.8937	729
1	3	0	2.0398	2919

ϵ_M 7.6 ϵ_L 0

concn, mmol/L				
[M_{tot}]	[L_{tot}]	A	A_{calcd}	$A - A_{calcd}$
5.706 29	1.64643	0.0499	0.078 2314	−0.0283314
5.706 29	3.29286	0.0871	0.112 731	−0.0256315
5.706 29	6.58572	0.1761	0.181 22	−5.12037E−03
5.706 29	8.23215	0.2068	0.214 977	−8.17694E−03
5.706 29	9.87858	0.2546	0.248 635	5.96501E−03
5.706 29	11.525	0.2909	0.282 107	8.79276E-03
5.706 29	13.1714	0.3221	0.315 408	6.69244E−03
5.706 29	14.8179	0.3535	0.348 551	4.94888E−03
5.706 29	16.4643	0.3902	0.381 546	8.65406E−03
5.706 29	18.1107	0.4212	0.414 405	6.79547E−03
5.706 29	21.4036	0.4841	0.479 955	4.14458E−03
5.706 29	2315	0.5144	0.514 207	1.93179E−04
5.706 29	24.6964	0.552	0.544 695	7.30544E−03
5.706 29	26.3429	0.5901	0.576 983	0.0131168
5.706 29	27.9893	0.6145	0.609 208	5.29158E−03
5.706 29	29.6357	0.6347	0.641 352	−6.652E−03
5.706 29	31.2822	0.6877	0.673 421	0.0142787
5.706 29	32.9286	0.7148	0.705 417	9.38278E−03
5.706 29	34.575	0.739	0.737 346	1.65403E−03
5.706 29	37.8679	0.7982	0.801 291	−3.09062E−03
5.706 29	41.1607	0.8567	0.864 748	−8.04776E−03

square of residuals 2.53982E−03 std dev 0.112 69

absorbances at the appropriate wavelengths for the mixtures (A_m). This program then calculates the best combinations of p and q, the extinction coefficients of each complex, and the overall complexation constants. The program minimizes the differences between the measured and calculated absorbances in the following manner:

$$U = \sum(A_{m,i} - A_{calcd,i})^2 \tag{8}$$

where i represents each of the data points. One assumes a given number of complexes (j), the stoichiometry (qp), β values, and ϵ values, and the program refines and modifies them. The program does not weight the experimental data. The main part of the program written for the refinement of parameters has been constructed as a unit that can be used for the calculation of the correction vector elements and of the error in each parameter. In our version of the program a maximum of five parameters can be refined simultaneously. It is possible to "search" for the initial values of parameters, either within a given interval or around their assumed values. This portion of the program can sometimes be used to find the value of a parameter when its contribution to the measured absorbance is small, as is expected for the tetrakis complex, although under some conditions the program cannot refine this parameter if it is too small.

The EQUSOLV subroutine is written for the solution of the appropriate mass balance equations.

$$C_M = [M] + \sum(q\beta_{qp}[M]^q[L]^p)_j \tag{9}$$

$$C_L = [L] + \sum(p\beta_{qp}[M]^q[L]^p)_j \tag{10}$$

In the experimental system q was found to be 1 for all complexes, and in the presence of inert electrolyte at an ionic strength of 0.5 M, p = 1, 2, and 3 at all solvent compositions. The tetrakis complex is dealt with separately. The program has two built-in iterative procedures. The first, the Newton–Raphson method, is quick but often diverges. In this case the program automatically goes into a more extended convergence program, which modifies the starting values for the unknown free concentrations of metal and ligand and then systematically alternates increments until the required convergence is obtained. Although this latter method always appears to achieve convergence, it may take 80–150 iteration cycles.

The EXTCALC subroutine calculates the absorbances with the concentrations of the species calculated by the EQUSOLV routine and with their measured extinction coefficients. This subroutine also calculates the sum of squares according to eq 8.

We have modified Gaizer's program to make it easier to correct errors and to save or recall data from the disk, and most importantly we have added a subroutine that allows for random selection of the parameter to be refined, which removes any program user bias in the selection of the best fit. Table I summarizes the results for the set of data corresponding to the reaction conditions from Figure 1 obtained by using this program.

Results

Table II is a summary of the results obtained for the CoNCS$^+$ complex obtained when the concentration of cobalt is in excess of that of the ligand, as described by eq 4. In methanol (X_w = 0.03) there was some difficulty in preventing perchlorate precipitation under the reaction conditions at an ionic strength of 0.5. The 25 °C results reported in methanol are considerably less reliable than those at the other solvent conditions. However, this problem was eliminated in the computer calculations by switching to NaSCN in place of KSCN, and in the solutions used in the complete evaluation no precipitate is formed after this change. At each solvent composition, the equilibrium constants decreased as the temperature increased, whereas the variation of the molar extinction coefficient is different at different solvent compositions. An examination of the results in Figure 2 shows that although eq 4 appears to be obeyed, the extrapolation to obtain ϵ_1 can cause a significant error to be obtained. Table III summarizes the results for the first three complexes obtained from the computer program. Although each K_1 is within experimental error of the respective value reported in Table II, each is systematically lower than that obtained by using eq 4. In addition, the calculated ϵ_1 from eq 4 is significantly higher than that obtained from the computer program. Two possible explanations for this result are possible. First, the length of the extrapolation shown in Figure 2 can result in significant error. Second, and more importantly, the assumption that only the mono complex is formed may not be valid. If a small amount of the bis complex forms, then not only would K_1 calculated by eq 4 be slightly higher than the real value but also, with the much larger magnitude of ϵ_2 compared to that of ϵ_1, the calculated extinction coefficient would be significantly higher. A comparison of the values shown in Tables II and III for the extinction coefficients and the equilibrium constants is consistent with this latter explanation. Hence the reported values in Table II were only utilized as first approximations in the computer program. Similarly, eq 5 was used to develop estimates for both K_3 and ϵ_3, and the computer program resolved the final values; these estimates are not reported here.

At several solvent compositions in the water-rich regions, only by elimination of the NaClO$_4$ could measurable concentrations of the tetrakis complex be obtained. However, if the value of K_4 was estimated from the literature, solutions at ionic strength of 0.5 could be made that contained only the cobalt and thiocyanate,

Table II. Evaluation of E_1 and ϵ_1 as a Function of Temperature Using Eq 4[a]

	15.0 °C		20.0 °C		25.0 °C		37.0 °C	
X_w	K_1	ϵ_1	K_1	ϵ_1	K_1	ϵ_1	K_1	ϵ_1
1.00	17.78 ± 1.32	252.8 ± 13.4	14.61 ± 1.68	276.0 ± 30.5	12.01 ± 0.82	289.6 ± 28.0	10.10 ± 0.79	297.0 ± 31.0
0.90	17.63 ± 1.64	304.0 ± 30.0	15.53 ± 1.50	311.0 ± 35.0	14.81 ± 0.62	307.0 ± 38.0	11.93 ± 1.17	321.0 ± 46.0
0.77	17.83 ± 0.49	346.9 ± 10.2	16.67 ± 0.49	350.3 ± 9.9	15.15 ± 1.65	357.0 ± 14.0	13.17 ± 3.20	366.0 ± 12.4
0.59	37.60 ± 1.71	359.5 ± 9.0	34.34 ± 1.34	364.1 ± 8.4	32.81 ± 1.31	365.0 ± 9.0	31.09 ± 1.38	357.0 ± 10.4
0.36	100.25 ± 11.30	426.0 ± 4.6	95.96 ± 7.00	422.0 ± 10.8	91.67 ± 8.0	423.0 ± 9.0	90.68 ± 11.3	414.0 ± 8.7
0.03					325.01 ± 75.6	890.6 ± 300.0		

[a] KSCN was used as the inert electrolyte, and some precipitation occurred at X_w = 0.03.

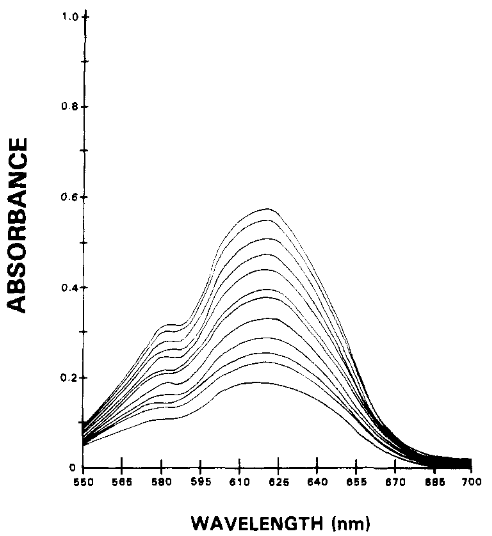

Figure 3. Some of the absorption data used to calculate K_4 at 25 °C in methanol with total [Co(II)] at 2.199 × 10^{-3} M. [SCN^-], from lowest to highest absorbance: 0.0370, 0.039 47, 0.041 94, 0.044 41, 0.049 34, 0.051 81, 0.054 27, 0.056 74, 0.059 21, 0.061 68, and 0.064 14 M.

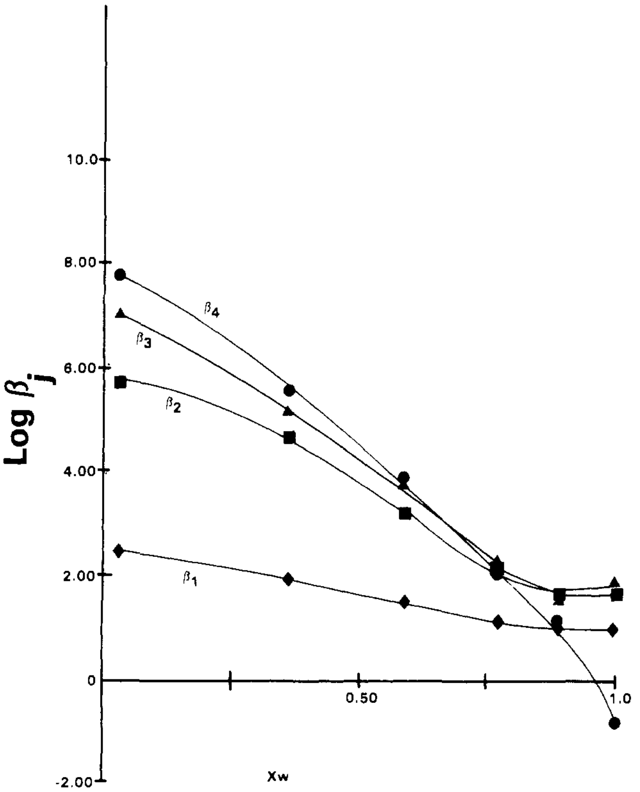

Figure 4. Variation of β at 25 °C as a function of solvent composition. Key: ◆, β_1; ■, β_2; ▲, β_3; ●, β_4.

and no $NaClO_4$. In methanol, when the ratio of SCN^- to Co(II) exceeded 8 to 1, a blue solution could be formed. In the solvent mixtures containing more water, the ratio of ligand to metal ion had to be greater in order to obtain the tetrakis complex. At X_w of 0.77, a ratio of 30 to 1 must be exceeded to obtain measurable quantities of this complex, and at higher water contents, a ratio of more than 60 to 1 was required. Because of the concentrations of metal ion and ligand required to obtain the tetrahedral complex at the two highest water mole fractions, the ionic strengths exceeded 0.5, which was used for all other solutions. The formation of the tetrakis complex can be monitored by observing either the disappearance of free Co^{2+} at 580 nm or the appearance of the blue complex at 620 nm. Because of the increased sensitivity due to the high extinction coefficient of the tetrakis complex, the absorbance at 620 nm was utilized in this portion of the study.

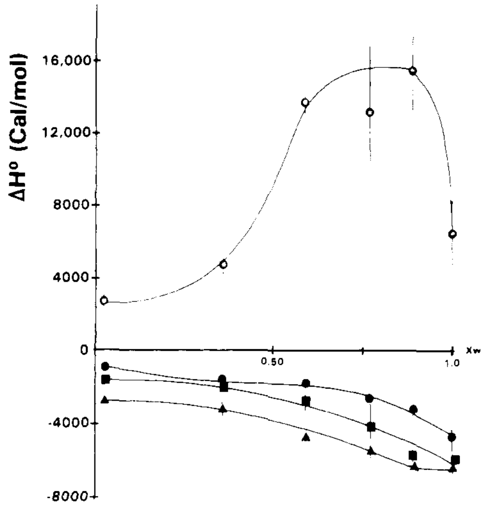

Figure 5. Variation in ΔH as a function of solvent composition for each of the complexes. Key: ●, mono complex; ■, bis complex; ▲, tris complex; ○, tetrakis complex.

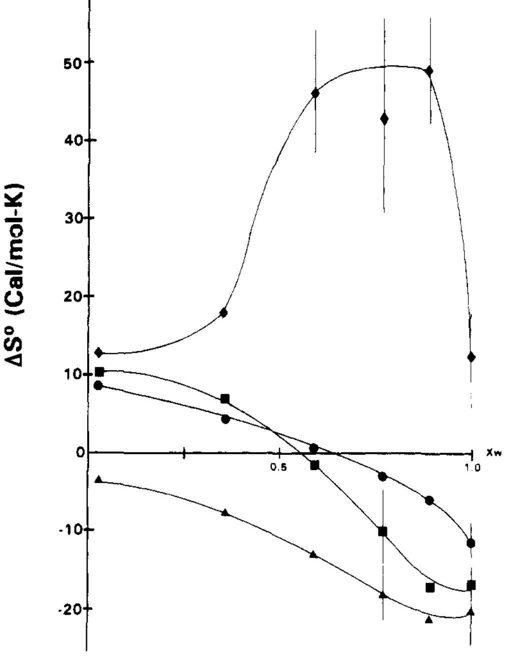

Figure 6. Variation of ΔS as a function of solvent composition for each of the complexes. Key: ●, mono complex; ■, bis complex; ▲, tris complex; ◆, tetrakis complex.

The other three complexes did not absorb in this region. Hence, the data for the first three complexes at 280 nm were used in the computer program in order to determine the best fits for the tetrakis complex at 620 nm. These results are also summarized in Table III. Figure 3 is a plot of the absorbance of a one set of typical solutions at constant Co(II) concentration, containing all four complexes. In order for the computer program to minimize U, several sets of data at different Co(II) concentrations were required in order to calculate the best K_4.

Since each of the four complexes was independently measured as a function of temperature, the thermodynamics of the complexation reactions can be calculated by using the standard equations for the variation of the equilibrium constants as a function of temperature. Table IV summarizes the thermodynamic data. The variations in β, ΔH, ΔS, and ΔG_{298} with solvent composition are summarized in Figures 4–7.

Information about the chemistry of what particular chemical species participate in a given chemical reaction can be obtained by examining distribution diagrams for the complexes at any solvent composition and temperature. Although differences are

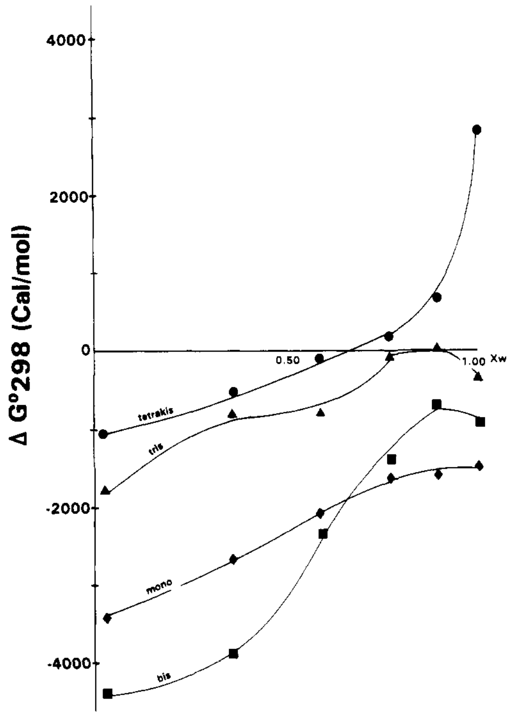

Figure 7. Variation of the Gibbs free energy at 25 °C as a function of solvent composition for each of the complexes. Key: ♦, mono complex; ■, bis complex; ▲, tris complex; ●, tetrakis complex.

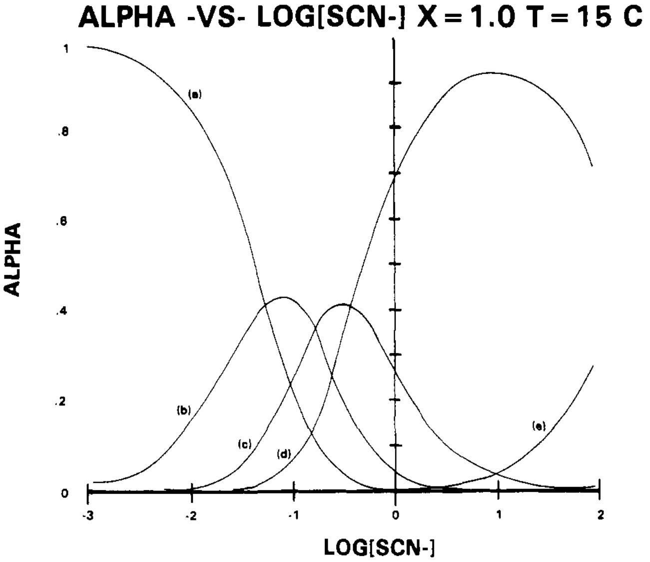

Figure 8. Distribution of species in water at 15 °C. Key: (a) free Co(II); (b) $[CoSCN]^+$; (c) $[Co(SCN)_2]$; (d) = $[Co(SCN)_3]^-$; (e) $[Co(SCN)_4]^{2-}$.

observed at each particular condition, only representative plots are shown in Figures 8–10.

Discussion

Among the parameters used to characterize the effect of solvent on metallic salts are the solvent donor number[35] and the solvent dielectric constant. Water has a donor number of 18, whereas methanol has a slightly higher number of 19. A much greater difference is observed in dielectric constants, where water has a value of 78.5 and the methanol value is 32.6. An early solvation study of cobalt(II) perchlorates in aqueous ethanol and aqueous acetone established the fact that the order of ligand field stabilization is greater for water than for the alcohol but that no appreciable symmetry differences occurred during complexation, with all of the species being octahedral.[27] Although significant kinetic differences have been observed for cobalt(II) perchlorates as a function of solvent composition in mixtures of methanol and DMF, these differences are not always reflected in the equilibrium measurements.[27,36] Thus, when the inner solvation shell of a Co(II) ion contains only organic molecules or a mixture with water, there need not be a geometry change. The absence of major spectral differences in each of the first three complexes observed in this study as a function of methanol–water composition differences is consistent with this observation. Thus, we believe that at all solvent compositions the geometries of the pink species corresponding to the mono, bis, and tris complexes are octahedral. Similarly, the blue solutions corresponding to the tetrakis complex indicate that this species is tetrahedral in water, methanol, and mixed-solvent compositions. This means that the addition of

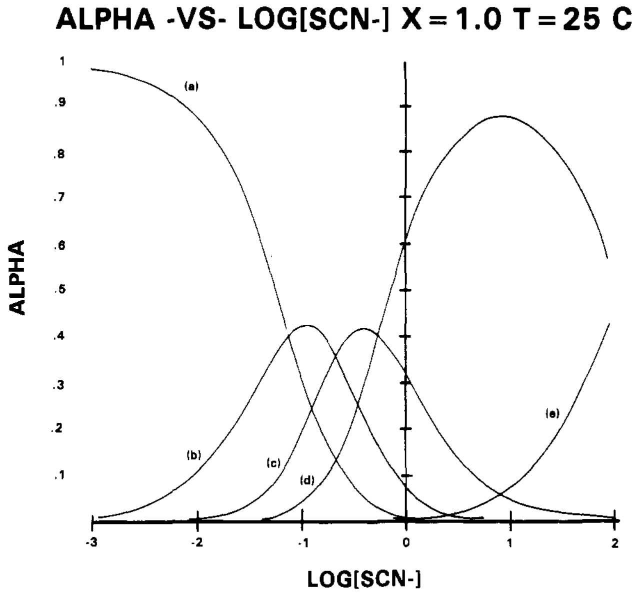

Figure 9. Distribution of species in water at 25 °C. Key: (a) free Co(II); (b) $[CoSCN]^+$; (c) $[Co(SCN)_2]$; (d) $[Co(SCN)_3]^-$; (e) $[Co(SCN)_4]^{2-}$.

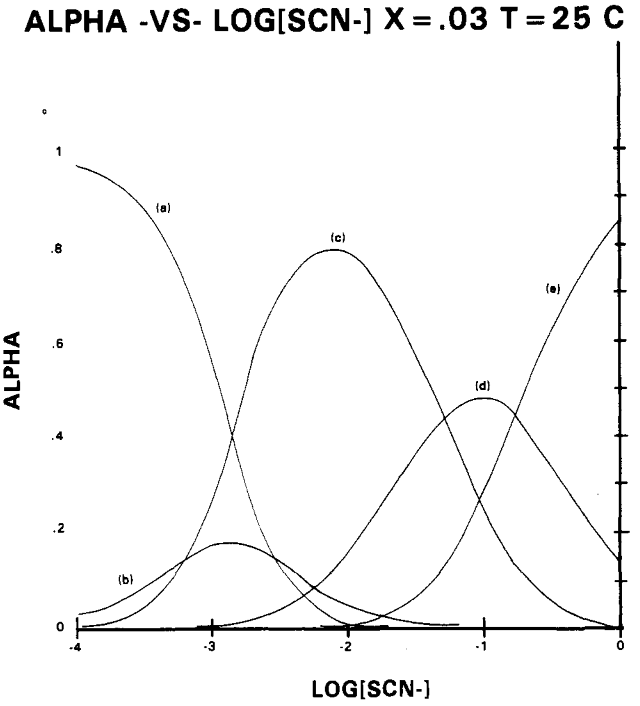

Figure 10. Distribution of species in methanol (X_w = 0.03) at 25 °C. Key: free Co(II); (b) $[CoSCN]^+$; (c) $[Co(SCN)_2]$; (d) $[Co(SCN)_3]^-$; (e) $[Co(SCN)_4]^{2-}$. A considerable difference exists in the regions of stability compared to the results in water.

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Table III. Computer Evaluation of the Complexation Constants and Extinction Coefficients at $I = 0.5$

	15 °C	20 °C	25 °C	37 °C
		$X_w = 1.00$		
K_1	17.70 ± 0.85	14.52 ± 0.75	11.93 ± 0.65	9.60 ± 0.68
K_2	6.22 ± 0.50	5.99 ± 0.54	4.55 ± 0.50	13.07 ± 0.49
K_3	2.63 ± 0.41	2.14 ± 0.40	1.79 ± 0.36	1.19 ± 0.34
K_4^a	0.0044 ± 0.0002	0.0068 ± 0.0001	0.0086 ± 0.0002	0.0104 ± 0.0003
ϵ_1^b	150 ± 3	171 ± 3	216 ± 4	223 ± 4
ϵ_2	835 ± 25	899 ± 29	992 ± 48	1553 ± 777
ϵ_3	2748 ± 480	3234 ± 661	3722 ± 1315	5689 ± 3160
ϵ_4	3664 ± 86	2745 ± 70	2615 ± 66	3096 ± 83
		$X_w = 0.89$		
K_1	17.40 ± 0.55	15.52 ± 0.20	14.60 ± 0.45	11.57 ± 0.41
K_2	4.52 ± 0.30	3.79 ± 0.18	3.30 ± 0.30	2.22 ± 0.61
K_3	1.37 ± 0.25	1.18 ± 0.10	0.93 ± 0.10	0.62 ± 0.37
K_4^c	0.101 ± 0.003	0.146 ± 0.004	0.318 ± 0.008	0.65 ± 0.02
ϵ_1	243 ± 2	265 ± 2	266 ± 2	329 ± 2
ϵ_2	729 ± 15	740 ± 19	798 ± 23	900 ± 28
ϵ_3	2919 ± 347	3089 ± 516	3405 ± 779	5487 ± 1358
ϵ_4	789 ± 19	667 ± 17	420 ± 10	380 ± 9
		$X_w = 0.77$		
K_1	17.68 ± 0.62	16.55 ± 0.66	15.17 ± 0.59	12.94 ± 0.45
K_2	11.75 ± 0.60	11.80 ± 0.82	10.45 ± 0.74	7.10 ± 0.59
K_3	1.88 ± 0.81	1.48 ± 1.11	1.14 ± 0.80	0.93 ± 16.35
K_4	0.202 ± 0.01	0.488 ± 0.01	0.78 ± 0.01	1.17 ± 0.01
ϵ_1	291 ± 3	289 ± 3	311 ± 2	332 ± 3
ϵ_2	562 ± 10	568 ± 9	557 ± 9	706 ± 19
ϵ_3	505 ± 195	441 ± 228	464 ± 264	894 ± 697
ϵ_4	1288 ± 13	670 ± 7	544 ± 5	517 ± 5
		$X_w = 0.59$		
K_1	37.5 ± 6.0	35.83 ± 0.87	34.10 ± 1.44	34.01 ± 1.88
K_2	60.2 ± 10.9	55.87 ± 2.62	52.27 ± 3.54	42.67 ± 4.03
K_3	4.77 ± 1.21	4.11 ± 0.13	3.62 ± 0.30	2.65 ± 0.43
K_4	0.37 ± 0.02	0.76 ± 0.04	1.2 ± 0.05	2.2 ± 0.10
ϵ_1	210 ± 5	197 ± 4	206 ± 4	246 ± 5
ϵ_2	347 ± 7	354 ± 6	359 ± 6	389 ± 9
ϵ_3	989 ± 105	1436 ± 105	1560 ± 114	1780 ± 238
ϵ_4	2814 ± 91	1746 ± 53	1277 ± 37	945 ± 27
		$X_w = 0.36$		
K_1	100.4 ± 4.73	94.76 ± 3.28	90.92 ± 3.21	83.54 ± 7.50
K_2	773.6 ± 224.0	727.9 ± 46.5	716.6 ± 46.7	614.5 ± 81.2
K_3	4.67 ± 3.20	4.08 ± 0.97	3.89 ± 0.42	3.14 ± 1.27
K_4	1.9 ± 0.11	2.3 ± 0.16	2.4 ± 0.1	3.5 ± 0.2
ϵ_1	399 ± 22	379 ± 10	376 ± 8	371 ± 9
ϵ_2	248 ± 8	237 ± 4	231 ± 3	225 ± 4
ϵ_3	1044 ± 388	1230 ± 184	1046 ± 161	1283 ± 251
ϵ_4	4300 ± 281	3164 ± 250	3144 ± 154	2858 ± 128
		$X_w = 0.03$		
K_1	336.7 ± 7.0	328.4 ± 8.1	319.0 ± 7.1	302.9 ± 12.1
K_2	1779 ± 36	1712 ± 364	1646 ± 29	1494 ± 757
K_3	24.0 ± 5.9	22.00 ± 1.73	20.0 ± 6.2	17.05 ± 5.15
K_4	5.2 ± 0.3	5.4 ± 0.3	5.9 ± 0.6	7.2 ± 1.5
ϵ_1	1425 ± 31	1378 ± 31	1466 ± 25	1336 ± 29
ϵ_2	541 ± 9	540 ± 9	528 ± 7	500 ± 9
ϵ_3	552 ± 142	564 ± 156	635 ± 127	589 ± 199
ϵ_4	2217 ± 64	2162 ± 58	2075 ± 80	1900 ± 77

[a] $I = 10$. [b] ϵ_1–ϵ_3 were measured at 280 nm, and ϵ_4 was measured at 620 nm throughout. [c] $I = 1.5$.

methanol to aqueous solutions of cobalt thiocyanate does not change the geometry, but rather it is the addition of the fourth SCN^- ligand that induces the geometry change. Although the magnitude of K_4 at each solvent composition is significantly less than for the other three complexes, the difference may be attributed to a lower statistical probability of ligand replacement in a tetrahedral compiex compared to an octahedral one, a reflection of the difficulty of forming a tetrahedral Co(II) species in these solvent mixtures, a reflection of the difficulty of forming a more highly negative charged ion in theses solvent mixtures, or a combination of effects. K_4 differs from the first three complexation constants in that it represents the combination of two different equilibrium reactions coupled together. The first is the addition of the fourth ligand, and the second is the loss of two bound solvent molecules to form the tetrahedral tetrakis species. Since these experiments cannot separate the two effects upon the magnitude of K_4, further comparisons will not be fruitful. In our experiments, even much larger additions of SCN^- did not disrupt the tetrahedral species by forming the pentakis complex.

The variation of each respective equilibrium constant with solvent composition is summarized in Table III and Figures 4 and 7, in terms of K, β, and ΔG_{298}, respectively. At each temperature above X_w of 0.75, relatively small changes were observed in K_1, K_2, and K_3 as a function of solvent composition. Below that water mole fraction, a significant increase is observed for the formation constants of the first two complexes, with a smaller magnitude change observed for K_3. In water at the four temperatures studied, $K_1 > K_2 > K_3 >> K_4$, and this same relationship holds at X_w of 0.77 and above. As additional methanol is added to the solvent mixtures, a new variation in equilibrium constants appears: $K_2 >> K_1 > K_3 >> K_4$. This change in the relative values of the successive stability constants should not be a function of the small difference between effective donor numbers in the aqueous methanol solutions. Rather, we believe it reflects the effect of solvent dielectric constant on the equilibrium determinations at constant ionic strength. The unusually large values of K_2 occur because they represent the formation of a neutral complex from two charged species, a process that should be favored at the lower dielectric constants obtained when significant amounts of methanol are present in the solvent system.

An examination of the enthalpy of successive complexations from Table IV and Figure 5 reveals interesting variations. For each of the first three complexes up to the tris complex, the complexation reactions are exothermic. The tetrakis complex formation is different from the other three in that it is endothermic, consistent with the assumption that the addition of the fourth ligand is of a nature different from that of the other three complexes and involves a different mechanism, the proposed geometry change. Recently, Kojima[37,38] studied the effect of temperature and pressure on the octahedral–tetrahedral equilibria of Co(II) solutions with Cl^-, Br^-, and I^- in pyridine. Using visible absorption spectra, they followed the equilibrium between the tetrahedral species, $CoX_2(py)_2$, and the octahedral species, $CoX_2(py)_4$. Kojima's results are similar to those in our system in that higher temperatures favored the tetrahedral species, as their reaction was also endothermic.

At each solvent composition, the enthalpy becomes more negative as each SCN^- ligand bonds to the Co(II) through the formation of the tris complex, until the geometry change occurs upon the addition of the fourth ligand. As methanol replaces water in the bulk solvation shell, the enthalpy increases for each of the first three complexes. Since the bond formation enthalpy for the Co(II)–SCN^- bonds should be approximately the same at each solvent composition, the increasing enthalpy is a measure of the decreased stabilization in methanol compared to that in water. This is consistent with the earlier observation of the increased ligand field stabilization in water compared to that in ethanol for Co–perchlorate solutions.[27] We have no conclusive reason for the apparent maximum in the complexation enthalpy at high water

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Table IV. Thermodynamics of Successive Complexation Steps

	mono	bis	tris	tetrakis
		$X_w = 1.00$		
$\Delta G°_{298}$, cal/mol	−1468.6 ± 32.0	−897.6 ± 61.0	−349.9 ± 108.0	+2817.6 ± 13.6
$\Delta H°$, cal/mol	−4866.4 ± 665.7	−6024.7 ± 807.7	−6360.8 ± 103.8	+6482 ± 1879
$\Delta S°$, cal/(mol K)	−11.2 ± 2.2	−17.2 ± 2.7	−20.1 ± 3.5	+12.0 ± 6.3
		$X_w = 0.89$		
$\Delta G°_{298}$, cal/mol	−1588.3 ± 18.0	−707.3 ± 51.0	+40.4 ± 60.2	+678.0 ± 14.7
$\Delta H°$, cal/mol	−3228.1 ± 178.6	−5695.8 ± 184.0	−6347.6 ± 70.0	+15400 ± 2000
$\Delta S°$, cal/(mol K)	−5.6 ± 0.6	−16.8 ± 0.6	−21.4 ± 0.2	+49.0 ± 6.7
		$X_w = 0.77$		
$\Delta G°_{298}$, cal/mol	−1610.9 ± 22.7	−1390.1 ± 40.7	−77.6 ± 315.0	+139.6 ± 7.5
$\Delta H°$, cal/mol	−2545.8 ± 73.2	−4265 ± 1539	−5591 ± 1070	+13200 ± 3700
$\Delta S°$, cal/(mol K)	−3.1 ± 0.2	−9.7 ± 5.2	−18.3 ± 3.6	+43.2 ± 12.5
		$X_w = 0.59$		
$\Delta G°_{298}$, cal/mol	−2090.8 ± 25.0	−2343.0 ± 39.0	−762.1 ± 47.0	−108.0 ± 24.2
$\Delta H°$, cal/mol	−1813.7 ± 70.5	−2779.3 ± 140.0	−4727.6 ± 46.3	+13800 ± 2400
$\Delta S°$, cal/(mol K)	+0.9 ± 0.2	−1.5 ± 0.5	−13.3 ± 0.2	+46.3 ± 8.0
		$X_w = 0.36$		
$\Delta G°_{298}$, cal/mol	−2671.8 ± 20.5	−3894.8 ± 37.4	−804.7 ± 60.7	−518.6 ± 24.2
$\Delta H°$, cal/mol	−1460.9 ± 102.4	−1827.6 ± 228.4	−3089.8 ± 270.0	+4771 ± 532
$\Delta S°$, cal/(mol K)	+4.1 ± 0.3	+6.9 ± 0.8	−7.6 ± 0.9	+17.8 ± 1.8
		$X_w = 0.03$		
$\Delta G°_{298}$, cal/mol	−3415.4 ± 13.0	−4387.5 ± 10.2	−1774.7 ± 161.0	−1051.5 ± 230.1
$\Delta H°$, cal/mol	−839.9 ± 13.1	−1417.7 ± 31.2	−2765.6 ± 125.2	+2837.3 ± 255.0
$\Delta S°$, cal/(mol K)	+8.6 ± 0.1	+9.9 ± 0.1	−3.3 ± 0.4	+13.1 ± 0.9

mole fractions for the formation of the tetrakis complex, coupled to the observed geometry change.

If our model for the geometry change being coupled to the addition of the fourth ligand is correct, then this should also be reflected in the variation of the entropy of reaction with solvent composition shown in Figure 6. In many metal ion complexation reactions the entropy is negative, which means that the most favorable reactions are those least disfavored by entropy. In water, each of the first three complexes are entropy disfavored, as expected. The entropy becomes more negative as each ligand is added through the formation of the tetrakis complex. For the tris complex, as methanol is added, the entropy becomes less negative but never favors the complexation reaction. For the formation of both the bis and tris complexes below a water mole fraction of approximately 0.6, the complex formation becomes entropy favored. One explanation for this is that the solvent composition in the inner solvation shell after complexation is different from that of the bulk solvent, suggesting that water preferentially leaves the inner shell over methanol. This is consistent with the slower rate of Co(II) solvent exchange in methanol compared to that in water. Just below a water mole fraction of 0.5, the formation of the bis complex becomes more entropy favored than the formation of tris complex, a reversal of the observations at higher water compositions.

Only for the first three complexes are the reactions enthalpy favored, as shown in Figure 5. Indeed, above a water mole fraction of 0.6, they are entropy disfavored. However, the Gibbs free energies of these complexes, shown in Figure 7, are favorable within experimental error for the mono, bis, and tris complexes, with results close to zero at high water mole fractions only for the tris complex. On the other hand, the formation of the tetrakis complex is enthalpy disfavored at all solvent compositions. The driving force for the tetrakis complexes is the positive entropy of complexation of all solvent compositions, a feature not observed for the other three complexes. This favorable entropy does not come from the addition of the fourth ligand, which is expected to also be disfavored by entropy. Rather, it occurs because of the release of two bound solvent molecules from the octahedral complex to form the tetrahedral complex. In water and in the almost anhydrous methanol solutions the numerical values of the entropy for the tetrakis complex are within experimental error of each other, 12.0 ± 6.3 and 13.1 ± 0.9 cal/(mol deg), respectively. These results are within the range of values expected for the loss of two solvent molecules from the metal ion to the bulk solvent. In the mixed solvents, the complexation entropy for the tetrakis complex is significantly higher. If the average solvent composition released by the solvation metal ion resembled the bulk solvent, then one would expect entropy values similar to those in the pure solvents. Since this is not observed, rather a larger entropy is observed in the mixed solvents, we believe that the composition of the bound solvent in the tris complex is different from that of the bulk solvent. Furthermore, since the highest magnitudes of the entropies are observed in the aqueous solvent regions, we believe that the Co(II) complexes preferentially bind methanol compared to water. This is consistent with our enthalpy data and the slower rates for cation solvent exchange in methanol compared to those in water. In the regions of low water content, the released bound solvent closely resembles the bulk solvent, and the magnitude of the entropy decreases to a value closer to that of the pure solvent.

At 25 °C, the free energy clearly is most favorable for the mono complex in water and for the bis complex in methanol, as seen in Figure 8. This reversal in methanol is a reflection of the increased entropy stabilization for the neutral bis complex in methanol. This entropy stabilization for the pseudohalide ligand, SCN^-, reacting with Co(II) in organic solvents has also been characterized for chloride complexes with Zn(II), Cd(II), Ag(I), and Cu(I) in Me_2SO compared to water.[39,40] The explanation advanced for the entropy effect in the organic solvents is that the removal of solvent molecules from the solvated metal ion is easier in solvents like methanol or Me_2SO than in water with its higher ligand field stabilization. This result would also hold in a solvated metal ion–ligand complex that undergoes further complexation.

With the equilibrium data generated by this study in aqueous methanol, it is now possible to get further insight into Swift's temperature-jump investigation of the octahedral–tetrahedral conversion for solvated Co(II).[7] The wavelength Swift used in his study was 500 nm in the absence of SCN^- and 580 nm for those Co(II) solutions containing SCN^-. Swift's solutions contained 0.01 M $Co(NO_3)_2$, 0.1 M KSCN, and 0.01 M HNO_3. The distribution of species present in water at 15 and 25 °C (Figure

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8 and 9) does indeed show a shift. At 15 °C the predominant Co(II) species at [SCN$^-$] = 0.1 M are the mono complex, the bis complex, and a small concentration of tris complexes. An increase in temperature to 25 °C increases the amount of the $CoSCN^+$ complex relative to that of the bis and tris forms. At 15 °C approximately 20% of the Co(II) exists as the aquo ion, and this increases to about 30% at 25 °C. There will be no measurable concentration of the tetrakis complex. Thus, the major change in complexed Co(II) species does not involve a geometry change, as would be expected for the formation of the tetrakis complex. Since the absorption peak corresponding to the various complexes extends through 580 nm, the wavelength in the temperature-jump study, we believe that the first absorption change corresponds to a rapid interchange of Co(II) complexes (<20 μs). However, the NMR and spectroscopic investigations of $Co(ClO_4)_2$ complexation in water and mixed solvents, which were not available for the temperature-jump study, indicate that the predominant solvated Co(II) species is octahedral in nature. This spectroscopic investigation cannot give any structural information about the nature of the aqeuous Co(II) solvated ion but does suggest that if significant concentrations of a tetrahedral species, $Co(H_2O)_4{}^{2+}$, were present, an observable color change should occur. However, it should be noted that the optical absorbance measured in a temperature-jump experiment is highly sensitive and might be able to detect a small concentration of $Co(H_2O)_4{}^{2+}$. Although this investigation does not eliminate the possibility that the earlier observations are correct, it does suggest that a temperature-jump relaxation reinvestigation of the Co(II)-SCN$^-$ system is in order. The reaction conditions should be modified to ensure for some of the experiments that only the mono complex is present and for others that the tetrakis complex is formed. Examination of Figures 8-10 reveals that as methanol is added to the solvent system, the range of stability of the tetrakis complex increases, suggesting that it may be possible to study the kinetics of the known octahedral-tetrahedral change for the Co(II)-SCN$^-$ system. With the more sensitive electronics presently available, the existence of the tetrahedral solvated Co(II) species should either be confirmed or eliminated.

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Photochemistry of Nickel(II) Azido Complexes: Singlet Nitrene

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The near-ultraviolet irradiation of $Ni(tet\text{-}a)(N_3)_2$ directly excites the $n \rightarrow \pi^*$ transition of the azido group, which yields a singlet nitrene intermediate. This intermediate scavenges ammonia to yield hydrazine. Because the primary quantum yield for nitrene formation is 0.042 and the quantum yield for azido group photodecomposition is 0.15, it is suggested that the remainder of the photodecomposition occurs via a triplet nitrene intermediate. It is shown that the formation of triplet nitrene is spin-allowed and energetically accessible.

Introduction

The photodecomposition of azido complexes has drawn a great deal of attention in recent years.[1-17] Among the reasons for this interest is the variety of modes of photodecomposition thus far demonstrated for azido complexes. Among those observed thus far are azide aquation, trans ligand aquation, azide radical formation, and coordinated nitrene formation. The quantum efficiencies for these reactions are wavelength-dependent, and often more than one mode is observed for the same complex. Much attention has been focused on the kinetic and thermodynamic factors that determine the patterns of reactivity with the hope of understanding the behavior of these complexes.

Much of the impetus for the more recent interest in azido group photochemistry results from the discovery by Basolo and coworkers of the nitrene photodecomposition pathway.[2-4] In contrast to organic azides, prior to these reports, azido group photodecomposition occurred exclusively via azide radical formation. In their original report Basolo and co-workers proposed that nitrene formation is favored for metals not having a stable one lower oxidation state and for metals having filled d orbitals that can back-donate into the vacant nitrogen orbitals of the nitrene and thus stabilize the metal nitrene. The importance of the former has been developed by Endicott and co-workers[21] in their quasi-thermodynamic treatment of redox photoreactivity. The importance of the latter has been demonstrated by Mansuy and co-workers,[10] who were able to isolate a stable iron porphyrin nitrene.

The first reported occurrence of metal nitrene intermediacy, both thermal[22,23] and photochemical,[2-4] employed metals of the

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