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# Preferential Solvation and Solvent Interchange in Water–Alkyl Sulfoxide Solutions of Pentaammine Complexes of Chromium(III) and Cobalt(III)

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The (dimethyl sulfoxide)pentaamminechromium(III) and aquopentaamminechromium(III) complex ions were preferentially solvated by dimethyl sulfoxide in water–dimethyl sulfoxide mixtures. Application of the Covington theory to the measured proton line broadenings of the solvents gave the solvation number, stepwise formation constants for the replacement of one solvent by the other, and the increment in the free energy change for each successive replacement step for each complex. The information concerning the composition of the solvation shells was applied to studies of the solvent-interchange reactions between aquopentaamminecobalt(III) and (dimethyl sulfoxide)pentaamminecobalt(III) in water–dimethyl sulfoxide binary solvent mixtures and between aquopentaamminecobalt(III) and (tetramethylene sulfoxide)pentaamminecobalt(III) in water–tetramethylene sulfoxide binary solvent mixtures. The pseudo-first-order rate constants, $k_W$, for the reaction of water with the sulfoxide complex ions were proportional to the first power of the probability that the solvation shell of the complex ion contained a water molecule. The pseudo-first-order rate constant, $k_S$, for the reaction of a sulfoxide molecule with the aquo complex ion was proportional to the second power of the probability that the solvation shell of the complex ion contained a sulfoxide molecule. The thermodynamic equilibrium constants for the solvent-interchange reactions were also obtained.

## Introduction

The composition of solvation shells (solvent cages) of transition-metal complexes in solvent mixtures is known in only a relatively few cases. Yet the composition of the solvation shell outside the first, or inner, coordination shell of these complexes can be of great importance in the study of thermal and photochemical substitution reactions in the first coordination shell, enzyme mechanisms, homogeneous catalysis, and solvent effects on Raman, infrared, visible, and ultraviolet spectra and in the theoretical study of solutions where comparisons of theoretical predictions with experimental data are all too few as a result of the scarcity of the latter.

Frankel, Stengle, and Langford[1] suggested the use of the chemical shift of the central metal resonance or of the line broadening of bulk solvent lines in nuclear magnetic resonance (NMR) spectra for studying the composition of solvation shells in place of the older, less effective, thermodynamic and kinetic methods. Langford and co-workers then went on to determine the fraction $n_S/n_0$ of a solvent Sol in the solvation shell of a metal complex for several complexes in binary solvent mixtures. (Here $n_S$ is the number of Sol molecules in the solvation shell in the solvent mixture and $n_0$ is the analogous number in the neat solvent Sol). Absolute solvation numbers were not determined. Langford and White[2] found that *trans*-$Cr(NH_3)_2(NCS)_4^-$ is preferentially solvated by acetone in water–acetone mixtures but that the pseudo-first-order rate constant for aquation was proportional to $(n_W/n_0)^2$, where the subscript w refers to water. In acetonitrile–water mixtures[3] the acetonitrile strongly preferentially solvated the same complex but the pseudo-first-order rate constant for aquation was approximately proportional to $n_W/n_0$. Also in acetonitrile–water mixtures[4] $Cr(NCS)_6^{3-}$ was strongly preferentially solvated by acetonitrile but the pseudo-first-order rate constant for aquation was again proportional to $n_W/n_0$. In dimethyl sulfoxide–water mixtures[5] the dimethyl sulfoxide strongly preferentially solvated $Cr(C_2O_4)_3^{3-}$ and also strongly retarded the rate of racemization. The pseudo-first-order rate constant for the latter depended strongly on $n_W/n_0$, a fact that was interpreted to mean that several water molecules were used to solvate (by H-bonding) the dechelating end of an oxalate ring in the transition state whereas dimethyl sulfoxide could not be used for this purpose. In nitromethane–dimethyl sulfoxide mixtures dimethyl sulfoxide was somewhat preferentially excluded from the solvation shell of $Cr(OS(CH_3)_2)_6^{3+}$ yet the dimethyl sulfoxide self-exchange rate constant was nearly independent of mole fraction of dimethyl sulfoxide until well below the value of 0.5.[6] This fact was interpreted to mean that one dimethyl sulfoxide molecule is unique in the solvation shell and is moderately tightly bonded to the complex ion. This interpretation was supported by the report[7] that there was a relatively slow exchange of some dimethyl sulfoxide molecules between the bulk solvent and solvation shell, which is detectable under certain circumstances. The two complexes $Co(acac)_3$ and $Cr(acac)_3$ (acac$^-$ = acetylacetonate ion) showed very similar preferential solvation behavior, as might be expected, in a number of binary solvent mixtures.[8] This observation is very important because it shows that when the charges and ligands are the same and the sizes are very similar, the solvation behaviors of two different complex ions with different metals are the same. This result will be used in the present paper.

Caminiti and co-workers have used X-ray diffraction to study structure in aqueous solutions of salts and have found 12 water molecules in the solvation shells of $Fe(H_2O)_6^{3+}$,[9] $Cr(H_2O)_6^{3+}$,[10] $Cd(H_2O)_5NO_3^+$,[11] $Al(H_2O)_6^{3+}$,[12,13] $Zn(H_2O)_6^{2+}$,[14] $Ni(H_2O)_6^{2+}$,[15] and $Mg(H_2O)_6^{2+}$,[15] approximately 10 in the solvation shell of $In(H_2O)_5(SO_4)^+$,[16] $Mn(H_2O)_5(SO_4)$,[17] and $Cd(H_2O)_5(SO_4)$,[18] and approximately 15 in the solvation shell of $Ce(H_2O)_8^{3+}$.[19] Thus one may expect 10–12 solvent molecules in a solvation shell of an octahedral complex ion if the solvent molecules are not too large. The water molecules in the solvation shells of these complexes were apparently strongly H-bonded to the first-coordination-shell water molecules as evidenced by the relatively short oxygen–oxygen distance between the two shells. Solvent mixtures were not examined.

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(1) Frankel, L. S.; Stengle, T. R.; Langford, C. H. *Chem. Commun.* **1965**, 393.
(2) Langford, C. H.; White, J. F. *Can. J. Chem.* **1967**, *45*, 3049.
(3) Sastri, V. S.; Henwood, R. W.; Behrendt, S.; Langford, C. H. *J. Am. Chem. Soc.* **1972**, *94*, 753.
(4) Behrendt, S.; Langford, C. H.; Frankel, L. S. *J. Am. Chem. Soc.* **1969**, *91*, 2236.
(5) Sastri, V. S.; Langford, C. H. *J. Phys. Chem.* **1970**, *74*, 3945.
(6) Langford, C. H.; Scharfe, R.; Jackson, R. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 1033.
(7) Vigee, G. S.; Ng, P. *J. Inorg. Nucl. Chem.* **1971**, *33*, 2477.
(8) Frankel, L. S.; Langford, C. H.; Stengle, T. R. *J. Phys. Chem.* **1970**, *74*, 1376.
(9) Caminiti, R.; Magini, M. *Chem. Phys. Lett.* **1979**, *61*, 40.
(10) Caminiti, R.; Licheri, G.; Piccaluga, G.; Pinna, G. *J. Chem. Phys.* **1978**, *69*, 1; **1976**, *65*, 3134.
(11) Caminiti, R.; Cucca, P.; Radnai, T. *J. Phys. Chem.* **1984**, *88*, 2382.
(12) Caminiti, R.; Radnai, T. *Z. Naturforsch., A* **1980**, *35A*, 1368.
(13) Caminiti, R.; Licheri, G.; Piccaluga, G.; Pinna, G.; Radnai, T. *J. Chem. Phys.* **1979**, *71*, 2473.
(14) Radnai, T.; Palinkas, G.; Caminiti, R. *Z. Naturforsch., A* **1982**, *37A*, 1247.
(15) Caminiti, R.; Licheri, G.; Piccalyuga, G.; Pinna, G. *Z. Naturforsch., A* **1980**, *35A*, 1361.
(16) Caminiti, R.; Paschina, G. *Chem. Phys. Lett.* **1981**, *82*, 487.
(17) Caminiti, R.; Marongiu, G.; Paschina, G. *Z. Naturforsch., A* **1982**, *37A*, 581.
(18) Caminiti, R. *Z. Naturforsch., A* **1981**, *36A*, 1062.
(19) Caminiti, R.; Cucca, P.; D'Andrea, A. *Z. Naturforsch., A* **1983**, *38A*, 533.

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Here we report a study of the composition of the solvation shells of $Cr(NH_3)_5(OS(CH_3)_2)^{3+}$ and $Cr(NH_3)_5(OH_2)_3{}^+$ in water–dimethyl sulfoxide mixtures using the line broadening of solvent proton NMR peaks[20] and the Covington–Thain equation. A corrected form of this equation is given in eq 1, where $n$ is the

$$\frac{\Delta}{\Delta_p} = \frac{\sum_{i=1}^{n} K^{1/n} Y^i k^{i(i-1)/2-i(n-1)/2} \frac{(n-1)!}{(n-i)!(i-1)!}}{1 + \sum_{i=1}^{n} K^{1/n} Y^i k^{i(i-1)/2-i(n-1)/2} \frac{n!}{(n-i)!i!}} \tag{1}$$

total number of solvent molecules in the solvation shell (the zero subscript has been omitted for clarity) of the Cr(III) complex, $K$ is the overall equilibrium constant for the replacement of $n_0$ water molecules in the solvation shell by $n_0$ dimethyl sulfoxide molecules, $Y$ is the ratio $a_D/a_W$ of the activities of dimethyl sulfoxide to water in the bulk solvent phase, $k$ is related to the increment in the free energy change with each successive replacement of a water molecule by a dimethyl sulfoxide molecule exclusive of the statistical factors involved in the successive, stepwise replacements, and $\Delta$ and $\Delta_p$ are measured line broadenings for a proton NMR peak in a solvent mixture and in the neat solvent, respectively, corrected[2,5] for composition and viscosity effects.

## Experimental Section

**Chemicals.** Tetramethylene sulfoxide from Aldrich Chemical Co. was distilled and collected under reduced pressure. Deuterated dimethyl sulfoxide (99.5 atom % D) from Stohler Isotope Chemicals and deuterium oxide (99.8 atom % D) from Bio-Rad Laboratories were used as received. Deionized water was used where ordinary water was required. *p*-Toluenesulfonic acid (PTSA) from Eastman Kodak Co. was purified by recrystallization from ethanol. All other chemicals were reagent grade and were used without special purification.

Aquopentaamminechromium(III) nitrate–ammonium nitrate double salt was prepared by literature methods.[21] Aquopentaamminechromium(III) perchlorate was prepared by treating the double nitrate salt with concentrated perchloric acid as suggested by Riccieri and Zinato.[22] Magnetic susceptibility measurements gave an effective magnetic moment of 3.9 $\mu_B$, with $HgCo(NCS)_4$ as standard, in agreement with the expected value. The absorption maxima and molar extinction coefficients were in good agreement with literature values.[22] (Dimethyl sulfoxide)pentaamminechromium(III) perchlorate was prepared from the aquo complex by the method outlined by Riccieri and Zinato[22] and precipitated with 3 M $LiClO_4$ in methanol. The absorption maxima and molar extinction coefficients were in good agreement with the published values.[22]

Aquopentaamminecobalt(III) perchlorate was prepared as previously described.[23] (Tetramethylene sulfoxide)pentaamminecobalt(III) perchlorate was prepared as described for the dimethyl sulfoxide complex[24] except that acetone dimethyl acetal was added to remove water present in the reaction mixture.

**Preferential Solvation Studies.** The solvent mixtures were prepared with accurately known weights of each of the protonated and deuterated solvents in a known volume of the resultant mixture. Thus the number of moles of each protonated and deuterated solvent present in each solution was accurately known. The solutions always contained 20.0 M total protons from all sources, but the ratio of total moles of water to total moles of dimethyl sulfoxide was varied to cover the total range of solvent compositions. For a line-broadening measurement a known weight of the desired Cr(III) complex was dissolved in a known weight and composition of solvent mixture. For a unbroadened line width measurement an equal number of moles of the analogous Co(III) complex was dissolved in the same weight and composition of solvent mixture. The NMR spectra of the two solutions were taken with a Varian FT 80 spectrometer at 40 °C as rapidly as possible after preparation of the solutions to ensure negligible substitution of the water and sulfoxide ligands in the first coordination shell of the Cr(III) complexes. The concentrations of the metal complexes were varied between 0.0050 and 0.020 M; thus the amount of a solvent in the paramagnetic solvation shell environment was usually less than 1–2%. The line broadening in a given solvent mixture was strictly proportional to the concentration of the Cr(III) complex over the range 0–0.075 M.

**Solvent-Interchange Studies.** The interchange of water and tetramethylene sulfoxide ligands in water–tetramethylene sulfoxide (Sol) solutions of pentaamminecobalt(III) complexes was followed spectrophotometrically with a Beckman Model 25 automatic sample changing and recording spectrophotometer with thermostated cells and with a Beckman DU spectrophotometer with thermostated cell compartment. The plots of ln $(A - A_\infty)$ vs. time followed the first-order rate law

$$\ln (A - A_\infty) = \ln (A_0 - A_\infty) - k_0 t$$

where $A$, $A_0$, and $A_\infty$ are absorbances at time $t$, zero time and 10 half-lives, respectively, accurately to 5 half-lives. The first-order rate constant for approach to equilibrium, $k_0$, is the sum of $k_S$, the first-order rate constant for sulfoxide replacing water, and $k_W$, the first-order rate constant for water replacing sulfoxide in the first coordination shell. The individual rate constants, $k_S$ and $k_W$, were obtained in the usual manner by determining the equilibrium quotient, $Q = [Co(NH_3)_5Sol^{3+}]/[Co(NH_3)_5OH_2{}^{3+}]$, after 10 half-lives from absorbance measurements at 480 nm, where the two complexes have an isobestic point, and at 550 nm, where the aquo complex has a very small absorbance. The molar extinction coefficients listed in the supplementary material were used to calculate concentrations. The sum of the two complex concentrations was always >97% of the initial amount of complex taken.

The rate constant $k_0$ was independent of pH at pH $\leq 4.0$, independent of whether perchloric acid or *p*-toluenesulfonic acid was used to control pH, and independent of ionic strength, $\mu$, in the range employed, $\mu \leq 0.12$ M.

## Results and Discussion

**Composition of the Solvation Shells of $Cr(NH_3)_5(OS(CH_3)_2)^{3+}$ and $Cr(NH_3)_5OH_2{}^{3+}$.** Fast exchange of solvent molecules between diamagnetic bulk-phase sites and paramagnetic solvation-shell sites around the complex ion is expected so that McConnell's equation[25] for fast exchange given in eq 2 should apply for the observed half-width at half-height of a solvent proton resonance. The

$$\frac{1}{T_2} = \frac{P_D}{T_{2D}} + \frac{P_M}{T_{2M}} \tag{2}$$

fraction $P_M$ of a given solvent component in the paramagnetic environment is rather small compared to the fraction $P_D$ of that solvent in the diamagnetic environment so that $P_D \simeq 1$; the line width $T_{2D}^{-1}$ in the absence of paramagnetic solute is small and the difference between correcting $T_2^{-1}$ for $T_{2D}^{-1}$ or $P_D T_{2D}^{-1}$ lies within the error of reproducibility of measuring the line widths. Therefore, the experimental line broadening to a good approximation is given by eq 3. The ratio of the line broadening in the

$$\pi \Delta \nu' = \frac{1}{T_2} - \frac{1}{T_{2D}} = \frac{P_M}{T_{2M}} \tag{3}$$

solvent mixture to the line broadening in a neat solvent is given by eq 4, where the subscript zero refers to the neat solvent. In

$$\frac{\Delta \nu'}{\Delta \nu'_0} = \frac{P_M T_{2M_0}}{P_{M_0} T_{2M}} \tag{4}$$

water–dimethyl sulfoxide mixtures there is a large change in viscosity $\eta$ over the entire range of compositions and it cannot be assumed that $T_{2M} = T_{2M_0}$. Therefore, the line broadenings should all be normalized to a common viscosity[5] $\eta_0$, e.g. that of the neat solvent. This is readily done with use of eq 5, where $\Delta\nu$ is the

$$\Delta \nu = (\Delta \nu')\eta_0/\eta \tag{5}$$

line broadening in a solvent mixture corrected for the viscosity change. Since $\Delta\nu_0 = (\Delta\nu'_0)\eta_0/\eta_0 = \Delta\nu'_0$, eq 4 in terms of the corrected line broadenings becomes eq 6, where $n$ and $n_0$ are the

$$\frac{\Delta \nu}{\Delta \nu_0} = \frac{P_M}{P_{M_0}} = \frac{n}{n_0}\frac{N_0}{N} \tag{6}$$

numbers of molecules of the solvent of interest in solvation shells in the mixture and in the neat solvent, respectively, and $N$ and $N_0$ are the total numbers of molecules of the same solvent in the

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(20) Covington, A. K.; Thain, J. M. *J. Chem. Soc., Faraday Trans. 1* **1974**, *70*, 1879. Equation 6 in this paper has an error in the exponent of the *k* factor, which was corrected before use.

(21) Mori, M. *Inorg. Synth.* **1957**, *5*, 131.

(22) Riccieri, P.; Zinato, E. *Inorg. Chem.* **1980**, *19*, 853.

(23) Gould, E. S.; Taube, H. *J. Am. Chem. Soc.* **1964**, *86*, 1318.

(24) Mac-Coll, C. R. P.; Beyer, L. *Inorg. Chem.* **1973**, *12*, 7.

(25) McConnell, H. M. *J. Chem. Phys.* **1958**, *28*, 430.

**Table I.** Activities of Dimethyl Sulfoxide, $a_D$, and of Water, $a_W$, and Values of $Y = a_D/a_W$, of the Excess Free Energy of Mixing, $\Delta G^E$, and of the Viscosities, $\eta$, at 40 °C for Water–Dimethyl Sulfoxide Mixtures

| $X_D$ | $a_D$ | $a_W$ | $Y$ | $\Delta G^E$/ cal mol$^{-1}$ | $\eta$/cP |
|---|---|---|---|---|---|
| 0 | 0 | 1.000 | 0 | 0 | 0.661 |
| 0.1 | 0.015 | 0.841 | 0.0181 | −146.2 | 1.30 |
| 0.2 | 0.058 | 0.668 | 0.0872 | −226.0 | 1.95 |
| 0.3 | 0.137 | 0.503 | 0.2732 | −277.7 | 2.41 |
| 0.4 | 0.247 | 0.367 | 0.6712 | −294.9 | 2.47 |
| 0.5 | 0.373 | 0.263 | 1.417 | −284.5 | 2.31 |
| 0.6 | 0.502 | 0.183 | 2.750 | −252.4 | 2.10 |
| 0.7 | 0.630 | 0.120 | 5.257 | −205.3 | 1.90 |
| 0.8 | 0.755 | 0.070 | 10.85 | −145.6 | 1.73 |
| 0.9 | 0.874 | 0.030 | 29.59 | −82.7 | 1.60 |
| 1.0 | 1.000 | 0 | | 0 | 1.52 |

mixture and in the neat solvent, respectively. Equation 6 is readily rearranged to give $n/n_0$, the ratio of the number of molecules of the solvent of interest in the solvation shell of the complex ion in a solvent mixture to the same number in the neat solvent; thus

$$\frac{n}{n_0} = \frac{\Delta\nu}{\Delta\nu_0}\frac{N}{N_0} \tag{7}$$

The viscosity corrections for line broadening were made with use of eq 5 and the viscosities for 40 °C obtained from the 25, 45, and 65 °C viscosities given by Cowie and Toporowski.[26] The viscosity was assumed to have a exponential dependence on temperature, and the least-squares fit for $\ln \eta$ and $T^{-1}$ was obtained for each solvent mixture. Then values of $\eta$ at 40 °C were calculated for these mixtures as given in Table I.

The activities of dimethyl sulfoxide and water for use in $Y = a_D/a_W$ were calculated from the excess free energies of mixing of these solvents and the Duhem–Margules equation. The excess free energies of mixing were calculated from the measured enthalpies of mixing and the excess entropies of mixing given by Kenttamaa and Lindberg.[27] As a function of the mole fraction, $X_D$, of dimethyl sulfoxide the excess free energies, $\Delta G^E$, of mixing were given by eq 8, where the least-squares values of the coefficients were $A = -0.8418$, $B = +0.3419$, and $C = -0.1497$ for 30 °C, $A = -0.7827$, $B = +0.3028$, and $C = -0.1436$ for 40 °C, and $A = -0.7245$, $B = +0.2646$, and $C = -0.1381$ for 50 °C.

$$\Delta G^E = RTX_D(1 - X_D)(\ln 10)[A + B(2X_D - 1) + C(2X_D - 1)^2] \tag{8}$$

The calculation of activities was carried out with 0.01 mole fraction changes in the amounts of the two solvents in the composition ranges $0 \leqslant X_D \leqslant 0.1$ and $0.9 \leqslant X_D \leqslant 1.0$ and 0.02 mole fraction changes in the range $0.1 < X_D < 0.9$. At 40 °C mole fraction changes of 0.001 were also made in the ranges $0 \leqslant X_D \leqslant 0.01$ and $0.99 \leqslant X_D \leqslant 1.0$; this did not produce an important change in the activities. At 40 °C the calculations were made in both the forward (starting with pure $H_2O$) and reverse (starting with pure dimethyl sulfoxide) directions. The activities differed somewhat, and the average values were used as given in Table I for mole fractions of interest.

Equation 7 applies to the water proton line broadenings and to the dimethyl sulfoxide proton line broadenings over the whole range of possible solvent mixtures. If we assume that the Covington–Thain[20] theory is valid, then we can replace the left-hand side of eq 1 by the ratio $n_D/n_0$ for dimethyl sulfoxide to obtain one equation and by the ratio $n_W/n_0$ for water to obtain another. We have now assumed that the number $n_0$ of solvent molecules in the solvation shell is constant (for a given complex) and independent of its composition. The two equations obtained from eq 1 are of the forms given in eq 9

$$\frac{n_D}{n_0} = \frac{A'}{B} \quad \text{or} \quad 1 = \frac{A}{B} \tag{9a}$$

where $A = A'n_0/n_D$ and

$$\frac{n_W}{n_0} = \frac{C'}{D} \quad \text{or} \quad 1 = \frac{C}{D} \tag{9b}$$

where $C = C'n_0/n_W$. Therefore

$$AD = BC \tag{10}$$

By selecting a value of $n_0$, inserting the activity ratio $Y$ for the particular solvent composition, and systematically processing $K^{1/n_0}$ and $k$ sets of values with the aid of a computer program, one can find the set(s) of $K^{1/n_0}$ and $k$ values (if there are any) which makes(make) the two sides of eq 10 equal to within 1% error for *all* solvent compositions within the experimentally accessible range. In the case of water–dimethyl sulfoxide mixtures, which are highly nonideal, the change from 0.1 mole fraction to 0.9 mole fraction dimethyl sulfoxide involves a change in $Y$ of >1600-fold. As a result, when the solvation number is (for example) 10, the magnitude of $Y^{10}$ is $1.1 \times 10^{32}$ times larger for the 0.9 mole fraction solution than for the 0.1 mole fraction solution. The coefficients in the terms involving $K^{1/n_0}$ and $k$ in eq 1 thus cover very wide ranges in fitting experimental data gathered across the range of solvent compositions and subject the Covington–Thain equation to a rather severe test.

In our applications of eq 1 we made use of the fact that[20]

$$K^{1/n_0} = K'k^{n_0(n_0-1)/2} \tag{11}$$

where $K'$ is the first stepwise formation constant of the outer-sphere complex with the statistical factor removed and we recast eq 1 to obtain $K'$ (instead of $K^{1/n_0}$) from the calculations. This change does not invalidate any of the preceding statements since the equation obtained also gave equations of the form of eq 9 from the two proton line broadenings. All stepwise formation constants $K_i$ for the outer-sphere complex were then simply calculated from[20]

$$K_i = \frac{(n_0 + 1 - i)}{i}K'k^{i-1} \tag{12}$$

for $i = 1, ..., n_0$, and used to calculate $n_D/n_0$ and $n_W/n_0$ values for comparison with experimental values at all solvent compositions. For the entire range of the 1600-fold change in the activity ratio $Y$ we found the best fit of the input $Y$ and $n/n_0$ values to be given by $n_0 = 10$, $k = 0.565$, and $K' = 155.193 \pm 12.3\%$ for dimethyl sulfoxide replacing water in the solvation shell of $Cr(NH_3)_5(OS(CH_3)_2)^{3+}$. The constancy of $K'$ is very satisfactory when it is recalled that $K'$ (or a power of $K'$) is a major factor in the overall formation constants $\beta = \prod_i K_i$ of all dominant species in solution in any mixture, i.e., the terms involving $K'$ are never negligible in any part of the range of solvent composition.

The corresponding values for dimethyl sulfoxide replacing water in the solvation shell of $Cr(NH_3)_5OH_2{}^{3+}$ were $n_0 = 12$, $k = 0.760$, and $K' = 23.889 \pm 21.39\%$. For this complex only line broadening for the dimethyl sulfoxide protons could be obtained; the water protons were exchanged between bulk solvent and the first-coordination-shell $H_2O$ as well as between bulk solvent and solvation shell sites.

The use of $k = 0.565$ and $K' = 155.193$ for 40 °C in eq 12 allows one to calculate the 10 stepwise outer-sphere formation constants for $Cr(NH_3)_5(OS(CH_3)_2)^{3+}$ with dimethyl sulfoxide replacing water; they are $K_{1D} = 1.55 \times 10^3$ $K_{2D} = 395$, $K_{3D} = 132$, $K_{4D} = 49.0$, $K_{5D} = 19.0$, $K_{6D} = 7.45$, $K_{7D} = 2.88$, $K_{8D} = 1.07$, $K_{9D} = 0.358$, and $K_{10D} = 9.11 \times 10^{-2}$. From these, values of $n_D/n_0$ were calculated to compare with the experimental values obtained from line broadening after viscosity and composition corrections according to eq 5 and 7, respectively, were made and are listed in Table II. The 10 stepwise constants for replacement of dimethyl sulfoxide by water in the reverse reactions are given here for convenience; they are $K_{1W} = 11.0$, $K_{2W} = 2.79$, $K_{3W} = 0.934$, $K_{4W} = 0.347$, $K_{5W} = 0.134$, $K_{6W} = 5.27 \times 10^{-2}$, $K_{7W} = 2.04 \times 10^{-2}$, $K_{8W} = 7.57 \times 10^{-3}$, $K_{9W} = 2.53 \times 10^{-3}$, and $K_{10W} = 6.44 \times 10^{-4}$. The values of $n_W/n_0$ calculated from these constants are also given in Table II for comparison with the appropriately corrected experimental values.

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[26] Cowie, J. M. G.; Toporowski, P. M. *Can. J. Chem.* **1961**, *39*, 2240.

[27] Kenttamaa, J.; Lindberg, J. J. *Suom. Kemistil. B* **1960**, *33*, 98.

**Table II.** Calculated and Experimental Values of the Fractions $n_D/n_0$ and $n_W/n_0$ of Dimethyl Sulfoxide and of Water, Respectively, in the Second Coordination Shells of $Cr(NH_3)_5(OS(CH_3)_2)^{3+}$ and $Cr(NH_3)_5OH_2^{3+}$

| | $Cr(NH_3)_5(OS(CH_3)_2)^{3+}$ | | | | $Cr(NH_3)_5OH_2^{3+}$ | |
|---|---|---|---|---|---|---|
| $X_D$ | $(n_D/n_0)_{calcd}$ | $(n_D/n_0)_{exptl}$ | $(n_W/n_0)_{calcd}$ | $(n_W/n_0)_{exptl}$ | $(n_D/n_0)_{calcd}$ | $(n_D/n_0)_{exptl}$ |
| 0 | 0 | 0 | 1.0 | 1.0 | 0 | 0 |
| 0.1 | 0.34 | 0.27 | 0.66 | 0.57 | 0.20 | 0.32 |
| 0.2 | 0.50 | 0.43 | 0.50 | 0.40 | 0.39 | 0.41 |
| 0.3 | 0.62 | 0.52 | 0.38 | 0.32 | 0.55 | 0.53 |
| 0.4 | 0.71 | 0.60 | 0.29 | 0.25 | 0.67 | 0.67 |
| 0.5 | 0.78 | 0.67 | 0.22 | 0.19 | 0.77 | 0.76 |
| 0.6 | 0.84 | 0.74 | 0.16 | 0.14 | 0.84 | 0.82 |
| 0.7 | 0.89 | 0.81 | 0.11 | 0.11 | 0.89 | 0.89 |
| 0.8 | 0.93 | 0.88 | 0.070 | 0.066 | 0.94 | 0.92 |
| 0.9 | 0.97 | 0.91 | 0.032 | 0.030 | 0.97 | 0.99 |
| 1.0 | 1.00 | 1.00 | 0 | 0 | 1.00 | 1.00 |

The value of 0.565 for $k$ for the dimethyl sulfoxide complex means that it is 1415 J/mol more difficult at 25 °C for a dimethyl sulfoxide molecule to replace a water molecule in the solvation shell with each successive replacement step. This means that the first dimethyl sulfoxide molecule is held most firmly of the 10. Qualitatively this result is in agreement with the conclusions of Langford, Scharfe, and Jackson[6] concerning a more tightly bonded first dimethyl sulfoxide molecule in the solvation shell of $Cr(OS(CH_3)_2)_6^{3+}$. In the reverse process the first water molecule is the most tightly bonded. For the $Cr(NH_3)_5OH_2^{3+}$ complex the value of $k = 0.760$ means that it is 680 J/mol more difficult for a dimethyl sulfoxide molecule to replace a water molecule in each successive step at 25 °C.

The use of $k = 0.760$ and $k' = 23.889$ for $Cr(NH_3)_5OH_2^{3+}$ in eq 12 allows one to calculate the 12 stepwise outer-sphere formation constants for dimethyl sulfoxide replacing water; they are $K_{1D} = 287$, $K_{2D} = 100$, $K_{3D} = 46.0$, $K_{4D} = 23.6$, $K_{5D} = 12.8$, $K_{6D} = 7.07$, $K_{7D} = 3.95$, $K_{8D} = 2.19$, $K_{9D} = 1.18$, $K_{10D} = 0.606$, $K_{11D} = 0.279$, and $K_{12D} = 0.0973$. The values of $n_D/n_0$ calculated from these constants are given in Table II for comparison with experimental values. Except for the $X_D = 0.1$ point for the aquo complex the agreement between the calculated and experimental values of $n/n_0$ in Table II is quite satisfactory considering the assumption that $k$ is independent of solvation shell composition, the viscosity corrections to the line widths, the approximations made in obtaining activities, the wide range of $Y$ values covered, and the high powers of $Y$ appearing in eq 1. The poor fit for the first point for the aquo complex may result from a lack of constancy for $k$ in the early stages of replacement so that the first stepwise formation constant is larger, relative to the rest, than is allowed for in the Covington-Thain equation.

The values of $(n_D/n_0)_{exptl}$ tend to be somewhat larger for the aquo complex than for the dimethyl sulfoxide complex (with the possible exception of one mixture). The difference is small, but it is consistent with the solvent-interchange studies made by Johnson and King[28] and by us as discussed in the next section.

**Solvent Interchange of $Co(NH_3)_5Sol^{3+}$ Complexes.** The interchange of water and tetramethylene sulfoxide (designated by Sol) is shown in eq 13. The rate of approach to equilibrium was

$$Co(NH_3)_5OH_2^{3+} + Sol \underset{k_W}{\overset{k_S}{\rightleftharpoons}} Co(NH_3)_5Sol^{3+} + H_2O \qquad (13)$$

strickly first order with respect to the complex concentration to 4–5 half-lives at each solvent composition over the range $0.1 \leqslant X_S \leqslant 0.9$. The observed first-order rate constant, $k_0$, was separated into its components with use of spectrophotometrically determined equilibrium concentrations of the two complexes in eq 13. The molar extinction coeffs. of the complexes are markedly dependent on solvent composition but quite independent of temperature in the range 30–50 °C. This is interpreted to mean that these coefficients change with change of solvation shell composition and that the solvation shell composition is not significantly dependent on temperature for a given bulk solvent composition. The molar extinction coefficients are given for both complexes for 29.9, 38.5, and 50.5 °C at various binary solvent compositions in the supplementary material.

**Table III.** Values of $Q = [Co(NH_3)_5Sol^{3+}]/[Co(NH_3)_5(OH_2)^{3+}]$ for the Solvent Interchange between Water and Tetramethylene Sulfoxide at Different Solvent Compositions and Temperatures

| $X_{T,D}$[a] | $Q$(29.9 °C) | $Q$(38.5 °C) | $Q$(50.5 °C) | $Q_D$(35.0 °C)[b] | $Q_D$(35.0 °C)[c] |
|---|---|---|---|---|---|
| 0.10 | 0.0491 | 0.0483 | 0.0847 | 0.0309 | |
| 0.20 | 0.0741 | 0.102 | 0.171 | 0.0753 | |
| 0.25 | | | | | 0.106 |
| 0.30 | 0.177 | 0.160 | 0.238 | 0.147 | |
| 0.40 | 0.271 | 0.315 | 0.380 | 0.253 | |
| 0.50 | 0.550 | 0.535 | 0.585 | 0.403 | 0.355 |
| 0.60 | 0.848 | 0.885 | 1.04 | 0.634 | |
| 0.70 | 1.61 | 1.46 | 1.80 | 1.02 | |
| 0.75 | | | | | 1.38 |
| 0.80 | 2.58 | 2.65 | 2.99 | 1.86 | |
| 0.90 | 5.65 | 5.24 | 6.80 | 4.49 | |

[a] Mole fraction of tetramethylene sulfoxide or dimethyl sulfoxide. [b] For water–dimethyl sulfoxide mixtures as calculated from the equations given in ref 28. [c] For water–dimethyl sulfoxide mixtures as found in this work.

The thermodynamic equilibrium constant for eq 13 is given by eq 14, where $f_S$ and $f_W$ are the activity coefficients of the tetramethylene sulfoxide and aquo complexes, respectively, $Q$ is the equilibrium molar concentration ratio (as given in the Experimental Section) of the two complexes, and $a_W$ and $a_S$ are the activities of bulk-phase water and tetramethylene sulfoxide solvents. It will be assumed that $f_S = f_W$ because of the similarity in charge, size, and ligands (five out of the six are the same).

$$K_0 = Q\frac{f_S a_W}{f_W a_S} \qquad (14)$$

Because of the similarities between dimethyl sulfoxide and tetramethylene sulfoxide it will also be assumed that the activity ratio $a_S/a_W$ for tetramethylene sulfoxide and water may be approximated by the activity ratio $a_D/a_W$ for dimethyl sulfoxide and water. (This assumption may not be as drastic as it first appears.) The activities for use in this ratio at 30, 38.5, and 50.5 °C were obtained from excess free energies of mixing.[27] The values of $Q$ for use in eq 14 are given in Table III. The values of $K_0$ from eq 14 decreased in the manner found by Johnson and King[28] for the water–dimethyl sulfoxide solvent interchange. However, examination of the $n_D/n_0$ values in Table II shows that $Co(NH_3)_5OH_2^{3+}$ tends to bind more dimethyl sulfoxide in the solvation shell than does $Co(NH_3)_5(OS(CH_3)_2)^{3+}$. Therefore, the inner-shell substitution of the water ligand is accompanied by some release of dimethyl sulfoxide from the solvation shell and replacement by water. As a result, the power of $a_D/a_W$ should be less than unity and

$$K_0 = \frac{Q}{Y^z} \qquad (15)$$

or

$$\ln Q = \ln K_0 + z \ln Y \qquad (16)$$

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[28] Johnson, R. W.; King, E. L. *Inorg. Chem.* **1977**, *16*, 2584.

**Table IV.** Values of $k_W$ and $k_S$ for Water–Tetramethylene Sulfoxide Solvent Systems at Different Solvent Compositions and Temperatures

| | 29.9 °C | | 38.5 °C | | 50.5 °C | |
|---|---|---|---|---|---|---|
| $X_{H_2O}$ | $10^5k_W{}^a/s^{-1}$ | $10^5k_S/s^{-1}$ | $10^5k_W/s^{-1}$ | $10^5k_S/s^{-1}$ | $10^5k_W/s^{-1}$ | $10^5k_S/s^{-1}$ |
| 1.00 | 1.50 | | 4.35 | | 19.6 | |
| 0.90 | 1.52 | 0.075 | 4.66 | 0.255 | 23.5 | 2.00 |
| 0.80 | 1.43 | 0.106 | 4.24 | 0.434 | 22.2 | 3.80 |
| 0.70 | 1.24 | 0.219 | 3.93 | 0.629 | 20.6 | 4.90 |
| 0.60 | 0.980 | 0.265 | 3.07 | 0.966 | 16.9 | 6.41 |
| 0.50 | 0.713 | 0.392 | 2.31 | 1.24 | 13.6 | 7.98 |
| 0.40 | 0.563 | 0.476 | 1.73 | 1.53 | 9.67 | 10.1 |
| 0.30 | 0.373 | 0.602 | 1.33 | 1.94 | 6.12 | 11.0 |
| 0.20 | 0.270 | 0.696 | 0.833 | 2.20 | 3.88 | 11.6 |
| 0.10 | 0.140 | 0.788 | 0.465 | 2.43 | 1.90 | 12.9 |
| 0.00 | | 0.818 | | 2.64 | | 13.1 |

[a] Repeated experiments (up to five times) gave first-order rate constants for approach to equilibrium with a standard deviation for a single measurement of ±1%. The rate constants $k_W$ and $k_S$ had a maximum standard deviation of ±4%

where $z < 1$. A least-squares treatment of the data yields the following: for water–tetramethylene sulfoxide systems $z = 0.64 \pm 0.03$, $\ln K_0 = -0.722 \pm 0.078$ at 29.9 °C, $z = 0.65 \pm 0.03$, $\ln K_0 = -0.718 \pm 0.061$ at 38.5 °C, and $z = 0.61 \pm 0.04$, $\ln K_0 = -0.407 \pm 0.070$ at 50.5 °C; for water–dimethyl sulfoxide systems $z = 0.67 \pm 0.04$, $\ln K_0 = -0.995 \pm 0.036$ at 35 °C. The results for the water–dimethyl sulfoxide system were obtained from equations given in ref 28 and from results in our laboratory which agreed satisfactorily with those of ref 28. A difference in $K_0$ between the two sulfoxides is not surprising because at least a small difference in bond energies between Co(III) and the two sulfoxides is expected. More worthy of notice is the value and constancy of $z$. If the solvation shells of the Co(III) complexes have the same composition as those of the corresponding Cr(III) complexes, as found[8] for other Co(III) and Cr(III) complexes, the value of $z$ deduced from $Q$ values obtained across the whole range of solvent compositions at a given temperature is consistent with the $n_D/n_0$ ratios obtained from independent line-broadeing measurements. The latter are not sufficiently precise to predict precisely the net change in the dimethyl sulfoxide content of the solvation shell upon changing an aquo complex to a dimethyl sulfoxide complex, but both $z$ and $n_D/n_0$ values indicate that some nonaqueous solvent is lost from the solvation shell in the forward reaction of eq 13; when this is taken into account in the thermodynamic equilibrium constant, the result is a satisfactorily constant quantity.

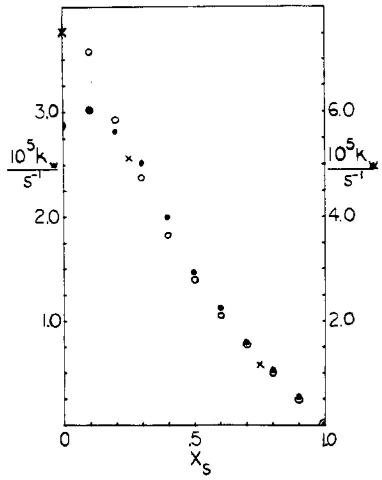

**Figure 1.** Plot of $10^5k_W$ vs. the mole fraction, $X_S$, of nonaqueous solvent component (35 °C): (closed circles) left-hand ordinate, water–tetramethylene sulfoxide media; (open circles) right-hand ordinate, water–dimethyl sulfoxide media, rate constants calculated from the equations given in ref 28; (crosses) right-hand ordinate, water–dimethyl sulfoxide media, rate constants found in this work.

**Table V.** Enthalpies and Entropies of Activation for $k_W$ and $k_S$ in Water–Tetramethylene Sulfoxide Mixtures

| $X_S$ | $\Delta H_W{}^{\ddagger}$/ (kJ/mol)[a] | $\Delta S_W{}^{\ddagger}$/ (J/mol K) | $\Delta H_S{}^{\ddagger}$/ (kJ/mol)[a] | $\Delta S_S{}^{\ddagger}$/ (J/mol K) |
|---|---|---|---|---|
| 0.00 | 99.5 | -9.2 | | |
| 0.10 | 106.2 | +13.1 | 128.5 | +61.1 |
| 0.20 | 106.5 | +13.5 | 139.9 | +101.7 |
| 0.30 | 109.1 | +20.9 | 121.7 | +47.4 |
| 0.40 | 110.7 | +24.0 | 124.1 | +57.4 |
| 0.50 | 114.7 | +34.7 | 117.5 | +38.6 |
| 0.60 | 110.6 | +19.0 | 119.2 | +45.9 |
| 0.70 | 108.1 | +7.9 | 113.3 | +28.7 |
| 0.80 | 103.2 | -11.1 | 109.2 | +16.5 |
| 0.90 | 100.6 | -24.9 | 108.6 | +15.3 |
| 1.00 | | | 107.5 | +12.3 |

[a] Average standard deviation for a single measurement was 3.3% for $\Delta H_W{}^{\ddagger}$ and 4.8% for $\Delta H_S{}^{\ddagger}$ throughout the solvent range.

The constancy of $z$ with change of temperature shows that the relative compositions of the two solvation shells are remaining approximately constant with temperature. Since the energy involved in replacing one solvent molecule with another in the solvation shell is small, the composition of a solvation shell is probably not significantly dependent on the temperature.

The rate constants $k_W$ and $k_S$ obtained at different temperatures across the range of solvent compositions are given in Table IV. The rate constants $k_W$ for tetramethylene sulfoxide–water and dimethyl sulfoxide–water[28] systems at 35 °C are plotted in Figure 1 against the mole fraction of the nonaqueous component. The plots show a remarkable similarity in the behavior of the two rate constants as the mole fraction of water, $X_W = 1 - X_S$, increases from zero to 0.8; $k_W$ for the dimethyl sulfoxide–water system remains equal to twice $k_W$ for the tetramethylene sulfoxide–water system over this range. It is not surprising that the magnitudes of the two rate constants differ since one does not expect the Co(III)–sulfoxide bond energy to be identical for the two sulfoxides. It is much more interesting that the two rate constants change with solvent composition in such a similar manner. It is widely accepted that the thermal substitution reactions of ligandopentaamminecobalt(III) complexes proceed by an $I_d$[29] mechanism where the entering ligand is chosen from the solvation shell because the $Co(NH_3)_5{}^{3+}$ group is not sufficiently stable to look for ligands outside the solvation shell. Since we have shown above that the solvation shell of $Co(NH_3)_5(OS(CH_3)_2)^{3+}$ is much poorer in fractional water content than the bulk solvent phase over the range $0.9 \geq X_W \geq 0.1$, the parallel behavior of the two $k_w$ values indicates that the solvation shell of $Co(NH_3)_5(OS(CH_2)_4)^{3+}$ is similarly poor in fractional water content over the range $0.8 \geq X_W \geq 0.1$. Certainly if the water contents of the two solvation shells diverged over this range it is likely that the two $k_W$ values would also have diverged. This indication of similar fractional water contents for the two solvation shells of the two sulfoxide complexes is consistent with the common value of $z$ that was found.

The $k_W$ values found for water–tetramethylene sulfoxide systems showed slight maxima at small $X_S$ values. This can be seen in Figure 1 for example. The maximum increased in height somewhat and broadened with increasing temperature. The same behavior of $k_W$ is observed for water–dimethyl sulfoxide media.

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(29) Langford, C. H.; Gray, H. B. "Ligand Substitution Processes"; W. A. Benjamin: New York, 1965.

At 35 °C, as seen in Figure 1, $k_W$ for dimethyl sulfoxide shows no maximum, only a decrease in slope; at 60 °C the maximum has become quite pronounced and has broadened.

The least-squares values of the enthalpies and entropies of activation listed in Table V were calculated for each solvent mixture by using eq 17, where $k_B$ is the Boltzmann constant and the other symbols have their usual meaning. Several rate constant

$$\ln \frac{k_i}{T_i} = \ln \frac{k_B}{h} + \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT_i} \qquad (17)$$

determinations were made at each temperature in each solvent mixture. The enthalpy of activation, $\Delta H_W^\ddagger$, for $k_W$ clearly shows a dependence on solvent composition. It is at a maximum at $X_S = X_W = 0.5$ and decreases with approach to either neat solvent. Johnson and King[28] reported a qualitatively similar trend for $k_0 = k_W + k_S$ for dimethyl sulfoxide mole fractions less than 0.5 (temperature data for mole fractions greater than 0.5 were not reported) in water–dimethyl sulfoxide mixtures. Since $k_W$ contributes to $k_0$ much more importantly than $k_S$ in this composition range, it is highly probable that the two sulfoxide systems are again showing similar behavior. The enthalpy of activation, $\Delta H_S^\ddagger$, for $k_S$ shows a dependence on solvent composition also with a maximum at $X_S = 0.2$. The activation parameters listed in Table V can be used to calculate $k_S$ and $k_W$ values for each solvent mixture at 29.9, 38.5, and 50.5 °C. The ratios $k_S/k_W$ of these values can be then compared to the spectrophotometrically determined $[Co(NH_3)_5Sol^{3+}]/[Co(NH_3)_5OH_2^{3+}]$ ratios. When this is done, satisfactory agreement is obtained between the two sets of $Q$ values.

The first-order rate constant $k_W$ for either sulfoxide complex, $Co(NH_3)_5Sol^{3+}$, reacting with water is a function of the solvent composition but it is *not a function of any integral power of the mole fraction or activity of either solvent; instead* $k_W$ *is proportional to the first power of* $n_W/n_0$ as the ratio was determined from the water proton line broadenings in $Cr(NH_3)_5(OS(CH)_2)_3{}^+$ solutions. The least-squares linear equations are

$$\log (10^5 k_W) = (1.11 \pm 0.05) + (0.92 \pm 0.02) \log (n_W/n_0)$$

for the water–dimethyl sulfoxide system and

$$\log (10^5 k_W) = (1.01 \pm 0.03) + (0.91 \pm 0.03) \log (n_W/n_0)$$

for the water–tetramethylene sulfoxide system.

The first-order rate constants $k_S$ for sulfoxide replacing water in $Co(NH_3)_5OH_2^{3+}$ are also a function of solvent composition but are not a function of any integral power of the mole fraction or activity of either solvent in the binary mixture. Instead they are dependent on the second power of $n_D/n_0$ as determined from the dimethyl sulfoxide proton line broadenings for $Cr(NH_3)_5OH_2^{3+}$ solutions. The least-squares linear equations are

$$\log (10^5 k_S) = (0.332 \pm 0.017) + (1.95 \pm 0.08) \log (n_D/n_0)$$

for water–dimethyl sulfoxide systems and

$$\log (10^5 k_s) = (0.371 \pm 0.017) + (1.98 \pm 0.07) \log (n_D/n_0)$$

for water–tetramethylene sulfoxide systems.

The specific rate of the reverse reaction in eq 13 is proportional to the probability that there is a water molecule in the solvation shell of $Co(NH_3)_5Sol^{3+}$. This is strong evidence that the substitution reaction has an $I_d$ mechanism because the water molecule must be in the solvation shell around $Co(NH_3)_5Sol^{3+}$ when the transition state is reached or substitution will not occur. Also it is strongly indicated that one water molecule is a stoichiometric component of the activated complex and is most probably the one entering (leaving) the first coordination shell in the solvent interchange. In an analogous fashion the specific rate of the forward reaction in eq 13 is proportional to the square of the probability that there is a sulfoxide molecule in the solvation shell of $Co(NH_3)_5OH_2^{3+}$. Thus two sulfoxide molecules appear to be stoichiometric components of the activated complex. One molecule presumably is the entering (leaving) molecule in the solvent-interchange reaction and the second performs some necessary function such as interacting with one or the other of the entering (leaving) ligand molecules or perhaps both in turn. Thus preferential solvation studies can provide information that brings meaning to an otherwise rather meaningless dependence of rate constants and overall equilibrium constants on solvent composition.

**Supplementary Material Available:** Tables showing the molar extinction coefficients for $Co(NH_3)_5OH_2^{3+}$ and for $Co(NH_3)_5(OS(CH_2)_4)^{3+}$ in water–tetramethylene sulfoxide systems at 29.9, 38.5, and 50.5 °C (2 pages). Ordering information is given on any current masthead page.

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# Stable, Chelated, Tetrahedral Silver(I) Complexes with Bidentate Phosphine Ligands. A Novel Application of INEPT to $^{109}Ag\{^{31}P\}$ NMR

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By the use of $^{109}Ag\{^{31}P\}$ INEPT pulse sequences, $^{109}Ag$ NMR spectra with good signal-to-noise ratios were obtained from bisphosphine complexes in relatively dilute solutions (e.g. 65 mM) in short times (1 h). They substantiated the existence of stable, chelated complexes of the type $[Ag(L_2)_2]NO_3$, where $L_2$ is $Ph_2PCH_2CH_2PPh_2$ (dppe), $Et_2PCH_2CH_2PPh_2$ (eppe), $Et_2PCH_2CH_2PEt_2$ (depe), $Ph_2PCH{=}CHPPh_2$ (dppey), and $Ph_2P(CH_2)_3PPh_2$ (dppp). Some of these complexes were isolated and further characterized. The difficulties of interpreting the $^{109}Ag\{^{31}P\}$ INEPT spectra arising from the second-order spin system of the eppe complex are discussed and clarified by the use of similar DEPT experiments.

## Introduction

Tetrakis complexes of the group 1B (11[21]) metal ions Cu(I), Ag(I), and Au(I) containing monodentate phosphines are usually considered to be of low thermodynamic stability and high kinetic lability.[2]

However, we have recently shown that such four-coordinate Au(I) complexes containing bidentate bis(tertiary phosphines)

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[1] (a) Birkbeck College. (b) Bruker Spectrospin.

[2] (a) Muetterties, E. L.; Alegranti, C. W. *J. Am. Chem. Soc.* **1970**, *92*, 4114. (b) Lippard, S. J.; Mayerle, J. J. *Inorg. Chem.* **1972**, *11*, 753. (c) Mays, M. J.; Vergnano, P. A. *J. Chem. Soc., Dalton Trans.* **1979**, 1112. (d) Parish, R. V.; Parry, O.; McAuliffe, C. A. *J. Chem. Soc., Dalton Trans.* **1981**, 2098.

0020-1669/85/1324-4278$01.50/0