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Solvation of Chloropentaamminecobalt(III) Ion in Water-Dimethyl Sulfoxide Mixtures

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The composition of the solvation shell of chloropentaamminecobalt(III) was investigated for water + dimethyl sulfoxide solvent mixtures using the Gibbs free energy of transfer and PMR solvent line broadening data. Strong evidence was found for the formation of solvated species with a unique dimethyl sulfoxide molecule in the solvation shell, which substantiates a previous conclusion concerning the existence of such species.

INTRODUCTION

The solvation of metal ions in solution is an important aspect of their chemistry. For example, in the solvent interchange reaction shown in eq. (1) (where Me represents the methyl group) the pseudo first-order rate constant k_s for the

$$Co(NH_3)_5OH_2^{3+} + Me_2SO \underset{k_w}{\overset{k_s}{\rightleftharpoons}} Co(NH_3)_5(OSMe_2)^{3+} + H_2O \qquad (1)$$

forward reaction has a strictly second-order dependence on (n_D/n_o), the mol fraction of dimethyl sulfoxide in the solvation shell of aquopentaamminecobalt(III),[1] over the entire range of mol fractions of dimethyl sulfoxide in the bulk solvent. Similarly, the pseudo first-order rate constant k_w for the reverse reaction has a strictly first-order dependence on (n_w/n_o), the mol fraction of water in the solvation shell of the (dimethyl sulfoxide)pentaamminecobalt(III) ion.[1] These two results clearly support the I_d mechanism, rather than the D mechanism,[2] for the reaction; the $Co(NH_3)_5{}^{3+}$ moiety cannot survive sufficiently long to escape the solvation shells and react with water and dimethyl sulfoxide in the bulk solvent phase where their mol fractions are very different from what they are in the solvation shells. Previously, Johnson and King[3] had searched for, but could not discover, simple relationships between these two rate constants and the concentrations, mol fractions and/or activities of the two solvents in the mixture.

In another study, it has been found[4] that the ratio $[Co(NH_3)_5(OSMe_2)^{3+}]/$ $/[Co(NH_3)_5OH_2^{3+}]$ of the two products formed in the mercury(II)-assisted removal of Cl^- from $Co(NH_3)_5Cl^{2+}$ in water and dimethyl sulfoxide mixtures was very different from (n_D/n_w), the ratio of the mol fractions of the two solvent components in the solvation shell of $Co(NH_3)_5Cl^{2+}$ as given by PMR line-broadening of the two solvent components in $Cr(NH_3)_5Cl^{2+}$ solutions. This result suggests that the removal of Cl^- from the metal complex by Hg^{2+} is not rapid enough for $Co(NH_3)_5^{3+}$ to be formed in the solvation shell surrounding the $Co(NH_3)_5Cl^{2+}$ ion.

More generally, a knowledge of the solvation shell of metal ions will be of much importance in the field of homogeneous catalysis, where the substrate is one of the components of the bulk solvent phase and must form part of the solvation shell of the metal catalyst prior to the reaction between substrate and metal.

In the results reported here, the composition of the solvation shell of chloropentaamminecobalt(III), designated by MCl^{2+}, was studied over the dimethyl sulfoxide mol fraction range $0.05 \leq X_D \leq 1.0$ using the PMR line-broadening results previously reported[4] and the free energies of transfer, $\Delta G_t^o(MCl^{2+})$, from purely aqueous solution to water + dimethyl sulfoxide mixed solvents as reported herein. The free energies of transfer were obtained from solubilities of $[MCl]Cl_2$ in the mixed solvents and were corrected to zero ionic strength at 25.0 °C. The results thus obtained from the two independent data sources are compared.

EXPERIMENTAL

Chemicals

Chloropentaamminecobalt(III) chloride, for brevity designated as $[MCl]Cl_2$, where MCl represents the $Co(NH_3)_5$ moiety, was prepared by literature methods.[5] De-ionized water was used throughout. Reagent grade dimethyl sulfoxide was used without further purification; traces of water in it were negligible, compared to the quantities of water added to obtain the desired solvent mixtures.

Solubility Determinations

Solid $[MCl]Cl_2$ was added to a saturated $[MCl]Cl_2$ solution in the solvent mixture. After a short time, an aliquot of solution was withdrawn, passed through a finely fritted sintered glass filter and analyzed for MCl^{2+} and Cl^-. Solubility determinations were performed in triplicate. For purely aqueous medium, our solubility determinations gave $(228.0 \pm 2.6) \times 10^{-4}$ mol dm^{-3} at 25 °C, compared to the literature value[6] of 225×10^{-4} mol dm^{-3}. Equally good agreement was obtained at 45.0 and 50.0 ° but these determinations will be reported later.

The spectrum of every filtrate was taken from 450 to 600 nm. The ratio A(532)/A(490) of the absorbances at 532 and 490 nm was never significantly less the 1.33, showing that no significant conversion of chloro to aqua or dimethyl sulfoxide complex had occurred. The concentration of MCl^{2+} in each filtrate was determined spectrophotometrically at 532 nm using the molar extinction coefficient, ε_{max}, determined for the relevant solvent mixture. (There is a small change in this coefficient over the range $0 \leq X_D \leq 1.0$.)

One aliquot of filtrate in each triplicate solubility determination was titrated with a 0.0500 M $Hg(NO_3)_2$ solution, using diphenylcarbazone as indicator to determine the Cl^- content. The Cl^- concentration was always twice the MCl^{2+} concentration within experimental error.

RESULTS AND DISCUSSION

Free Energies of Transfer

The experimentally determined solubilities, S, and their accompanying standard deviation for a single measurement, are listed in Table I for the mol fractions, X_D, of dimethyl sulfoxide used in the binary solvent mixtures. These solubilities were converted to activity solubility products K_a given in eq. (2) using Davies' equation,[7] relating activity coefficients to ionic strength because this equation has no arbitrary parameters. Constant A in Davies' equation was corrected for the change in dielectric constant of the liquid medium. For this purpose both sets of dielectric constants reported by Wolford[8] and by Lindberg and Kenttamaa[9] were used and fitted to a sixth degree polynomial. The relative percent error between the calculated and experimental dielectric constants at any one data point was not greater than 0.2%. Hence, the dielectric constant of any mixture could be accurately calculated for all mixtures in the range $0 \leq X_D \leq 1.0$.

$$K_a = a_{2+}\, a_{2-} \tag{2}$$

The K_a are listed in Table I. The first value listed for $X_D = 0$ is K_{aw}, the activity solubility product for purely aqueous medium. The remainder of the listed values are for K_{as}, the activity solubility products for media containing solvent S. As is well known, the Gibbs energy of transfer for $[MCl]Cl_2$ from a purely aqueous medium to a solvent S is given by eq. (3) which is readily converted to eq. (4). In eq. (4), the Gibbs free energy of transfer of Cl^- is readily obtained from the data of Cox, Natarajan and Waghorne[10] with the division $\Delta G_t^o(Ph_4As^+) = 1.08$; $\Delta G_t^o(BPh_4^-)$ recommended by Kim.[11] Gibbs free energies of transfer of MCl^{2+} calculated from eq. (4) for selected solvent compositions are listed in Table I and can be rounded off as needed. These Gibbs free energies of transfer were fitted to the polynomial in eq. (5) with a standard deviation of 94 J/mol. All ΔG_t^o values for points lying between the experimental points fall on the experimental $\Delta G_t^o - X_D$ curve, as indeed they should if eq. (5) adequately describes the dependence of ΔG_t^o on X_D.

TABLE I

The molar solubilities and activity solubility products of chloropentaamminecobalt(III) chloride and the Gibbs energies of transfer of the cation from water to water + dimethyl sulfoxide media at 25 °C

X^a_D	$10^4 \cdot S^b$/M	K_a/M^3	ΔG^o_t(exptl)/J mol
0.0	228.0 ±2.6	1.27×10^{-5}	
0.1	138.7 ±2.1	3.425×10^{-6}	-5742
0.2	90.2 ±0.8	1.07×10^{-6}	-13679
0.3	64.1 ±1.2	4.11×10^{-7}	-22296
0.4	51.4 ±1.0	2.15×10^{-7}	-30824
0.5	41.8 ±0.5	1.15×10^{-7}	-37966
0.6	32.3 ±0.6	5.45×10^{-8}	-43172
0.7	24.0 ±0.15	2.32×10^{-8}	-46736
0.8	18.3 ±0.4	1.05×10^{-8}	-49742
0.9	12.0 ±0.1	3.19×10^{-9}	-52106
1.0	8.41±0.11	1.15×10^{-9}	-56776

[a] Mol fraction of dimethyl sulfoxide based on binary solvent composition.
[b] Solubility in mol dm^{-3} ±standard deviation for a single determination.

$$\Delta G_t^o(\mathrm{MCl\cdot Cl_2}) = RT\ \ln(K_{aw}/K_{as}) \tag{3}$$

$$\Delta G_t^o(\mathrm{MCl^{2+}}) = -2\Delta G_t^o(\mathrm{Cl^-}) + RT\ \ln(K_{aw}/K_{as}) \tag{4}$$

$$\Delta G_t^o(\mathrm{MCl^{2+}}) = \sum a(\mathrm{i})X_\mathrm{D}{}^\mathrm{i} \tag{5}$$

The equilibria giving rise to the Gibbs free energies of transfer of $\mathrm{MCl^{2+}}$ can be written in a manner similar to the one used previously[12] for $\mathrm{K^+}$ as in eqs (6) to (9), where the bar over a symbol refers to species in purely aqueous medium.

$$\overline{\mathrm{MCl^{2+}}} + \overline{\mathrm{iW}} \rightleftharpoons \overline{\mathrm{MCl^{2+}\cdot W_i}},\ \gamma_\mathrm{i} \tag{6}$$

$$\overline{\mathrm{MCl^{2+}}} \rightleftharpoons \mathrm{MCl^{2+}},\ \beta_\mathrm{o} \tag{7}$$

$$\mathrm{MCl^{2+} + jW + kD} \rightleftharpoons \mathrm{MCl^{2+}\cdot W_jD_k},\quad \beta_\mathrm{jk} \tag{8}$$

$$\overline{\mathrm{MCl^{2+}}} + \mathrm{jW + kD} \rightleftharpoons \mathrm{MCl^{2+}\cdot W_jD_k},\quad \overline{\beta_\mathrm{jk}} = \beta_\mathrm{o}\beta_\mathrm{jk} \tag{9}$$

For convenience, the reference state here is chosen to be the bare, unsolvated, $\mathrm{MCl^{2+}}$ ion, not the fully hydrated one as in the earlier study[12] of $\mathrm{K^+}$.

In the purely aqueous phase with a total concentration C of all hydrated species, the concentration of the $\overline{\mathrm{MCl^{2+}\cdot W_i}}$ ion (i = 0,1,2, ...,p) is given by eq. (10):

$$\overline{[\mathrm{MCl^{2+}\cdot W_i}]} = \gamma_\mathrm{i}C/\sum \gamma_\mathrm{i} \tag{10}$$

When ΔC mol dm^{-3} of the complex are transferred out of the aqueous phase the change in the concentration of each $\overline{\mathrm{MCl^{2+}\cdot W_i}}$ ion is given by eq. (11) and the accompanying Gibbs free energy change is given by eq. (12). The total Gibbs free energy change in the aqueous phase per mol of complex transferred is given by eq. (13) and is a constant for a given T, regardless of the destination of the complex.

$$\Delta[\mathrm{MCl^{2+}\cdot W_i}] = (\Delta C)\gamma_\mathrm{i}/\sum_\mathrm{i} \gamma_\mathrm{i} \tag{11}$$

$$\Delta G_\mathrm{i} = -RT(\Delta C)\gamma_\mathrm{i}\ln\gamma_\mathrm{i}/\sum_\mathrm{i}\gamma_\mathrm{i} \tag{12}$$

$$\Delta G_\mathrm{W}{}^\mathrm{o} = -RT\left[\frac{\sum_\mathrm{i}\gamma_\mathrm{i}\ln\gamma_\mathrm{i}}{\sum_\mathrm{i}\gamma_\mathrm{i}}\right] \tag{13}$$

The distribution coefficient of $\mathrm{MCl^{2+}}$ between the aqueous phase and the mixed solvent S in eq. (7) is β_o. In the mixed solvent the various solvated species $\mathrm{MCl^{2+}\cdot W_jD_k}$ with j water (W) molecules and k dimethyl sulfoxide (D) molecules in the solvation shell are formed in eq. (8) with formation constants β_jk. In eq. (9), the $\mathrm{MCl^{2+}\cdot W_jD_k}$

ions in the mixed solvent are considered to be formed from $\overline{MCl^{2+}}$ ions in the aqueous phase and W and D molecules in the mixed solvent with formation constants $\beta_o\beta_{jk}$.

Note that the total solvation number of the complex ion in the mixed solvent is $(j + k)$, that this number can be variable, and that this number need not to be equal to p, the maximum hydration number in aqueous medium.

The Gibbs free energy change accompanying the formation of an equilibrium concentration of $MCl^{2+} \cdot W_jD_k$ from MCl^{2+} in the aqueous phase and W and D in the mixed solvent is given by eq. (14) and the total of all such contributions per mol of complex transferred is given by eq. (15).

$$\Delta G_i = [MCl^{2+} \cdot W_jD_k]\left\{-RT\ln(\beta_o\beta_{jk})\right\} \tag{14}$$

$$\Delta G_s{}^o = -RT\left[\frac{\sum_{j=0}^{n}\sum_{k=0}^{m}\beta_{jk}a_W^j a_D^k \ln\beta_o\beta_{jk}}{\sum_{j=0}^{n}\sum_{k=0}^{m}\beta_{jk}a_W^j a_D^k}\right] \tag{15}$$

It follows that the Gibbs free energy of transfer per mol of complex from its equilibrium hydration states in purely aqueous medium to its equilibrium solvation states in mixed solvent S is given by eq. (16). In eq. (16), the maximum numbers of water and dimethyl sulfoxide molecules to occupy a solvation shell are n and m, respectively. The first term within the braces is a constant and will be designated a. The second term, $\ln\beta_o$, may be replaced by a polynomial in X_D; we have found a quadratic to be satisfactory. In the third therm, the activities of water a_w, and of dimethyl sulfoxide, a_D are known for the solvent range $0 \le X_D \le 1.0$, as previously described.[13] The numerator and denominator of this term will be designated by $g(n,m,s)$ and $f(n,m,s)$, respectively, so that eq. (16) can be written more concisely as eq. (17) for the sth mixed solution.

$$\Delta G_t{}^o = -RT\left[\frac{\sum_{i=0}^{P}\gamma_i\ln\gamma_i}{\sum_{i=0}^{P}\gamma_i} + \ln\beta_o + \frac{\sum_{j=0}^{n}\sum_{k=0}^{m}\beta_{jk}a_W^j a_D^k\ln\beta_{jk}}{\sum_{j=0}^{n}\sum_{k=0}^{m}\beta_{jk}a_W^j a_{D,S}^k}\right] \tag{16}$$

$$\Delta G^o_{t,s} = -RT\left\{a + bX_{D,s} + cX^2_{D,s} + \frac{g(n,m,s)}{f(n,m,s)}\right\} \tag{17}$$

In the latter equation, the values of a, b, c and the $(n+1)(m+1) - 1$ β_{jk} must be determined. (The value of β_{oo} is necessarily unity). This is done using a minimization technique for the sum of the squares of the relative error for each solvent mixture s given in eq. (18).

$$\chi^2 = \sum_S\left[\frac{\Delta G^o_{t,s}\,(\text{expt}) - \Delta G^o_{t,s}\,(\text{calc})}{\Delta G^o_{t,s}\,(\text{expt})}\right]^2 \tag{18}$$

As many equations as unknowns are generated by differentiation of (18) with respect to the unknowns and setting the result equal to zero.

The a, b, c values for minimum error were

$$a = -0.40334557,\ b = 21.27162268,\ c = -1.18801461.$$

There are two results of note: (1) The value of $\Delta G_w{}^o$ is positive, as expected for the conversion of differently hydrated species to one species prior to transfer of that species to mixed solvent s. (2) The term $-RT \ln \beta_o$ accounts for much of $\Delta G^o{}_{t,s}$ (expt), as might be expected because the solvent cannot enter the first coordination shell of cobalt(III) to interact with the Co^{3+} center.

Abbreviated ln β_{jk} values are given in Table II. At $X_D = 0.05$, 45% of the complex ion was present as $MCl^{2+} \cdot W_{10}D_0$, which disappeared as X_D increased and was absent when the W:D ratio reached 2:1. Formation of the well-known 2:1 water:dimethyl sulfoxide complex in the bulk solvent competes successfully for the water and removes the decahydrate. Numerous solvated ions appear with small j and k values along with appreciable amounts of solvates, for which the total solvation number $(j+k) = 10$. For example, at $X_D = 0.65$, the percentage of $MCl^{2+} \cdot W_4D_6$, $MCl^{2+} \cdot W_3D_7$ and $MCl^{2+} \cdot W_2D_8$ were 14, 10 and 14%, respectively, while the remaining ions had 2 water molecules at the most and varying numbers of dimethyl sulfoxide molecules so that $(j+k) < 10$. Solvation numbers greater than 10 were not found. At $X_D = 0.95$, 71% of the complex ion was present as $MCl^{2+} \cdot W_0D_9$; the one-for-one replacement of water by dimethylsulfoxide did not persist up to $X_D = 0.95$ although those species were important at smaller X_D values.

TABLE II

ln β_{jk} values from Gibbs energy of transfer, ΔG_t^o (MCl^{2+})*

j	*k*=0	1	2	3	4	5	6	7	8	9
0	0.00	1.29	1.03	0.49	–0.31	–1.85				3.66
1	–0.81	1.33	2.87	2.17	2.23	2.25	2.15	1.84	1.38	1.39
2	–3.19	1.14	5.02	–0.03	–0.02	0.03	0.08	0.09	8.71	
3	–6.18	0.89	2.04	0.12	–0.01	–0.01	–0.01	9.95		
4	–7.30	0.60	1.15	0.06			11.76			
5		0.25	0.72	0.05		11.46				
6		–0.20	0.51	0.03	11.48					
7		–0.65	0.39	5.82						
8		–1.04	7.74							
9		–1.30								
10	0.96									

* Where values were too small to determine, no number was entered.

PMR Line Broadening for Mixed Solvent Components

Langford[14] and co-workers have shown the utility of line broadening studies of solvent components for yielding solvent ratios in solvation shells of inert Cr(III) and Co(III) complexes. In their studies it was reasonably assumed that the solvation states of Cr(III) complexes would be models for the solvation states of the corresponding Co(III) complexes because of similarity in size, charge and atoms (groups) exposed to the surrounding solvent. The mol fractions of dimethyl sulfoxide (n_D/n_o) and of water (n_w/n_o) in the solvation shell of chloropentaamminecobalt(III) reported earlier[4] can be also used to obtain distributions of solvated species for comparison purposes when corrected to 25 °C for the known viscosity changes of water + dimethyl sulfoxide mixtures.[15]

When the unsolvated ion is used as the reference state, it is easily shown that the mol fraction of sulfoxide in the solvation shell for solvent mixture s $(n_D/n_o)_s$ is given by eq. (19) and that the mol fraction of water in the solvation shell $(n_w/n_o)_s$ for the same solvent is given by eq. (20).

$$\left(\frac{n_D}{n_O}\right)_S = \frac{\sum_{j=0}^{n} \sum_{k=0}^{m} k\, a^j_{W,S}\, a^k_{D,S}\, \beta_{jk}}{\sum_{j=0}^{n} \sum_{k=0}^{m} (j+k)\, a^j_{W,S}\, a^k_{D,S}\, \beta_{jk}} \tag{19}$$

$$\left(\frac{n_W}{n_O}\right)_S = \frac{\sum_{j=0}^{n} \sum_{k=0}^{m} j\, a^j_{W,S}\, a^k_{D,S}\, \beta_{jk}}{\sum_{j=0}^{n} \sum_{k=0}^{m} (j+k)\, a^j_{W,S}\, a^k_{D,S}\, \beta_{jk}} \tag{20}$$

The relative errors between the experimental and calculated values of these two mol fractions were squared, summed and minimized. Again, as many equations as there are unknowns can be generated by differentiation with respect to β_{jk} and equation of the derivatives to zero. For minimum error, the abbreviated ln β_{jk} given in Table III were obtained. Distributions of solvated ions for some solvent compositions are shown in Table IV.

Like in the free-energies-of-transfer study, it would appear that the solvated species in purely aqueous solution is $MCl^{2+} \cdot W_{10}$ and that a considerable amount of this species is still present at $X_D = 0.05$. This solvated species is absent when the W:D ratio has decreased to 2:1. As X_D increases $MCl^{2+} \cdot W_{10-k}D_k$ species appear up to $k = 9$. No solvated species with $k = 10$ is formed, as was also found in the free-energy-of-transfer study. Attempts to introduce a $k = 10$ species resulted only in poorer fits with the experimental data.

In many respects the distributions of solvated species at various solvent compositions obtained from line broadenings are very different from those obtained from Gibbs energies of transfer. Initially, we naively expected that similar distributions should be obtained from the two independent sets of experimental data and we intro-

TABLE III

ln β_{jk} values from PMR line broadening of solvent components*

j	*k*=0	1	2	3	4	5	6	7	8	9
0	0.00	12.90	−2.00	−2.00	−2.00	−1.04				−5.00
1	0.15	5.07	−1.00	−2.00	−2.00	−9.00				14.04
2	−4.00	9.60	−1.00	−2.00	−2.00	−8.00			−2.00	
3	−7.00	14.03	−0.50	−2.00	−2.00	−7.00		−5.00	14.78	
4	−6.50	11.06	−0.50	−0.50	−0.50	−0.50	−0.50	19.14		
5	−5.00	6.55	−0.50	0.02	−0.40	21.08	14.45			
6	−5.00	3.00	0.10	0.02	20.10					
7	−4.25	3.00	0.10	16.65						
8	−0.84	3.00	15.24							
9	−0.83	12.86								
10	9.26									

* Where values were too small to determine, no number was entered.

TABLE IV

Distribution of the $MCl^{2+} \cdot W_jD_k$ species at various bulk mol fractions, X_D, of dimethyl sulfoxide at 25 °C

	Sets of (j,k) subscripts[a]													
X^b_D	10,0	0,1	2,1	3,1	4,1	9,1	8,2	7,3	6,4	5,5	3,7	2,8	1,9	Sum
0.05	36.2	15.1	0.5	38.0	1.8	7.8	0.5							99.9
0.15	3.7	34.1	0.8	53.0	2.2	4.2	1.4	0.2	0.2					99.8
0.25	0.1	57.2	0.7	36.8	1.1	0.7	0.7	0.4	1.8	0.6				100.1
0.35		74.0	0.5	17.8	0.4		0.1	0.2	3.3	3.6	0.1			100.0
0.45		84.1	0.3	6.3	0.1			0.1	2.1	6.1	1.1			100.2
0.55		88.7	0.1	2.2					0.7	4.5	3.4	0.1	0.1	99.8
0.65		91.2	0.1	0.7					0.2	1.8	5.2	0.3	0.6	100.1
0.75		92.6		0.2						0.4	4.4	0.5	2.0	100.1
0.85		94.1									1.8	0.4	3.7	100.0
0.95		97.0									0.1	0.1	2.8	100.0

[a] Only those species whose percent mol fractions, based on total cobalt(III) present, rounded off to 0.1 or greater are listed.

[b] Dimethyl sulfoxide mol fractions based on total solvents present only.

duced β_{jk} values from the ΔG^o_t study into eqs. (19) and (20). Very large errors were obtained, which decreased until the results given in Tables III and IV were obtained. A closer consideration leads to the conclusion that these two distributions need not be the same. For example, $MCl^{2+} \cdot W_0D_0$ is not present in line broadening results because it cannot contribute to solvent line broadening when it has neither W or D molecules acting in solvating roles. It can be present in the ΔG^o_t results because the change of solvent structure, which accompanies enclosing the MCl^{2+} ion in a clathrate-like cage,[16] can result in a significant Gibbs energy contribution. In a similar manner, other solvated ions may contribute considerably to one of the measured quantities but less significantly to the other.

Worthy of note are the unique complexes containing one dimethyl sulfoxide molecule, $MCl^{2+} \cdot W_jD_j$ (j = 0, 2, 3, 4, 9), formed. In particular, one solvated complex $MCl^{2+} \cdot W_0D_1$ is formed over the whole range of solvent compositions used. Long ago, Langford, Scharfe and Jackson[17] suggested the existence of a unique outer-shell dimethyl sulfoxide complex formed with octahedral inner-sphere transition metal complex ions such as hexakis(dimethyl sulfoxide)nickel(II) and -chromium(III). They proposed that one D molecule was uniquely bound or positioned in the second, or outer, coordination shell of the central metal as a result of examining the kinetic and preferred solvation data of Frankel,[18] of Vigee and Ng[19] and of Langford and co-workers.[17] Our results from the line width study show that species containing one D molecule in the solvation shell predominate in percentage abundance (see column 2 in Table V) of species important to line broadening.

In Table V, we have tabulated total mol fraction F_1 of species containing one D, the total number N_{Db} of bound D per 100 MCl^{2+} present, and the fraction F_{Db} in column 4. F_{Db} is defined as the ratio of N_{Db} at X_D to the number of D bound at X_D = 0.75, where N_{Db} is a maximum. In Figure 1 we have plotted F_{Db} *versus* X_D along with the values of the D self-exchange rate constant given by Langford *et al.*[17] The two plots are very similar and the similarity may be fortuitous. If it were not, the rate constants would be proportional to the fraction F_{Db} of bound D and the rate constant would attain its maximum value when the maximum number of D were in the solvation shell.

TABLE V

Distribution of bound dimethyl sulfoxide in the solvation shell of MCl^{2+} at various X_D

X_D	F_1[a]	N_{Db}	F_{Db}
0.05	63.2	64.2	0.435
0.15	94.3	98.5	0.67
0.25	96.5	109.3	0.74
0.35	92.7	125.4	0.85
0.45	90.8	137.7	0.93
0.55	91.0	141.8	0.96
0.65	92.0	146.0	0.99
0.75	92.8	147.6	1.00
0.85	94.1	143.2	0.97
0.95	97.0	123.7	0.84

[a] Sum of mol fraction of $MCl^{2+} \cdot W_jD_l$ ($j = 0,1,\ldots, 10$) species

[b] N_{Db} = number of bound dimethyl sulfoxide molecules per 100 MCl^{2+}.

[c] $F_{Db} = N_{Db}/147.6$.

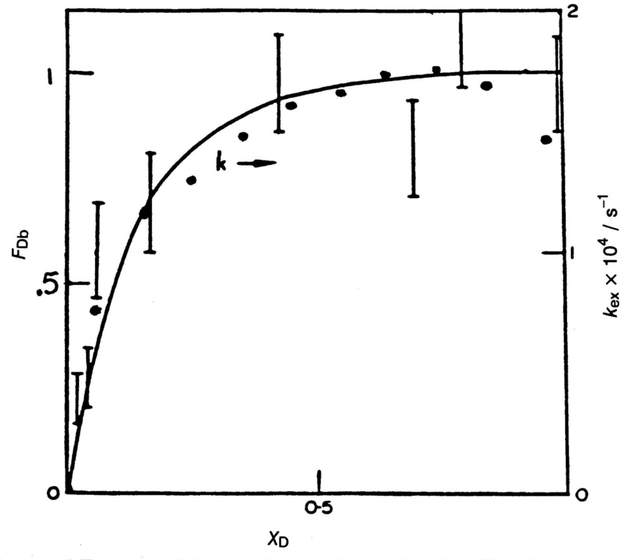

Figure 1. Dependence of F_{Db} and of k_{ex} on the total mol fraction X_D of dimethyl sulfoxide based on total solvents only.

In Figure 1, the vertical bars give ranges of k_{ex} for the CrD_6^{3+} + D self-exchange and the smooth curve was drawn through them so as to reach a maximum value at $X_D = 1$ in accordance with the ideas prevailing at that time. At that time, it was assumed that the number of D molecules in the solvation shell would be maximum at $X_D = 1$; at $X_D < 1$ k_{ex} would decrease as X_D decreased. Our values of F_{Db} would suggest that k_{ex} should reach a maximum at $X_D < 1$ and that k_{ex} should decrease measurably from $X_D = 0.85$ to $X_D = 0.95$ if the precision of the k_{ex} values could be improved sufficiently; the vertical bars for the experimental values of k_{ex} at these two X_D values do show the suggested decrease. Unfortunately, the precision of the k_{ex} and line broadening measurements is insufficient to be certain of this decrease.

It should be noted that obtaining values for the mol fractions of solvents in coordination shells involves the assumption that T_{2M} remain constant with the change of composition of the coordination shell. Since this assumption appeared to be valid for the first-coordination shells of Co^{2+} and Ni^{2+} in water + dimethyl sulfoxide binary mixtures[20] and for the outer-coordination shells of inert octahedral Cr(III) complexes,[14,17] it should be a valid assumption also for $Cr(NH_3)_5Cl^{2+}$. In this case, the results of Table IV show that the total number of W and D solvent molecules in the solvation shell per 100 MCl^{2+} decreases continuously as X_D increases in the range 0.05 to 0.95. Also, at the point where $(n_D/n_0) = (n_w/n_0) = (1/2)$, there are many different solvated species in solution and solvent substitution cannot be represented by the single, overall substitution reaction:

$$M \cdot W_n + (n/2)D \rightleftharpoons M \cdot W_{n/2}D_{n/2} + (n/2)W$$

as it was tacitly assumed in the past when calculating equilibrium constants at the »half-way« point for solvent substitution.

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SAŽETAK

Solvatacija kloropentaamminkobalt(III)-iona u smjesama voda-dimetilsulfoksid

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Sastav solvatacijske ljuske kloropentaamminkobalt(III)-iona u smjesama vode i dimetilsulfoksida (DMSO) proučavane su određivanjem Gibbs-ovih energija prijenosa i širenja linija otapala u spektru ^{1}H-NMR. Dobiven je čvrst dokaz nastanka solvatne kemijske vrste sa samo jednom molekulom DMSO, u skladu s ranijim zaključcima o njezinu postojanju.