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Mechanism of Complexation of Ni^{2+} in Dimethyl Sulfoxide and of Cu^{2+} in Methanol with Monodentate Ligands

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Electrical conductance data for $Ni(NCS)_2$ in DMSO and $Cu(ClO_4)_2$ in MeOH at 25° are reported. They indicate the two electrolytes to be associated in the two solvents with association constants $K_{NiNCS^+} = 989\ M^{-1}$ in DMSO and $K_{CuClO_4^+} = 193\ M^{-1}$ in MeOH. Pressure-jump relaxation kinetic data are reported for $Ni(NCS)_2$ in DMSO at 20, 25, 30, and 35°. The analysis of the data reveals the mechanism to be interchange dissociative (Id) with the rate constant of ligand penetration in the first coordination sphere of Ni^{2+} to be of the same order of magnitude as the pseudo-first-order rate constant for solvent exchange. The activation enthalpy confirms the above. Ultrasonic relaxation data of $Cu(ClO_4)_2$ in MeOH at 25° also indicate the mechanism to be Id with $k_{23} \approx k_{exch}$. Previous findings in MeOH and DMSO indicating slower rates of substitution are suggested to be due to the structure of the ligand, specifically to the multidenticity of it in the case of previous studies in DMSO. The general validity of the Eigen interchange dissociative mechanism for monodentate ligands is reaffirmed.

Introduction

Conflicting results for the mechanism of solvent substitution around the first coordination sphere of first-row transition metals exist in the literature for the case of MeOH and DMSO.

Ellgen and Pearson showed that the dissociative interchange (Id) mechanism explains data of complexation of Ni^{2+} with several ligands in MeOH eminently well.[2] However, data for complexation of first-row transition metals and Mg^{2+} with metabenzenedisulfonate anions could not be fitted by this mechanism.[3] The doubt that some properties of the ligand were responsible for such behavior was confirmed by Hoffmann, *et al.*,[4] in a study of several metal cations with Cl^- in MeOH and Mg^{2+} with trifluoroacetate anion showing the Id mechanism to be operative. Similarly, Caldin and Bennetto[5] found rate constants far lower than expected on the basis of the product $K_{Fuoss}k_{exch}$ for Ni^{2+} in DMSO. They attributed this behavior to the structure of the solvent and found correlation between the parameter $n = k_f(\text{exptl})/K_{Fuoss}k_{exch}$ and properties of the solvents such as fluidity and heat of evaporation. However, Hoffmann[6] showed that Ni^{2+} with NCS^- and Cl^- complexed *via* an Id mechanism in DMSO.

It was of paramount interest to extend the work of Hofmann to Cu^{2+} in MeOH where recent nmr solvent-exchange data have become available.[7] Similarly, it was of interest to confirm the data and findings of Hoffmann[6] in DMSO by investigating the activation parameters of the reaction and performing equilibrium association measurements to make sure that indeed the first complexation step between Ni^{2+} and NCS^- had been measured.[6]

Ultrasonic relaxation for the case of Cu^{2+} with ClO_4^- in MeOH and *P*-jump relaxation for Ni^{2+} with NCS^- in DMSO proved to be appropriate tools to study the kinetics of complexation. Electrical conductance data provided equilibrium formation constants.

Experimental Part

Instrumentation. The instrumentation and procedure for the electrical conductance,[8] *P* jump,[3] and ultrasonics[9] have been described already.

Materials. $Ni(NCS)_2$ (K & K reagent) was dried at 102° to constant weight. DMSO (Fisher reagent) was distilled *in vacuo* twice over P_2O_5 collecting the middle third fraction only. MeOH (Fisher reagent) was distilled over Al amalgam in a 5-ft all-Pyrex Vigreaux column. $Cu(ClO_4)_2$ in MeOH was prepared in two ways. The first method[10] was metathesis of anhydrous $CuCl_2$ and $AgClO_4$ predried at 110° ($CuCl_2$ was anhydrous (Baker reagent); $AgClO_4$, anhydrous (Smith, Cleveland, Ohio)). The solution was filtered through a fine-fritted disk followed by analysis of the filtrate by cation exchange and acidimetry. The second method was refluxing $Cu(ClO_4)_2 \cdot 6H_2O$ in MeOH over molecular sieves by an extraction apparatus[11] already described[10] for at least 5 hr followed by analysis of the solution as before. Solutions prepared in both ways of the same concentration gave results for ultrasonic relaxation data within experimental error (±2%). On the other hand, solutions of $Cu(ClO_4)_2 \cdot 6H_2O$ of the same salt concentration as anhydrous ones gave the same results by ultrasonic relaxation showing that small quantities of water had no apparent effect on the data.

Similarly, solutions for conductance work, in the case of $Cu(ClO_4)_2$ in MeOH prepared either by the metathesis method or by partially dehydrating a salt (by exposure over P_2O_5 for several weeks), gave the same results within experimental error.

Solutions for kinetic work were prepared by volume dilutions of stocks for the case $Ni(NCS)_2$ in DMSO and by freshly prepared solutions for the case of $Cu(ClO_4)_2$ in MeOH. For conductance work, solutions were prepared by weight and analyzed by weight burets with EDTA solutions for the cations. For both salts additions of weighed samples of stock solutions to the solvent were performed directly in the conductance cell in a drybox.

The temperature was maintained within ±0.05° at room temperature and ±0.1° at −50° for the kinetic work. For the conductance work the temperature was maintained equal to 25.00 ± 0.001° as measured by a Mueller bridge and calibrated Pt thermometer.

The only change in equipment with respect to the previous work[3] was the material of the *P*-jump cell because of the use of DMSO. It was found that Delrin (acetal molding) was adequate in mechanical strength, chemical inertness, and rigidity to withstand the 30-atm transients with DMSO solutions. On the contrary, Teflon proved to be not rigid enough, the electrodes of the conductance cells[3] vibrating

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Table I. Equivalent Conductance (Ω^{-1} cm^2 equiv^{-1}) and Concentration (*M*) of $Ni(NCS)_2$ in DMSO and $Cu(ClO_4)_2$ in MeOH at 25°

10^4C	Λ	10^4C	Λ	10^4C	Λ
		Electrolyte $Ni(NCS)_2$			
0.2442_5	44.29_3	0.9065_8	41.13_2	4.057_6	35.22_3
0.3944_7	43.68_0	1.448_2	40.09_3	6.672_8	32.43_0
0.5871_0	42.73_4	2.403_6	37.63_7	9.791_6	29.53_0
0.7287_3	42.10_5				
		Electrolyte $Cu(ClO_4)_2$			
1st run				2nd run	
0.7655_4	121.50	2.2438	114.90	1.3507	118.44
1.2952	118.66	2.6259	113.56	2.7123	113.19
1.7821	116.61	3.2886	111.64	4.0194	109.46
				5.4215	106.17

excessively during the explosion (with a resulting noisy signal on the scope). Attempts to build a pressure-jump cell of stainless steel coated by Teflon were also unsuccessful because of electrical shortage at the edges of the cavities withholding the electrodes (the authors are grateful to Dr. G. Macri for these efforts which resulted in the construction of a Delrin cell).

Results and Calculations

Table I reports the electrical conductance data and the corresponding concentrations for $Ni(NCS)_2$ in DMSO and $Cu(ClO_4)_2$ in MeOH at 25°.

These data have been analyzed by the Fuoss-Edelson method[12] already described.[10] Plots of the quantity Λ^* *vs.* χ are shown in Figure 1 according to the equation[12]

$$\Lambda^* = \Lambda_0 - \frac{K_A}{\Lambda_0}\chi \qquad (1)$$

where K_A corresponds to the equilibrium $Me^{2+} + L^- \rightleftharpoons MeL^+$. The results for Λ_0 and K_A, after recycling with the calculated Λ_0 by least-squares analysis, are as follows: for $Ni(NCS)_2$, $\Lambda_0 = 46.55 \pm 0.08$ Ω^{-1} cm^2 equiv^{-1} and $K_A = 989 \pm 18$ M^{-1}; for $Cu(ClO_4)_2$, $\Lambda_0 = 129.67 \pm 0.05$ Ω^{-1} cm^2 equiv^{-1} and $K_A = 193 \pm 3$ M^{-1}. Data for the $\lambda^0{}_{NCS^-} = 29.20$ in DMSO[13a] and $\lambda^0{}_{ClO_4^-} = 70.8 \pm 0.2$[13b] in MeOH have been taken from the literature, in order to analyze the conductance data by eq 1.

Subtraction from the final Λ_0 values gives $\lambda^0{}_{Ni^{2+}} = 17.4 \pm 0.3$ Ω^{-1} cm^2 equiv^{-1} in DMSO and $\lambda^0{}_{Cu^{2+}} = 58.9 \pm 0.25$ Ω^{-1} cm^2 equiv^{-1} in MeOH. Previous results from the literature for limiting ionic conductances of the two cations are $\lambda^0{}_{Ni^{2+}} = 18.4$ Ω^{-1} cm^2 equiv^{-1} in DMSO[14] and $\lambda^0{}_{Cu^{2+}} = 60.9 \pm 1.2$ Ω^{-1} cm^2 equiv^{-1} in MeOH[8] at 25°. For the case of Cu^{2+}, the present figure is believed to be more reliable than the previous one[8] which was obtained by a long extrapolation of a Shedlovsky plot on CuBDS data. For the case of $Ni(NCS)_2$ the reported figure for K_A is in good accord with Hoffmann's kinetic result[6] for $K_A \simeq 10^3$ M^{-1} in DMSO at 20°.

Table II reports the relaxation times for $Ni(NCS)_2$ in DMSO at the various concentrations and temperatures investigated. The data at 20° are in excellent accord with the data by Hoffmann.[6]

For an unambiguous interpretation of the relaxation spectra for $Ni(NCS)_2$ in DMSO, attention must be given to the species present in solution at the concentration range of this work.

Table II. Relaxation Times at the Various Concentrations and Temperatures Investigated and $k_f \pm \Delta k_f$ and $k_r \pm \Delta k_r$ at the Corresponding Temperatures for $Ni(NCS)_2$ in DMSO

Temp, °C	*C, M*	$10^3\tau$, sec	10^4k_f, M^{-1} sec^{-1}	k_r, sec^{-1}
20	0.001	6.4 ± 0.08	$5.6_8 \pm 0.4_2$	89 ± 18
	0.005	3.4 ± 0.06		
	0.010	$2.3 \pm 0.00_2$		
	0.018	1.9 ± 0.11		
	0.025	1.6 ± 0.07		
	0.050	1.2 ± 0.02		
25	0.001	4.2 ± 0.06	$8.9_4 \pm 0.3_7$	136 ± 27
	0.005	2.2 ± 0.02		
	0.010	1.6 ± 0.04		
	0.018	1.3 ± 0.04		
	0.025	1.15 ± 0.02		
	0.050	0.82 ± 0.01		
30	0.001	2.6 ± 0.05	13.5 ± 0.4	196 ± 33
	0.005	1.5 ± 0.02		
	0.010	1.1 ± 0.03		
	0.018	0.86 ± 0.01		
	0.025	0.69 ± 0.01		
	0.050	0.55 ± 0.08		
35	0.001	1.9 ± 0.04	19.3 ± 0.4	302 ± 31
	0.005	0.95 ± 0.01		
	0.010	$0.75 \pm 0.00_7$		
	0.018	0.60 ± 0.01		
	0.025	0.51 ± 0.01		
	0.050	0.37 ± 0.01		

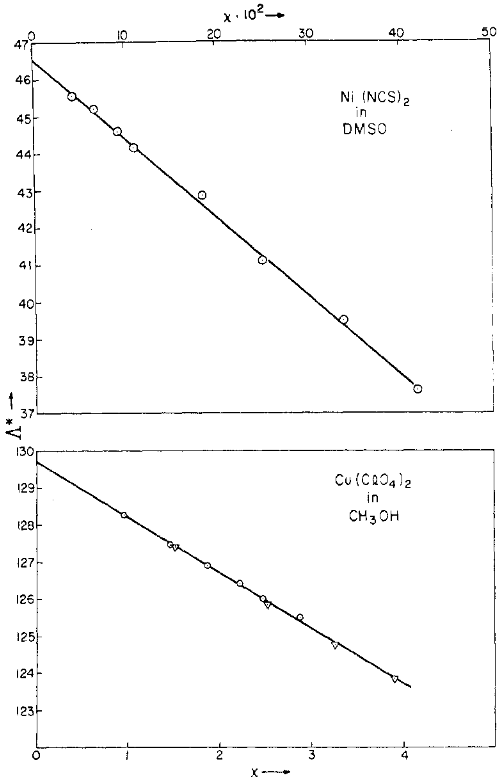

Figure 1. Fuoss-Edelson method: Λ^* *vs.* χ for $Ni(NCS)_2$ in DMSO and $Cu(ClO_4)_2$ in MeOH at 25°.

This problem has been already dealt with by Hoffmann, *et al.*[6] These authors noticed that two relaxation times were observable for this system in the concentration range 2×10^{-2}–10^{-1} *M*. The fast one on the order of 0.1 msec was measured by a shock tube; the slow one on the order of 1.0 msec was measured by the *P*-jump technique. At $C = 0.1$ *M*, the amplitude of the relaxation curve for the fast process was larger than for the slow process.[6] With increas-

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ing dilution toward $C = 10^{-2}\ M$ the amplitude of the fast process decreased rapidly while the amplitude of the slow process was slightly diminished.[6] The fast process was associated with the formation of the bis complex and the slow one with the formation of the mono complex. Further, since the relaxation times for the two processes are separated by a factor of 10, coupling between the two processes was neglected. Each process was treated as an independent step on a time scale. The two average formation constants from the kinetic data were[6] $K_1 = 1140$ and $K_2 = 35\ M^{-1}$. In this laboratory we also noticed, for concentrations larger than 0.05 M, that the relaxation spectra determined by the P-jump technique could not be fitted by a single relaxation process (nonlinearity of the log displacement *vs.* time). We therefore maintained the concentration of the electrolyte in the range where a single relaxation was observable, namely, up to 0.05 M.

Failure to observe a second relaxation however is not necessarily a proof of the existence of a single species. In fact it could be argued that such a criterion is dependent on the sensitivity of the method of detection of the relaxation process.

It is important therefore to check whether the observations by Hoffmann, *et al.*,[6] are consistent with the stoichiometric calculations. By combining the two mass action expressions $K_1 = [\mathrm{ML}]/[\mathrm{M}][\mathrm{L}]$ and $K_2 = [\mathrm{ML_2}]/[\mathrm{ML}][\mathrm{L}]$ with the mass balance equations $C^0{}_\mathrm{M} = [\mathrm{M}] + [\mathrm{ML}] + [\mathrm{ML_2}]$ and $C^0{}_\mathrm{L} = [\mathrm{L}] + [\mathrm{ML}] + 2[\mathrm{ML_2}]$, one can calculate the average ligand number n, where

$$n = \frac{C^0{}_\mathrm{L} - [\mathrm{L}]}{C^0{}_\mathrm{Me}} = \frac{K_1[\mathrm{L}] + 2K_1K_2[\mathrm{L}]^2}{1 + K_1[\mathrm{L}] + K_1K_2[\mathrm{L}]^2}$$

In the above [M] and [L] are the concentrations of free metal and free ligand. At $[\mathrm{L}] = 10^{-3}\ M$, $n = 0.56$ whereas at $[\mathrm{L}] = 10^{-2}\ M$, $n = 1.18$ retaining[6] $K_1 = 1140\ M^{-1}$ and $K_2 = 35\ M^{-1}$. Hence at $[\mathrm{L}] = 10^{-2}\ M$, since $n = 1.18$ the presence of the second complex should be observable. At the stoichiometric concentration $C^0{}_{\mathrm{Ni(NCS)_2}} = 2.5 \times 10^{-2}$ M the first complexation is almost complete, $[\mathrm{NiNCS^+}] \simeq [\mathrm{NCS^-}]$, while $[\mathrm{Ni^{2+}}]$ is one order of magnitude smaller. Therefore $[\mathrm{NCS^-}] \simeq 2 \times 10^{-2}\ M$. It is significant that Hoffmann noticed the presence of a second relaxation down to $C^0{}_{\mathrm{Ni(NCS)_2}} = 2.5 \times 10^{-2}\ M$. This is consistent with the above calculation.

The question to consider next is the possibility of coupling of the two processes.

If the equilibria

$$\mathrm{Ni^{2+} + NCS^-} \underset{k_{\mathrm{r}_1}}{\overset{k_{\mathrm{f}_1}}{\rightleftharpoons}} \mathrm{NiNCS^+}$$

$$\mathrm{NiNCS^+ + NCS^-} \underset{k_{\mathrm{r}_2}}{\overset{k_{\mathrm{f}_2}}{\rightleftharpoons}} \mathrm{Ni(NCS)_2}$$

are present at the highest concentrations used in this work (2×10^{-2} and $5 \times 10^{-2}\ M$), the reciprocal relaxation times should be given by the equation[15]

$$\tau^{-1}{}_{\mathrm{I,II}} = {}^1/_2\{(a_{11} + a_{22}) \pm \sqrt{(a_{11} + a_{22})^2 - 4(a_{11}a_{22} - a_{12}a_{21})}\}$$

where [15]

$$a_{11} = k_{\mathrm{r}_1} + k_{\mathrm{f}_1}\{[\mathrm{Ni^{2+}}] + [\mathrm{NCS^-}]\}$$

$$a_{22} = k_{\mathrm{r}_2} + k_{\mathrm{f}_2}\{[\mathrm{NiNCS^+}] + [\mathrm{NCS^-}]\}$$

$$a_{12} = k_{\mathrm{r}_1} - k_{\mathrm{f}_1}[\mathrm{Ni^{2+}}]$$

$$a_{21} = k_{\mathrm{f}_2}\{[\mathrm{NCS^-}] - [\mathrm{NiNCS^+}]\}$$

The expression for $\tau^{-1}{}_{\mathrm{I,II}}$ can be rearranged as

$$\tau^{-1}{}_{\mathrm{I,II}} = {}^1/_2\{(a_{11} + a_{22}) \pm \sqrt{(a_{22} - a_{11})^2 + 4a_{12}a_{21}}\}$$

As already stated at the stoichiometric concentration $C^0{}_{\mathrm{Ni(NCS)_2}} = 2 \times 10^{-2}\ M$, the first complexation is almost complete, $[\mathrm{NiNCS^+}] \approx [\mathrm{NCS^-}]$, while $[\mathrm{Ni^{2+}}]$ is much smaller. Then the product $a_{12}a_{21}$ under the square root in the above equation is negligible compared to $(a_{22} - a_{11})^2$.

Consequently

$$\tau^{-1}{}_{\mathrm{I,II}} = {}^1/_2\{(a_{11} + a_{22}) \pm (a_{22} - a_{11})\}$$

and

$$\tau^{-1}{}_\mathrm{I} = a_{22} = k_{\mathrm{r}_2} + k_{\mathrm{f}_2}\{[\mathrm{NiNCS^+}] + [\mathrm{NCS^-}]\}$$

$$\tau^{-1}{}_\mathrm{II} = a_{11} = k_{\mathrm{r}_1} + k_{\mathrm{f}_1}\{[\mathrm{Ni^{2+}}] + [\mathrm{NCS^-}]\}$$

The two processes are uncoupled (with the exception of the interdependence between the concentrations of the various species). The process we have observed by P-jump technique is the one corresponding to τ_II, namely, the long relaxation time.

The last aspect to consider is the possible presence of species such as the tetrahedral $\mathrm{Ni(NCS)_4}^{2-}$ or $\mathrm{Ni(NCS)_3}^-$. Evidence from visible spectra by Gutmann[16] for molar ratios $X = [\mathrm{NCS^-}]/[\mathrm{Ni^{2+}}] \leqslant 10$ seems to exclude such a possibility. In fact at the molar ratio $X = 10$ the spectrum is quite similar to the one reported by Libus[14] for $\mathrm{Ni(ClO_4)_2}$ in DMSO. Two peaks are clearly visible at λ 415 and 630 nm from the work of Gutmann,[16] with respective extintion coefficients $\epsilon \sim 15$ and $\epsilon \sim 4$. Large increases of these two peaks are only noticed for larger values of the molar ratio X. No evidence of the spin-allowed absorption spectrum due to tetrahedral species is evident for $X \leqslant 10$.

The analysis of the P-jump relaxation data has then been performed on the assumption that the equilibrium responsible for the observed relaxation is

$$\mathrm{Ni^{2+} + NCS^- = NiNCS^+}$$

Then[17,18]

$$\tau^{-1} = k_\mathrm{f}\theta + k_\mathrm{r} \tag{2}$$

where[10]

$$\theta = \frac{\gamma_\mathrm{Ni}\gamma_\mathrm{NCS}}{\gamma_\mathrm{NiNCS}}\left\{C_\mathrm{Ni} + C_\mathrm{NCS} + C_\mathrm{NCS}\frac{\mathrm{d}\ln(\gamma_\mathrm{Ni}\gamma_\mathrm{NCS}/\gamma_\mathrm{NiNCS})}{\mathrm{d}\ln C_\mathrm{Ni}}\right\}$$

θ has been calculated as shown before[10] for a 2:1 electrolyte. The τ^{-1} *vs.* θ plot is shown in Figure 2. Slopes and intercepts with their standard errors calculated by least-squares analysis, namely, $k_\mathrm{f} \pm \Delta k_\mathrm{f}$ and $k_\mathrm{r} \pm \Delta k_\mathrm{r}$, are reported in Table II. The various k_f's are correlated by means of the Eyring expression

$$k_\mathrm{f} = \frac{kT}{h}\exp\left(-\frac{\Delta H_\mathrm{f}^\ddagger}{RT}\right)\exp\left(\frac{\Delta S_\mathrm{f}^\ddagger}{R}\right)$$

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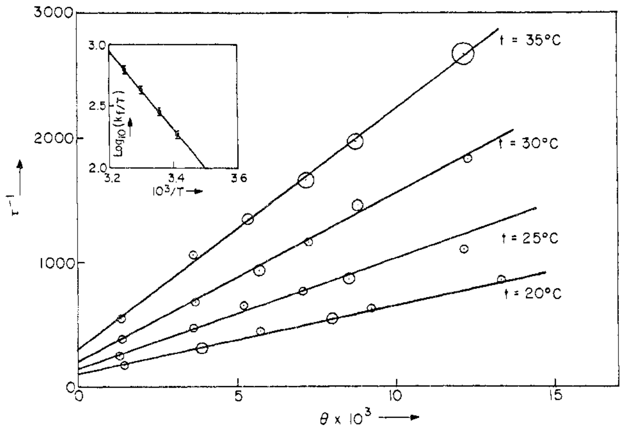

Figure 2. τ^{-1} *vs.* θ for $Ni(NCS)_2$ in DMSO at 20, 25, 30, and 35°. Insert shows log (k_f/T) *vs.* $1/T$ for $Ni(NCS)_2$ in DMSO.

as shown in the insert in Figure 2 where the plot of log (k_f/T) *vs.* $1/T$ is reported. This gives $\Delta H_f^{\ddagger} = 13.77 \pm 0.32$ kcal/mol and $\Delta S_f^{\ddagger} = 10.4 \pm 0.2$ eu.

We first notice that at 25° $k_f/k_r = 659\ M^{-1}$ in good accord with the conductance value of $K_A = 989\ M^{-1}$ considering the error involved in the ratio k_f/k_r. This ensures that the assumption of the measured process being expressed by eq 2 is correct. [Notice, in fact, that the Fuoss-Edelson approach for diluted unsymmetrical electrolytes is valid only if the first equilibrium step of complexation is present. Under these conditions linearity between Λ^* and χ is expected as reported in Figure 1.] Further, by calculating the hydrodynamic radii by the Stokes equation

$$R^0_{\pm} = \frac{0.82\,|Z_{\pm}|}{\lambda^0_{\pm}\eta}$$

one gets $R^0_+ + R^0_- = 6.1 \simeq 6$ Å. Assuming this to be the interionic distance in the outer-sphere ion pair, the Fuoss constant

$$K_F = \frac{4\pi N a^3}{3000}\exp(b)$$

in DMSO at 25° is $K_F = 30\ M^{-1}$ $(b = |Z_+Z_-|e^2/aDkT)$.

If one now assumes an interchange dissociative Eigen mechanism for the complexation of Ni^{2+} by NCS^- in DMSO

$$Ni^{2+}S_6 + NCS^- \overset{K_F}{\rightleftharpoons} Ni^{2+}S_6,NCS^- \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} NiS_5NCS^+ \qquad (3)$$

one obtains $k_f = K_F k_{23}$ and $k_{23} = 3 \times 10^3\ sec^{-1}$ at 25°. This figure is of the same order of magnitude of the rate constants for solvent exchange in DMSO for Ni^{2+} which have been reported by various authors to be $k_{exch} = 3.2 \times 10^3$,[19] 5.2×10^3,[20] 9.3×10^3,[21] and $7.5 \times 10^3\ sec^{-1}$ [22] at 25°.

Similarly, by virtue of the same mechanism (eq 3)

$$\Delta H_{23}^{\ddagger} = \Delta H_f^{\ddagger} - \Delta H^{\circ}$$

$$\Delta S_{23}^{\ddagger} = \Delta S_f^{\ddagger} - \Delta S^{\circ}$$

ΔH° and ΔS° are calculable as reported before[23] to be $\Delta H^{\circ} = 0.57$ kcal/mol and $\Delta S^{\circ} = 8.65$ eu, which give $\Delta H_{23}^{\ddagger} = 13.2$ kcal/mol and $\Delta S_{23}^{\ddagger} = 1.7$ eu.

Table III. Ultrasonic Results for $Cu(ClO_4)_2$ in MeOH at 25°[a]

C, M	f_r, MHz	$10^{17}A$, $cm^{-1}\ sec^2$	$10^{17}B$, $cm^{-1}\ sec^2$
0.195	18	225	40.0
0.133	15	164	36.0
0.090	12	121	36.5

[a] The values of B are estimated to be precise within $\pm 0.5 \times 10^{-17}$ $cm^{-1}\ sec^2$. The calculated A and f_r values are precise within ±5-10%.

Literature data for the $\Delta H^{\ddagger}_{exch}$ and $\Delta S^{\ddagger}_{exch}$ have been reported as $\Delta H^{\ddagger}_{exch} = 13.0$,[19] 12.1,[20] 7.3,[21] and 8.0 kcal/mol[22] and $\Delta S^{\ddagger}_{exch} = +3.2$,[19] -1.3,[20] -16 ± 2,[21] and -14 ± 7 eu.[22] At least for the $\Delta H^{\ddagger}_{exch}$ one can say that the values are of the same order of magnitude as $\Delta H^{\ddagger}_{23}$ reported above. For $\Delta S^{\ddagger}_{exch}$ the scatter is too large to arrive at any conclusion, except that $\Delta S^{\ddagger}_{23}$ is in reasonable accord with two of the reported figures.

Another check of the validity of our and Hoffmann's analysis for the $Ni(NCS)_2$ data is evident by comparing the value of the forward rate constant for $Ni(NCS)_2$ at 20° with the one for $NiCl_2$.[6] The two values $(5.6 \pm 0.4) \times 10^4$ (Table II) and $(7 \pm 1) \times 10^4\ M^{-1}\ sec^{-1}$, respectively, are in good accord. For $NiCl_2$ spectral evidence collected by Griffiths[24] shows unambiguously that for a ligand to metal ratio $X = 2$ only one complex species, namely, $NiCl^+$, is present in DMSO at 25°.

Figure 3 reports the ultrasonic absorption data as α/f^2 *vs.* f for $Cu(ClO_4)_2$ in MeOH at 25° at the three concentrations investigated. α is the sound absorption coefficient (neper cm^{-1}) and f the frequency (Hz).

The solid lines are calculated functions according to a single relaxation process[18]

$$\frac{\alpha}{f^2} = \frac{A}{1 + (f/f_r)^2} + B \qquad (4)$$

with $A = 2\mu_{max}/uf_r$, f_r the relaxation frequency, u the sound velocity, and μ_{max} the maximum excess sound absorption. B is the background absorption. Results for f_r, A, and B are reported in Table III.

It should be noticed that the values of B (Table III) are larger than the value of the solvent absorption since[9b] $\alpha^0/f^2 = 30 \times 10^{-7}\ cm^{-1}\ sec^2$ at 25°. Having taken $B > \alpha^0/f^2$ means to have cut off the presence of possible relaxations occurring at frequencies above our instrumental range. This may be seen in the insert of Figure 3 where, for $C = 0.195\ M$, the excess sound absorption μ *vs.* frequency f is reported. The solid line has been calculated according to the function for a single relaxation[18]

$$\mu = 2\mu_{max}\frac{f/f_r}{1 + (f/f_r)^2} \qquad (5)$$

where $\mu = \alpha_{exc}(u/f)$, $\alpha_{exc} = \alpha - Bf^2$, and μ_{max} has been calculated from the determined A in Table III (from which f_r is also taken). In Figure 3 the open circles correspond to $B = 40 \times 10^{-17}\ cm^{-1}\ sec^2$ whereas the triangles indicate the values of μ assuming $B = \alpha^0/f^2$. There are two possibilities to consider for $B > \alpha^0/f^2$. Either, as already suggested, other relaxations due to the solute exist or the solvent sound absorption is altered by the presence of the electrolyte because of structural modifications affecting its shear or volume viscosities.[9b,25]

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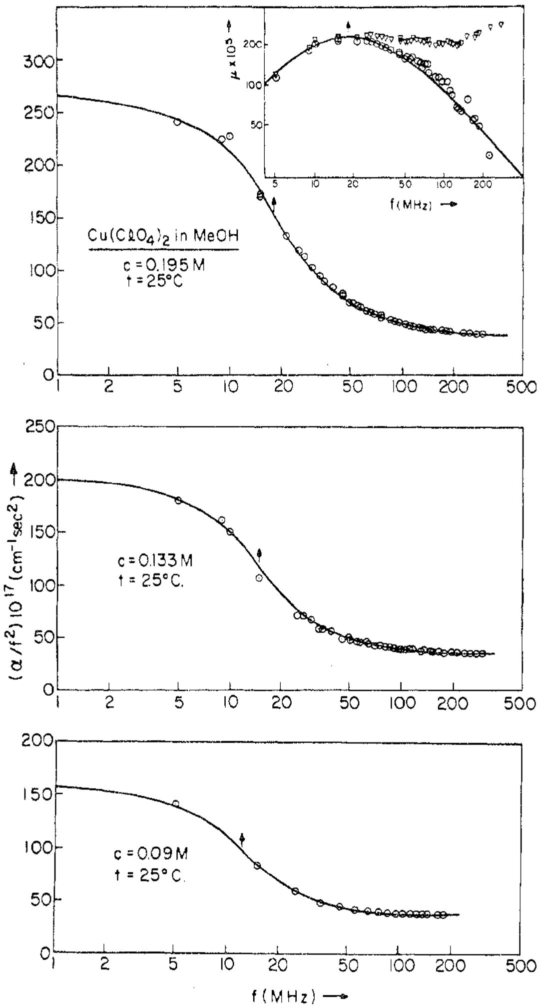

Figure 3. α/f^2 *vs.* f for Cu(ClO$_4$)$_2$ in MeOH at 25° at the various concentrations investigated. Insert shows $\mu \times 10^5$ *vs.* f for Cu(ClO$_4$)$_2$ at $C = 0.195\,M$: ○, $B = 40 \times 10^{-17}$ cm^{-1} sec^2; ▽, $B = 30 \times 10^{-17}$ cm^{-1} sec^2.

In the present case we lean toward the former hypothesis because of the evidence shown in Figure 4 of a relaxation process at very high frequency for the same systems at −50°. A quantitative interpretation of this process is not possible, unfortunately, from these data because at $f > 200$ MHz the solvent also starts showing a relaxation (Figure 4). However, the electrolyte absorption α/f^2 decreases (with increasing frequency) at frequencies below the one where the solvent shows an onset of downward inflection in α/f^2. This means that we probably are observing a process associated with Cu(ClO$_4$)$_2$ not observable at +25°.

In Figure 4 data for Zn(ClO$_4$)$_2$ and Ni(ClO$_4$)$_2$[26] at −50° show a similar behavior. For 0.11 M Zn(ClO$_4$)$_2$ at 25° no relaxation is observable (in contrast to Cu(ClO$_4$)$_2$) but only a constant excess absorption $\Delta\alpha/f^2 \simeq 6 \times 10^{-17}$ cm^{-1} sec^2 is seen in the frequency range 10-150 MHz. Similarly 0.14 M Ni(ClO$_4$)$_2$ shows no relaxation at +25° but a slight inflection of the excess $\Delta\alpha/f^2 \simeq 7 \times 10^{-17}$ cm^{-1} sec^2 at $f >$ 150 MHz.

We therefore advance the hypothesis that the relaxation observed for Cu(ClO$_4$)$_2$ at 25° is associated with the penetration of the ligand ClO$_4^-$ in the axial position of the tetragonally distorted Cu(MeOH)$_6^{2+}$, this process being loosely coupled to an outer-sphere diffusion-controlled process (having a relaxation frequency above the range of our instrumentation, as the evidence at −50° suggests). In fact the rate of solvent exchange for Ni(MeOH)$_6^{2+}$ is slower than for Cu(MeOH)$_6^{2+}$ (see Figure 6 below) and indeed no relaxation for the former cation is visible at +25°.

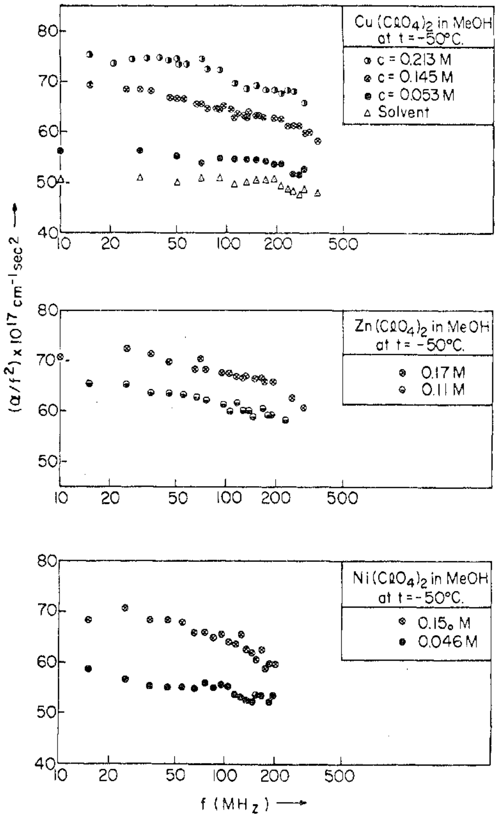

Figure 4. α/f^2 *vs.* f for Cu(ClO$_4$)$_2$, Zn(ClO$_4$)$_2$, and Ni(ClO$_4$)$_2$ at the various concentrations investigated in methanol at −50°.

The proposed process, similar to eq 3, is expressable as

$$\mathrm{CuS_6}^{2+} + \mathrm{ClO_4}^- \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \mathrm{CuS_6}^{2+},\mathrm{ClO_4}^- \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \mathrm{CuS_5ClO_4}^+ \qquad (6)$$

A plot of τ^{-1} ($=2\pi f_r$) *vs.* θ (calculated as in the case of Ni(NCS)$_2$) is shown in Figure 5.

In the calculation of θ the value of the approach distance between free ions, a, has been taken equal to 7×10^{-8} cm.[10] This figure is obtained as the sum of the two Stokes radii $R^0_{\mathrm{Cu}^{2+}} = 5.1 \times 10^{-8}$ cm and $R^0_{\mathrm{ClO_4}^-} = 2.1 \times 10^{-8}$ cm calculated through ionic conductance and the relation $R^0_\pm = |Z_\pm| 0.82/\lambda^0_\pm\eta$. The average slope forcing a straight line through the origin ($k_r \geqslant 0$) is $k_f = (1.1 \pm 0.1) \times 10^{10}\ M^{-1}$ sec^{-1}.

Similarly least-squares analysis (dotted line) according to eq 2 gives slope $k_f = (1.31 \pm 0.08) \times 10^{10}\ M^{-1}$ sec^{-1} and intercept $(-1.8 \pm 0.7) \times 10^{-1}$ sec^{-1}. Retaining $k_f = 1.1 \times 10^{10}\ M^{-1}$ sec^{-1} for the forward rate constant, according to eq 2, assuming the outer-sphere process to be faster than the solvent substitution, one gets

$$k_f = K_{12}k_{23}$$

By retaining for K_{12} the Fuoss constant, which in methanol at 25° is $K_F = 116.5\ M^{-1}$, gives $k_{23} = (9.4 \pm 0.1) \times 10^7$ sec^{-1}. This figure is in reasonable accord with the pseudo-first-order nmr solvent-exchange rate constant $k_{\mathrm{exch}} = 7.4 \times 10^7$ sec^{-1} reported recently by Luz.[6] This accord is expected on the basis of a dissociative mechanism.

Objections could be raised for having assumed the pre-

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[26] A. Fanelli, Ph.D. Thesis, Polytechnic Institute of Brooklyn, (1971).

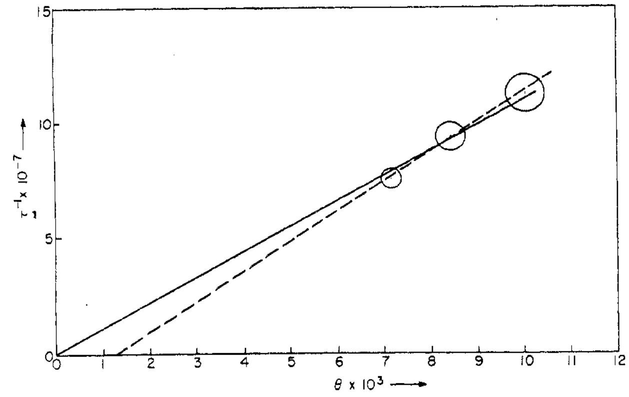

Figure 5. τ^{-1} *vs.* θ for $Cu(ClO_4)_2$ in MeOH at 25°.

equilibration condition leading to $k_f = K_{12}k_{23}$ for the case of a fast solvent-exchanging cation like Cu^{2+}. The more precise equation

$$k_f = k_{12}k_{23}/(k_{21} + k_{23}) \tag{7}$$

based on the steady state on the intermediate in (6) should be used.

Equation 7 reduces to the expression $k_f = K_{12}k_{23}$ only if $k_{21} >> k_{23}$. Retaining $a = 7 \times 10^{-8}$ cm and assuming the validity of the Debye-Smoluchowski[27] and Eigen[28] theories, we obtain

$$\begin{aligned} k_{12} &= k_D = \frac{8NkT}{3000\eta}\,\frac{b}{1 - e^{-b}} \\ k_{21} &= k_{-D} = \frac{2kT}{\pi\eta a^3}\,\frac{b}{e^b - 1} \end{aligned} \tag{8}$$

One gets in methanol at 25° $k_{12} = 5.99 \times 10^{10}\ M^{-1}\ \mathrm{sec}^{-1}$ and $k_{21} = 5.14 \times 10^8\ \mathrm{sec}^{-1}$. From eq 7 one then calculates $k_{23} = 1.1 \times 10^8\ \mathrm{sec}^{-1}$ in good agreement with the above figure for $k_{23} = 0.94 \times 10^8\ \mathrm{sec}^{-1}$. Further support of the dissociative Id mechanism is shown in Figure 6 where the k_{exch} values in MeOH, taken from the literature,[4,7,29-31] are plotted *vs.* the k_{subst} also in methanol. It may be seen that all the metal cations follow closely the straight line inclined at 45° which is required by a dissociative mechanism. Also Ni^{2+} being the slowest and Cu^{2+} the fastest exchanging cations is in accord with crystal field stabilization theory and Jahn-Teller theorem.

Discussion

The above work for Ni^{2+} in DMSO and Cu^{2+} in MeOH concurs with the hypothesis that the Eigen interchange dissociative mechanism is operative in these two solvents.

Previous results in CH_3CN support the same conclusions.[10] Still Caldin and Bennetto[5] reported a 200-fold change in the ratio

$$n = \frac{k_f}{k_{\mathrm{exch}}K_F}$$

from acetonitrile to DMSO. For all the ligands so far investigated in this laboratory and by Hoffmann,[6] namely,

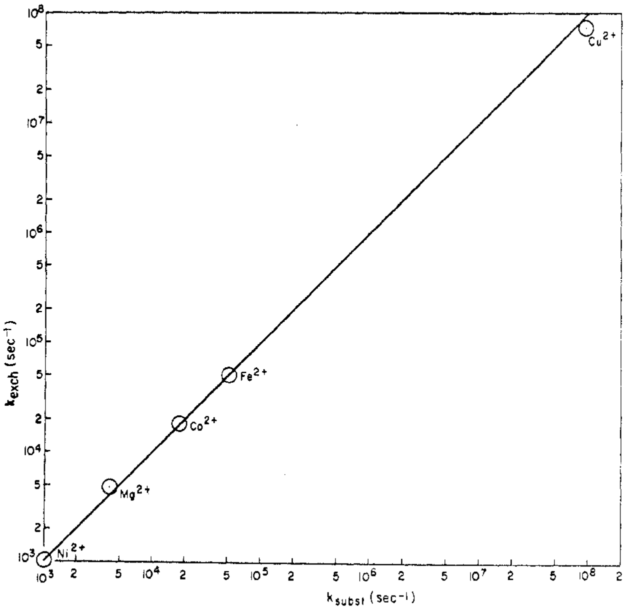

Figure 6. Plot of k_{exch}(MeOH), sec^{-1}, *vs.* k_{subst}(MeOH), sec^{-1}, for Ni^{2+}, Mg^{2+}, Co^{2+}, Fe^{2+}, and Cu^{2+} at 25°. The values used are as follows: Ni^{2+}, $k_{\mathrm{exch}} = 1.0 \times 10^3$,[29] $k_{\mathrm{subst}} = 1 \times 10^3\ \mathrm{sec}^{-1}$;[2] Mg^{2+}, $k_{\mathrm{exch}} = 4.7 \times 10^3$,[30] $k_{\mathrm{subst}} = 4 \times 10^3\ \mathrm{sec}^{-1}$;[4] Co^{2+}, $k_{\mathrm{exch}} = 1.8 \times 10^4$,[29] $k_{\mathrm{subst}} = 1.75 \times 10^4\ \mathrm{sec}^{-1}$;[4] Fe^{2+}, $k_{\mathrm{exch}} = 5.0 \times 10^4$,[31] $k_{\mathrm{subst}} = 5 \times 10^4\ \mathrm{sec}^{-1}$;[4] Cu^{2+}, $k_{\mathrm{exch}} = 7.4 \times 10^7$,[7] $k_{\mathrm{subst}} = 9.4 \times 10^7\ \mathrm{sec}^{-1}$ (this work). (The data for k_{subst} referring to Mg^{2+}, Co^{2+}, and Fe^{2+} are at 20°.[6])

ClO_4^- in acetonitrile and Cl^- and NCS^- in DMSO, the ratio n is about 1.

It is noteworthy that the ligands used in this laboratory previously[10] in CH_3CN and in the present work as well as by Hoffmann[6] are monodentate ligands whereas both Macri[3] and Bennetto[5] used potentially bidentate ligands. Whereas the structure of the metal disulfonate complexes is not known, it is well known that dipyridyl is a chelating ligand. So at least for the case of Bennetto's work it is possible to state that a chelate complex is the ultimate product of the reaction. But then[15]

$$k_f = K_{12}\frac{k_{23}k_{34}}{k_{32} + k_{34}}$$

where k_{34} is the rate constant for ring closure. Bennetto and Caldin by writing $k_f = K_{12}k_{23}$ assumed implicitly that $k_{34} >> k_{32}$ which has proven to be true in water.[32] It is at least conceivable that the quantity n

$$n = \frac{k_f}{K_{12}k_{23}} = \frac{k_{34}}{k_{32} + k_{34}}$$

may vary from solvent to solvent especially when, as in the case of DMSO, the converse condition $k_{32} > k_{34}$ may arise because of the high donor ability[33] of the solvent with respect to water.

If one writes the equilibrium including the solvent

$$\mathrm{Me^{2+}S_6} + \mathrm{LL} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \mathrm{MeS_6,LL} \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \mathrm{MeS_5\text{-}LL} + \mathrm{S} \underset{k_{43}}{\overset{k_{34}}{\rightleftharpoons}} \mathrm{MeS_4}\!<\!\begin{matrix}\mathrm{L}\\ | \\ \mathrm{L}\end{matrix} + \mathrm{S}$$

it is clear that the solvent and the second end of the ligand are in competion for the intermediate MeS_5-LL. This competition may shift from solvent to solvent, the case of DMSO

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(27) M. von Smoluchowski, *Z. Phys. Chem. (Frankfurt am Main)*, 92, 179 (1917); P. Debye, *Trans. Electrochem. Soc.*, 82, 265 (1942).

(28) M. Eigen, *Z. Phys. Chem. (Frankfurt am Main)*, 1, 176 (1954).

(29) Z. Luz and S. Meiboom, *J. Chem. Phys.*, 40, 2686 (1964).

(30) S. Nakamura and S. Meiboom, *J. Amer. Chem. Soc.*, 89, 1765 (1967).

(31) H. H. Glaeser, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, 4, 1061 (1965).

(32) R. H. Holyer, C. D. Hubbard, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, 4, 929 (1965); 5, 622 (1965).

(33) V. Gutmann, *Rec. Chem. Progr.*, 30, 171 (1969).

being possibly one in which the latter is favored over the ligand.

Although the above is speculative, it could rationalize some of the discrepancies noticed earlier[5] in terms of kinetic chelating effect already documented in aqueous solutions.[34] On the other hand, Wilkins[35] had warned in the first place that the findings by Caldin and Bennetto were subjected to the assumption of a "normal" substitution mechanism[35] for the bidentate ligands used.

As suggested also by Wilkins,[35] another source of possible discrepancy between the product $K_{12}k_{\text{exch}}$ and k_f could be having taken[5] K_{12} equal to a constant ($K = 0.1$) for all the solvents. This was[5] a consequence of having retained the Fuoss formula $K_F = (4\pi Na^3/3000)\exp(b)$ with $b = 0$ for a cation-neutral molecule interaction ($b = |Z_+Z_-|e^2/aDkT$). In fact objections could be raised for having taken the ion-dipole energy equal to zero. The Fuoss association theory[36] applied to the case of a cation associating with a dipole in a continuum of permittivity D would read

$$K = \frac{4\pi Na^3}{3000}e^{-U/kT}$$

where a would assume the significance of the distance between the center of the cation and the center of the dipole when at contact; U would be the ion-dipole potential energy.

According to Gurney,[37] the ion-dipole energy is

$$U(r) = -\frac{e\mu}{D(r^2 - d^2)}$$

where d is the dipole radius and r is the distance between the center of the cation and the center of the dipole. When at contact

$$U(a) = -\frac{e\mu}{D(a^2 - d^2)}$$

and

$$K_{12} = K = \frac{4\pi Na^3}{3000}\exp\left(\frac{e\mu}{D(a^2 - d^2)}\right)$$

Rationalization of a factor of 200 in the ratio of the parameter $n = k_f/K_{12}k_{\text{exch}}$,[5] between CH_3CH and DMSO, if attributable only to the K_{12}'s, would mean a ratio

$$\frac{\exp(-U_{\text{DMSO}}/kT)}{\exp(-U_{CH_3CN}/kT)} = 200$$

considering a to be independent of solvent nature. Stated in other terms $U_{CH_3CN} - U_{\text{DMSO}} = 5.30kT = 2.18 \times 10^{-3}$ erg. On a molar scale this converts to 3.1 kcal/mol. Such a quantity seems too large for this difference. To have an idea of the order of magnitude of the energy required one may calculate the ion-dipole energy for the hypothetical case where $D = 40$, $\mu \simeq 1 \times 10^{-18}$ esu,[38] $a = 5 \times 10^{-8}$ cm, and $d = 3 \times 10^{-8}$ cm, giving

$$U(a) = -\frac{4.8 \times 10^{-28}}{40(25 - 9) \times 10^{-16}} = -0.75 \times 10^{-14}\ \text{erg}$$
$$= -0.18kT$$

at 25° which, on a molar scale, converts to −108 cal/mol. [Notice that even using the 1959 triple ion or ion-dipole association theory of Fuoss,[39] as modified by Jagodzinski,[40] one obtains comparable results. In fact the modified Fuoss equation[39] reads

$$K_{12} = K_3 = \frac{Nv_2e^{-3/2}}{1000}e^{-U/kT}$$

and a factor of 200 between two n's is still expressable as

$$\frac{\exp(-U_{\text{DMSO}}/kT)}{\exp(-U_{CH_3CN}/kT)} = 200$$

if v_2 the volume of the ion-dipole complex is taken to be the same for all the solvents.]

The last possibility one ought to consider in trying to rationalize the data of Bennetto and Caldin[5] is to abandon the interchange mechanism of Eigen and assume a dissociative mechanism, ignoring the bidentate character of dipyridyl. This in fact is what Bennetto and Caldin[5] basically proposed.

Then one may write

$$MS_6 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MS_5 + S$$

$$MS_5 + L \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} MS_5L$$

Writing the rate equations for the mechanism, with the assumption of the steady-state condition for the intermediate $d[MeS_5]/dt = 0$, leads to the relation for the overall forward rate constant of complexation k_f

$$k_f = \frac{k_1k_2}{k_{-1} + k_2[L]}$$

Since Bennetto and Caldin[5] used small concentrations of ligands (10^{-5} M), one may assume the condition $k_{-1} \gg k_2[L]$

$$k_f = k_{\text{exch}}\frac{k_2}{k_{-1}}$$

with $k_{\text{exch}} = k_1$. According to this mechanism, one might speculate that the competition ratio k_2/k_{-1} between ligand and solvent for the intermediate MS_5 is ~1–10 for solvents like water and methanol and ≪1 for DMSO. This rationalization, however, fails to explain why, for the same solvent DMSO, in the case of NCS^- the ratio appears equal to 10–30 whereas for bipyridyl it is ≪1 (both ligands binding to Ni^{2+} through nitrogen atoms). [Notice also that in the P-jump work presented above, the ligand concentration is not negligible with respect to the metal cation and the condition $k_{-1} \gg k_2[L]$ may not be valid. However, this should lower k_f (in the case of NCS^-) with respect to the dipyridyl value (if the ratio k_2/k_{-1} were the same), contrary to what is found experimentally.]

Registry No. $Ni(NCS)_2$, 13689-92-4; $Cu(ClO_4)_2$, 13770-18-8; DMSO, 67-68-5; MeOH, 67-56-1; Ni^{2+}, 14701-22-5; Cu^{2+}, 15158-11-9; NCS^-, 302-04-5; ClO_4^-, 14797-73-0.

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(34) J. Williams and S. Petrucci, *J. Amer. Chem. Soc.*, **95**, 7619 (1973), and previous literature quoted therein.

(35) R. G. Wilkins, *Accounts Chem. Res.*, **3**, 408, (1970).

(36) R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience, New York, N. Y., 1959, Chapter XVI.

(37) R. W. Gurney, "Ionic Processes in Solutions," Dover Publications, New York, N. Y., 1953.

(38) μ(dipy) = 0.91 D in water: P. E. Fielding and R. W. J. Le Fevre, *J. Chem. Soc.*, 1811 (1951).

(39) R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience, New York, N. Y., 1959, Chapter XVIII.

(40) P. Jagodzinski, B.S. Thesis, Polytechnic Institute of Brooklyn, 1973; P. Jagodzinski and S. Petrucci, *J. Phys. Chem.*, **78**, 917 (1974).