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(23) Since one would expect generation of NH in solution to result in formation of NH_2Cl, $NHCl_2$, and/or NCl_3 under the photolysis conditions,[24-26] the observation that $\Delta[Rh(NH_3)_5N_3^{2+}] \geq$ equivalents of oxidant is qualitatively inconsistent with Zink's mechanism.
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(29) One would expect smaller net redox quantum yields for rhodium(III) complexes than for cobalt(III) complexes on the basis that rhodium(II) is likely to be a better reducing agent than cobalt(II), making cage recombination more likely (see ref 2, 3e). Furthermore, if the relative redox yields of $Co^{III}(NH_3)_5X$ complexes are roughly the same as those for $Rh^{III}(NH_3)_5X$ complexes (i.e., $\phi(X = I)/\phi(X = N_3) \approx 3$) one might expect a maximum value of $\phi_{redox} \approx 0.08$ for $Rh(NH_3)_5N_3^{2+}$. This value should decline to zero at the threshold, and one might expect $\phi_{redox} <$ 0.02 at 3.9 μm^{-1} even with a 3.5-μm^{-1} threshold energy. On the basis of our observations we would set $\phi_{redox} \leq 0.01$ at 3.9 μm^{-1}.
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Solvent Effects on Dissociation of the Monocomplex of Nickel(II) with Isoquinoline

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Dissociation rate constants and associated activation parameters for the monocomplex of nickel(II) with isoquinoline in acetonitrile and propylene carbonate as solvents were obtained from measurements by stopped-flow spectrophotometry. Overall equilibrium constants for formation of the complex in water, methanol, dimethyl sulfoxide, and *N,N*-dimethylformamide were obtained from spectrophotometric measurements. Dissociation rate constants and associated activation parameters in water, methanol, dimethyl sulfoxide, and *N,N*-dimethylformamide are calculated. Neither dissociation rate constants nor equilibrium constants for complex formation correlate with Gutmann's donicity scale for solvents, but the enthalpy of activation for dissociation of the complex ($\Delta H_b^{\ddagger}$) shows a linear relationship with solvent donicity.

Introduction

Although an improved understanding of solvent properties is emerging from recent studies on the formation of labile metal–ligand complexes in various solvents, few kinetic studies on the dissociation of labile complexes in solution, especially in nonaqueous solvents, have been made. Results of kinetic studies of substitution reactions in water,[1] methanol,[2] ethanol,[3] acetonitrile,[4] and *N,N*-dimethylformamide[5] indicate that formation of labile complexes of nickel(II) with many ligands proceeds by a dissociative type of interchange mechanism[6] (I_d), and the rate of solvent exchange between NiS_6^{2+} (where S is a solvent molecule) and bulk solvent is the rate-controlling step. The exact mechanism of substitution at nickel(II), however, even with "simple" monodentate ligands, has not been ascertained as yet in dimethyl sulfoxide.[5a] With nickel(II) and a monodentate ligand L, the pathways of an I_d type mechanism can be represented by

$$\underset{\mathrm{I}}{\mathrm{NiS_6{}^{2+} + L \overset{K_{12}}{\rightleftarrows} NiS_6{}^{2+},L}} \underset{\mathrm{II}}{\underset{k_{32}}{\overset{k_{23}}{\rightleftarrows}}} \mathrm{L\text{-}NiS_5{}^{2+},S} \tag{1}$$

In this pathway the rate-controlling step for the formation of an inner-sphere complex (process II, forward rate constant k_{23}) is preceded by the rapid formation of an outer-sphere complex (process I, equilibrium formation constant K_{12}). The charge on L has been omitted for simplicity. For a "normal" type of substitution,[4b] when $K_{12}[\mathrm{L}] \ll 1$, the second-order formation rate constant (k_f) and the equilibrium constant for formation of an inner-sphere from an outer-sphere complex (K^{i}_{eq}) are given by

$$k_f = K_{12}k_{23} \tag{2}$$

and

$$K^{i}_{eq} = k_{23}/k_b = k_f/K_{12}k_b = K_{eq}/K_{12} \tag{3}$$

where K_{eq} is the "overall" equilibrium constant for formation of the complex. K_{12} is estimated from the theoretical relationship[7]

$$K_{12} = \frac{4\pi N a^3}{3 \times 10^3} e^{-U(a)/kT} \tag{4}$$

where

$$U(a) = \frac{z_1 z_2 e^2}{Da} - \frac{|z_1 z_2 e^2 \kappa|}{(1 + \kappa a)D} \tag{5}$$

Here a is the closest distance of approach of the center of the solvated metal ion to the center of the ligand. Under pseudo-first-order conditions when $[\mathrm{Ni}^{2+}] \gg [\mathrm{L}]$, the observed pseudo-first-order rate constant (k_{obsd}) is given by[8]

$$k_{obsd} = k_f[\mathrm{Ni}^{2+}] + k_b \tag{6}$$

where the slope and intercept in pseudo-first-order kinetic plots equate to the formation and dissociation rate constants. The validity of eq 6 has been confirmed by Moore and Buck[9] by comparison of the results of directly measured dissociation rate constants with intercepts found in pseudo-first-order plots for formation of the monocomplex of 4-phenylpyridine with nickel(II) in dimethyl sulfoxide as solvent. However, intercepts have been encountered in kinetic studies in several nonaqueous solutions[5b] that do not give correct dissociation rate constant values. The reasons for this are not known with certainty, but the presence of trace impurities in the system may be a contributing factor. In any event, to obtain meaningful values, k_b should be either directly measured or calculated from directly measured K_{eq} and k_f values by eq 1, rather than being obtained from the intercepts of pseudo-first-order plots for formation of the complex.

Data on dissociation rate constants of labile complexes in water and nonaqueous solutions are meager. Moore and Wilkins[10] observed a linear correlation between k_b and acid dissociation constants of protonated ligands (pk_{LH^+}) for the monocomplexes of nickel(II) with 3- and 4-substituted pyridines in water as solvent. A similar relationship was also confirmed by Hoffmann[11] for nickel–carboxylate complexes. Rate constants and associated activation parameters for dissociation of various monosubstituted complexes of Mn(II) in methanol[12] have recently been reported by Benton and Moore. Studies directed particularly at solvent effects on the dissociation of labile complexes are few. One of these is the work of Dickert, Hoffmann, and Janjic,[5c] who investigated the dissociation of mono and bis complexes of nickel(II) with thiocyanate ion in various solvents and discussed their results in relation to the donicity scale for solvents proposed by Gutmann.[13] A survey of this area is included in a review by Hoffmann.[14]

We report here directly measured dissociation rate constants of the monosubstituted complex of nickel(II) with isoquinoline in acetonitrile and propylene carbonate as solvents, along with spectrophotometrically measured "overall" equilibrium constants for formation of the complex in water, methanol, dimethyl sulfoxide, and dimethylformamide. In addition, dissociation rate constants for this complex in water, methanol, dimethyl sulfoxide, and dimethylformamide have been calculated from K_{eq} and previously reported values[5a] of k_f in these solvents and are compared with the intercepts of pseudo-first-order kinetic plots for formation of the complex.

Experimental Section

Solvents. Sources and purification procedures for all solvents except propylene carbonate were as described before.[5a] Propylene carbonate (Jefferson Chemical Co.) was purified by the method of Krause and Kratochvil.[15]

Reagents. In all solvents nickel(II) was introduced as the perchlorate salt. For propylene carbonate it was hexakis(acetonitrile)nickel(II) perchlorate. For other solvents the methods of preparation of the corresponding nickel(II) perchlorate salts were similar to those described before.[5a] Concentrations of nickel(II) solutions were determined by EDTA titration with murexide indicator after dilution with water and buffering to pH 10 with ammonia–ammonium chloride. Copper(II) was introduced as hexakis(acetonitrile)copper(II) perchlorate.[16] All copper(II) solutions were standardized after dilution with water by iodometric titration using starch as indicator. Tetraethylammonium perchlorate (J. T. Baker Chemical Co.) was recrystallized three times from boiling deionized distilled water and dried under vacuum at 65 °C for 2 days. Isoquinoline was purified as described previously.[5a]

Instrumental and Experimental Procedure. The stopped-flow spectrophotometer (Durrum Instrument Co., Model D-110) used for the kinetic measurements of dissociation rate constants and the procedures for handling all nonaqueous solutions were described before.[5a] Equilibrium constants were measured spectrophotometrically with a double-beam uv–visible spectrophotometer (Unicam SP800) equipped with stoppered silica cells thermostated to ±0.1 °C. Equilibrium constants were measured at 325 nm in all solvents. Generally a set of five to eight complex solutions was prepared in each solvent for measurement at each temperature. In each set of solutions the ligand concentration was kept constant, usually between 1×10^{-4} and 2×10^{-4} M, and the nickel(II) concentration varied from about 0.005 to 0.1 M in water and methanol and from 5×10^{-3} to 5×10^{-2} M in dimethyl sulfoxide and dimethylformamide. Molar absorptivities of nickel(II) and ligand at 325 nm were measured at the corresponding temperatures in each solvent. All spectrophotometric measurements were repeated with different batches of reagents and solvents; the reproducibility of the results was within ±2%.

For kinetic measurements of dissociation rate constants by use of copper(II) as the decomposing ion, concentrations of nickel(II) and isoquinoline were held constant at 1.5×10^{-3} and 1×10^{-4} M, respectively, and the copper(II) concentrations varied in four steps from 5×10^{-3} to 15×10^{-3} M in propylene carbonate and by two different values, 13.2×10^{-3} and 22.5×10^{-3} M, in acetonitrile. Measurements were made at 330 nm in propylene carbonate and at 310 nm in acetonitrile. In propylene carbonate as solvent the total ionic concentrations were adjusted by addition of tetraethylammonium perchlorate. All concentrations refer to final values after mixing.

Results

Under the experimental conditions employed only the monocomplex was considered to be formed; also, isoquinoline was not considered to be protonated in any of the solvents studied.

Overall Equilibrium Constants of Formation. Equilibrium constants were measured spectrophotometrically at 325 nm, where the complex absorbs more strongly, but nickel(II) more weakly, than isoquinoline. Typical values of molar absorptivities of the complex, nickel(II), and isoquinoline in water at 25 °C are 3060, 0.1, and 743. Taking into account the contributions of each absorbing species, the total absorbance,

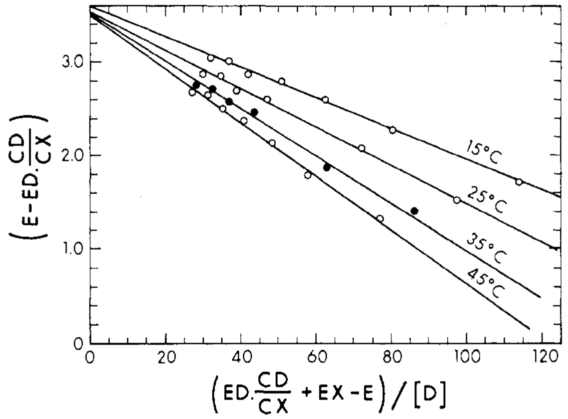

Figure 1. Evaluation of "overall" equilibrium constant for formation of the monocomplex of nickel(II) with isoquinoline in methanol as solvent at various temperatures.

A_T, of the complex solution can be shown[17] to be given by

$$A_T = EL(CX) \tag{7}$$

Also

$$E - ED\frac{CD}{CX} = (EDX - ED) + \frac{F}{K_{eq}}\,\frac{(ED)\frac{CD}{CX} + EX - E}{[D]} \tag{8}$$

and

$$[D] = CD - CX\,\frac{E - EX - ED\frac{CD}{CX}}{EDX - EX - ED} \tag{9}$$

Here D, X, and DX represent nickel(II), isoquinoline, and complex; ED, EX, and EDX are the molar absorptivities of nickel(II), isoquinoline, and the complex; CD and CX are the initial concentrations of nickel(II) and isoquinoline; [D] is the equilibrium concentration of nickel(II); E is termed the "apparent absorptivity"; L is the path length of the cell in cm; and F, the composite value of the collection of activity coefficients, is given by

$$F = f_{DX}/f_X f_D \tag{10}$$

The theory and algebra for deducing eq 7–9 and a computer program for calculating [D] have been described by Ramette.[17] Least-squares plots of (E − ED(CD/CX)) against (ED·(CD/CX) + EX − E)/[D], the slopes of which give F/K_{eq}, in methanol as solvent are shown in Figure 1. In all solvents good straight lines were obtained, indicating that F remained constant in all of the solutions measured. With isoquinoline as X, F from eq 11 will reduce closely to unity since $f_{DX} \approx f_D$, and the inverse of the slopes of the plots, as shown in Figure 1, gives K_{eq} directly. Values of K_{eq} are listed in Table I.

Dissociation Rate Constants. Kinetically observed pseudo-first-order rate constants for dissociation of the complex in acetonitrile and propylene carbonate as solvents, obtained by use of high concentrations of copper(II) as decomposing ion (Table II), are independent of the concentration of copper(II) and ionic strength of the medium. This indicates that the general scheme for copper(II)-induced decomposition of the monocomplex of nickel(II) with isoquinoline can be represented by (L = isoquinoline, and solvent molecules attached to Ni^{2+} and Cu^{2+} are omitted for convenience)

$$NiL^{2+} \underset{k_f}{\overset{k_b}{\rightleftarrows}} Ni^{2+} + L \tag{11}$$

$$Cu^{2+} + L \overset{k_1}{\rightleftarrows} CuL^{2+} \tag{12}$$

Table I. "Overall" Equilibrium Constants for Formation of the Monocomplex of Nickel(II) with Isoquinoline at Various Temperatures

Solvent	K_{eq}[a] 15 °C	20 °C	25 °C	30 °C	35 °C	45 °C
Water	86.8	76.8	68.3	61.0	54.6	44.3
Methanol	61.8	55.7	50.5	45.7	41.7	34.8
Dimethyl sulfoxide		37.1	31.0	27.5	21.9	
Dimethylformamide	100		91.2		82.8	79.7

[a] Reproducibility is ±2%; one additional significant figure given.

Table II. Rate Constants for Dissociation of the Monocomplex of Nickel(II) with Isoquinoline as a Function of Temperature, Concentration of Decomposing Ion, and Ionic Strength

10^3[Cu(II)],[a] M	Ionic strength[b]	Rate constants,[c] s^{-1} 25 °C	35 °C	45 °C	55 °C
		Propylene Carbonate Solvent			
2.5	0.012	0.0267	0.075	0.187	0.495
2.5	0.023	0.0277	0.075	0.192	0.495
5.0	0.023	0.0272	0.075	0.188	0.498
7.5	0.023	0.0283	0.074	0.188	0.498
		Acetonitrile Solvent			
13.2	0.044	0.136	0.385	0.949	
22.5	0.082	0.133[d]	0.389	0.924	

[a] Concentrations of nickel(II) and isoquinoline were held constant at 1.5 × 10^{-3} and 1 × 10^{-4} M. All concentrations and ionic strengths refer to final values (after mixing) in cuvette of spectrophotometer. [b] Ionic strength adjusted with tetraethylammonium perchlorate. [c] Reproducibility is ±2%; one additional significant figure is given. [d] Additional value: 0.0513 at 15 °C.

This scheme is the same as that observed by Benton and Moore[12] for dissociation of the monocomplex of manganese(II) with bipyridine, terpyridine, and phenanthroline using H^+ and mercury(II) as electrophiles. It also indicates that at high concentrations of copper(II), as used in this work, k_b is equal to k and is independent of the concentration of copper(II) and the ionic strength of the medium. From eq 6 and 7 it can be shown that, when $[Cu^{2+}] \gg [L]$, k is given by

$$k = k_b k_1[Cu^{2+}]/(k_f[Ni^{2+}] + k_1[Cu^{2+}]) \tag{13}$$

and if, at high concentrations of copper(II), $k_f[Ni^{2+}] \ll k_1[Cu^{2+}]$, then k is equal to k_b and is independent of the concentration of copper(II) and the ionic strength of the medium.

In Table III dissociation rate constants and associated activation parameters are tabulated. Intercepts of the pseudo-first-order plots for formation of the complex[5a] are included in Table III for comparison with the k_b values reported in this work.

Discussion

The important results in Table III are the following.

1. Intercepts found in the pseudo-first-order kinetic plots for formation of the nickel–isoquinoline complex agree with independently determined values of k_b in all of the solvents studied except dimethylformamide within the limits of experimental uncertainty. The agreement in water and methanol is especially good.
2. Neither dissociation rate constants nor equilibrium constants correlate with the donicity scale for solvents proposed by Gutmann.[13]
3. Values of $\Delta H_b^\ddagger$ in different solvents show a linear correlation with the donor number of the corresponding solvents according to the Gutmann donicity scale.

Turning first to the dissociation rate constants in Table III, the source of the discrepancy between values of k_b calculated

Table III. Rate Constants and Associated Activation Parameters for Dissociation of the Monocomplex of Nickel(II) with Isoquinoline[a]

Solvent	k_b,[b] s^{-1}	$K^i_{eq} = K_{eq}/K_{12}$,[c] l. mol^{-1}	$\Delta H_b^\ddagger$, kcal mol^{-1}	$\Delta S_b^\ddagger$ eu	K_{eq}, l. mol^{-1}	Donicity DN[d]
Water	2.99[e] (2.96)	216	16.1 ± 0.6	+2 ± 2	68.3	18.0
Methanol	1.91[e] (1.94)	92.6	19.3 ± 0.2	+7.5 ± 0.7	50.5	
Dimethyl sulfoxide	109[e] (112)	35.8	13.5 ± 0.4	−4 ± 1	31.0	29.6
Acetonitrile	0.135[f] (0)[g]	8.63 ± 10^3	17.2 ± 0.5	−5 ± 2	9.19 × 10^3 [h]	14.1
Propylene carbonate	0.275[f]		17.7 ± 0.5	−6 ± 2		15.1
Dimethylformamide	26.5[e] (19.5)	105	13.9 ± 0.4	−5 ± 1	91.2	26.8

[a] Temperature 25 °C. [b] Values in parentheses are intercepts found in pseudo-first-order plots for formation of the complex from ref 5a. [c] Values of *a* used: 5 Å in water, 6 Å in methanol, 7 Å in dimethyl sulfoxide and dimethylformamide, and 7.5 Å in acetonitrile. [d] Data from ref 13. [e] Calculated by eq 1 in text; k_f values taken from ref 5a. [f] Average of values in Table II. [g] Data from ref 4a. [h] Calculated by eq 1 in text; k_f taken from ref 4a.

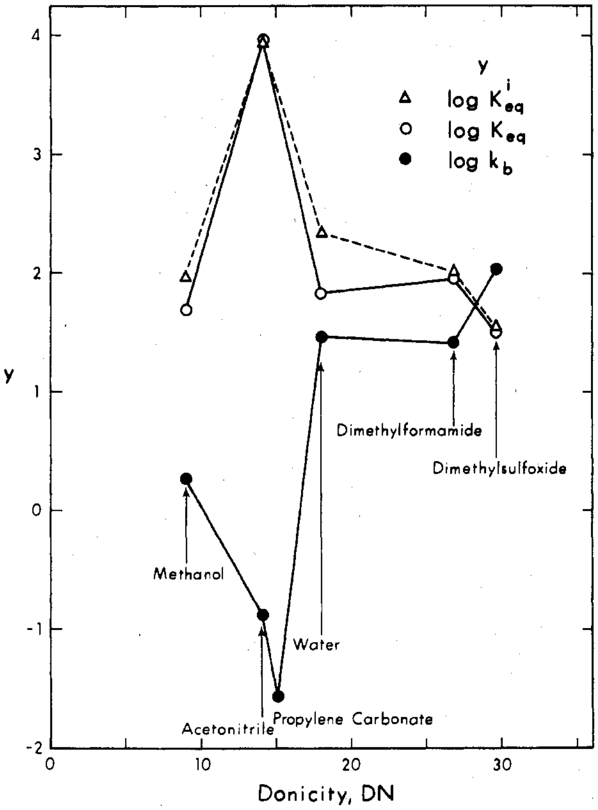

Figure 2. Relation between values of dissociation rate constants and equilibrium constants for formation of the monocomplex of nickel(II) with isoquinoline in various solvents and the donicity of the solvent.

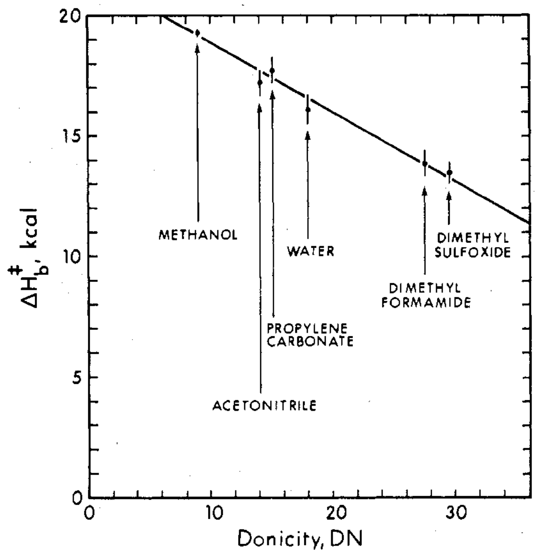

Figure 3. Relation between values of enthalpy of activation for dissociation of the monocomplex of nickel(II) with isoquinoline in various donor solvents and the donicity of the solvent.

from K_{eq} and k_f and values obtained from intercepts of the pseudo-first-order plots for formation of the complex in dimethylformamide cannot be identified with certainty at this time. Spectrophotometric measurements of K_{eq} were repeated with different batches of solvent and reagents in this solvent, as in other solvents, and the results were reproducible within ±2%. The possibility of the presence of impurities in the dimethylformamide solvent was discussed previously.[5a] Hence, we believe that dissociation rate constants in dimethylformamide are better represented by values calculated from directly measured K_{eq} and k_f values.

The solvent dependence of dissociation rate constants and equilibrium constants for formation of the mono and bis complexes of nickel(II) with thiocyanate ion has been considered by Dickert, Hoffmann, and Janjic[5c] in relation to the donicity of solvents. The important conclusions of their discussion are that (1) rate and equilibrium constants can be correlated with the Gutmann donicity scale for solvents, (2) the donor number of water in Gutmann's scale should be about 33 rather than the value of 18 reported by Gutmann, and (3) the donor number of methanol in Gutmann's scale is predicted to be 19. A value for methanol was not reported by Gutmann, but Popov and co-workers[21] suggested 25.7 on the basis of NMR measurements. Because isoquinoline is a monodentate ligand like thiocyanate ion, the results of the two systems can be compared mechanistically. Constants represented by the symbols k_b, K_{eq}, K_{12}, and K^i_{eq} in this work are equivalent to the symbols, k_{21}, K_1, K_{01}, and K^i_1 in the work of Dickert, Hoffmann, and Janjic.[5c]

Our results indicate that their conclusion (1) based on thiocyanate cannot be applied to isoquinoline. Figure 2 shows that none of our values of k_b, K^i_{eq}, or K_{eq} correlate with solvent donicity for the solvents studied. However, as shown in Figure 3, $\Delta H_b^\ddagger$ values in different solvents do show a linear relation with the donor number of the solvents as reported by Gutmann. As far as conclusions (2) and (3) are concerned, our results from Figure 3 indicate that the donor number of water in Gutmann's donicity scale for solvents is best represented by 18, the value reported also by Gutmann, and that the donor number of methanol should be on the order of 9.

The consistency observed between the donicity scale for solvents predicted from our kinetic studies with the nickel(II)–isoquinoline system and that using Gutmann's values, including water, is surprisingly good. Trends in polarographic and other properties indicate that nickel(II) ion is more strongly solvated in dimethyl sulfoxide,[17] but more weakly in methanol,[18] than in water. This trend is in the same order as that of the donicities of dimethyl sulfoxide, water, and methanol suggested here. The value of 9 predicted for methanol by the nickel(II)–isoquinoline correlation is lower than would be expected; it may be that extensive hydrogen bonding in hydroxylic solvents such as water and the alcohols has a significant effect on $\Delta H_b^\ddagger$ values in these solvents.

A scheme that fits our results for dissociation of the complex is represented by

$$S + L\text{-}NiS_5 \underset{III}{\rightleftharpoons} \underset{\substack{\text{outer-}\\ \text{sphere}\\ \text{complex}}}{S,S_5Ni\text{-}L} \underset{IV}{\rightleftharpoons} S\text{-}NiS_5,L \qquad (14)$$

In this pathway the rate-determining step (process IV, forward rate constant k_b), which leads to dissociation of the ligand from the central coordinating cation with simultaneous formation of an inner-sphere complex by introduction of a donor solvent molecule into the inner sphere of the cation, is preceded by rapid formation of an outer-sphere complex with solvent (process III). Process IV will likely be affected by the nature of the solvent molecules present in the inner sphere of the nickel ion as well as by the Lewis acid–base properties of the ligand relative to the solvent.[20] In eq 14, S and L represent the solvent molecule and isoquinoline, and charges on nickel(II) are omitted for convenience.

We now briefly discuss why the apparent donicities of water and methanol in Dickert, Hoffmann, and Janjic's work are higher than the corresponding values predicted from our work and their relation to some NMR chemical shift studies by Popov.[21] Plots of ^{23}Na NMR chemical shifts for $NaClO_4$ and $NaBF_4$ in several different donor solvents against solvent donicities have been shown to give a linear correlation, and by extrapolating this relation to the results of similar measurements in water and methanol as solvents, donicities of 33 for water and 25.7 for methanol were predicted.[21] Whether the results of ^{23}Na NMR chemical shifts measured in structureless or poorly structured dipolar aprotic solvents can be extrapolated to hydroxylic solvents having definite structure and pronounced hydrogen bonding is difficult to determine, however, and the donicities of water and methanol indicated by this approach may be somewhat uncertain also.

In Gutmann's donicity scale the donor number of any solvent represents the negative $\Delta H_{S\cdot SbCl_5}$ value in high dilution of 1,2-dichloroethane for the formation of a 1:1 adduct between the neutral donor solvent molecule S and $SbCl_5$. Experimentally, the change in heat content upon addition of a small amount of neutral donor to a dilute solution of $SbCl_5$ in dichloroethane is measured calorimetrically. Under these conditions and by keeping the molar ratio of antimony(V) chloride to donor solvent greater than unity, the heat of reaction approximates closely the heat of solvation of $SbCl_5$ by the donor solvent in the formation of a 1:1 donor–acceptor complex. If the strong electron-pair donor capacity of a solvent molecule gives rise to a large heat of reaction with $SbCl_5$, and thereby to a high donor number, that same property may stabilize the transition state in the dissociation of a metal–ligand complex and lower the activation energy for the reaction in eq 14. This could explain the inverse correlation seen between solvent donicity and $\Delta H_b^\ddagger$ for the nickel–isoquinoline system. Hydroxylic solvents such as water may present an additional factor through selective solvation of the leaving ligand. The nature of the ligand also requires consideration, as to both charge and conformation.

It is thus expected that (a) apparent donicities of solvents which strongly solvate the ligand will trend toward values higher than "normal" and (b) the stronger the interaction between ligand and solvent, the more positive will be the deviation from "normal" (the donicity of any solvent in Gutmann's scale being considered to be "normal"). The deviations of +15 for water and +10 for methanol observed by Dickert, Hoffmann, and Janjic[5c] from the corresponding values in Gutmann's scale are in agreement with the expectation that, of the solvents considered by Hoffmann and co-workers, water will solvate thiocyanate ion most strongly and methanol next most strongly. This may explain why the donicities of water and methanol predicted from the thiocyanate studies are higher than the corresponding values predicted from our work.

We conclude that the correlation observed between $\Delta H_b^\ddagger$ and solvent donicity can be rationalized from a mechanistic point of view by including the effects of solvent molecules coordinated to the metal ion on the stability of the transition state. It is significant that in this system more information on details of the reaction mechanism can be obtained from consideration of thermodynamic parameters than from consideration of rate constants at a single temperature.

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Registry No. $NiLS_5^{2+}$(S = water), 60489-00-1; $NiLS_5^{2+}$(S = methanol), 60489-01-2; $NiLS_5^{2+}$(S = dimethyl sulfoxide), 60489-02-3; $NiLS_5^{2+}$(S = acetonitrile), 60489-03-4; $NiLS_5^{2+}$(S = propylene carbonate), 60489-04-5; $NiLS_5^{2+}$(S = dimethylformamide), 60489-05-6.

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