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Solvent Dependence of Ligand Substitution Kinetics of Nickel(II)[1]

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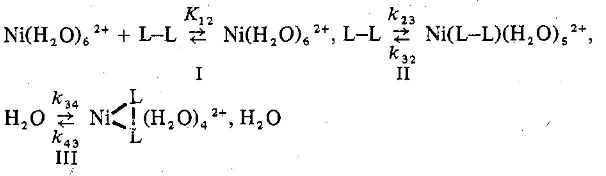
Rate constants and activation parameters are reported for the substitution reactions of nickel(II) ion with pyridine, 2,2'-bipyridine, 1,10-phenanthroline, and 2,2',2''-terpyridine, mainly in acetonitrile and dimethyl sulfoxide as solvents. In addition, similar data are reported for terpyridine in methanol and ethylene glycol and for bipyridine in ethanol–water and *tert*-butyl alcohol–water mixtures. In dimethyl sulfoxide substitution by pyridine appears to proceed by an I_d mechanism in which solvent exchange is rate limiting (as in water), but with the multidentate ligands at ordinary temperatures the possibility exists that the rate-controlling step is ring closure. There is some evidence that near 120° nickel(II) ion in dimethyl sulfoxide loses its ability to discriminate among the four ligands. In acetonitrile the unexpected result is obtained that the enthalpy and entropy of activation for substitution by the multidentate ligands, particularly phenanthroline, are much lower than for pyridine. In alcohol–water mixtures pronounced minima in the enthalpy and entropy of activation occur at the same solvent compositions at which the medium is known to possess maximum structure.

Extensive investigations[2] have indicated that in aqueous solution the rate-determining step in the reaction of many metal ions with numerous (but not all) ligands studied involves loss of a water molecule from the primary solvation sphere of the metal ion. In the majority of cases this step appears to involve an I_d mechanism, *i.e.*, a (concerted) interchange process characterized by a dissociative mode of activation.[3] As illustrated below for the reaction of nickel(II) with an uncharged unidentate ligand, it further appears that this rate-determining step which leads to formation of an inner-sphere complex (process II, forward rate constant k_{23}) is preceded by rapid formation of an outer-sphere complex (process I, equilibrium formation constant K_{12})

$$\mathrm{Ni(H_2O)_6}^{2+} + \mathrm{L} \underset{\mathrm{I}}{\overset{K_{12}}{\rightleftarrows}} \mathrm{Ni(H_2O)_6}^{2+}, \mathrm{L} \underset{\substack{k_{32}\\ \mathrm{II}}}{\overset{k_{23}}{\rightleftarrows}} \mathrm{NiL(H_2O)_5}^{2+}, \mathrm{H_2O} \qquad (1)$$

If the ligand is multidentate, additional steps leading to ring closure must be considered, as illustrated (process III) for the case of an uncharged bidentate ligand



$$\mathrm{Ni(H_2O)_6}^{2+} + \mathrm{L{-}L} \underset{\mathrm{I}}{\overset{K_{12}}{\rightleftarrows}} \mathrm{Ni(H_2O)_6}^{2+}, \mathrm{L{-}L} \underset{\substack{k_{32}\\ \mathrm{II}}}{\overset{k_{23}}{\rightleftarrows}} \mathrm{Ni(L{-}L)(H_2O)_5}^{2+}, \mathrm{H_2O} \underset{\substack{k_{43}\\ \mathrm{III}}}{\overset{k_{34}}{\rightleftarrows}} \mathrm{Ni}{<}\overset{\mathrm{L}}{\underset{\mathrm{L}}{|}}(\mathrm{H_2O})_4^{2+}, \mathrm{H_2O} \qquad (2)$$

It is usually assumed[2e] that for many multidentate ligands, including all three of those involved in the present study, $k_{34}/k_{32} \gg 1$ in aqueous solution, so that process II remains the rate-determining step, as it is for unidentate ligands. However, exceptions to this "normal" type of substitution have been found. For example, in the reaction of β-alanine with cobalt(II), ring closure is rate limiting; this behavior has been termed "sterically controlled substitution."[4] Other examples have been identified by several workers (Margerum, Rorabacher, Pearson, and others) and are listed by Wilkins.[2e] Finally, a (limiting) D-type process[3] characterized by a relatively long-lived intermediate $\mathrm{NiS_5}^{2+}$ (S = solvent) is generally not observed,[2b] although evidence has been presented in support of the existence of such an intermediate in dimethyl sulfoxide as solvent.[5]

In view of the crucial role attributed to water in reactions 1 and 2, studies in other solvents may be expected to provide useful new perspectives. Solvent-exchange rates (k_s), measured by nmr spectroscopy, are available for water and several nonaqueous solvents,[6] and these can be compared with observed ligand substitution rates (k_l) in each solvent. For the special case when $K_{12}[\mathrm{L}] \ll 1$, it can be shown that for "normal" substitution $k_l = K_{12}k_{23}$. In testing whether substitution is "normal," it is convenient to consider a ratio R given by

$$R = (4/3)k_{23}/k_s = (4/3)k_l/K_{12}k_s \qquad (3)$$

where $^3/_4$ appears to be a reasonable statistical factor[7] representing the probability that a ligand will enter a particular coordination site vacated by a solvent molecule. In eq 3, k_{23} and k_s are first-order rate constants while k_l is second order. If substitution is "normal," the (dimensionless) ratio R should have a value near unity. In addition, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values for ligand substitution should be similar to those for solvent exchange. Limitations of this type of analysis are that existing nmr data, particularly the activation parameters, are rather uncertain for the majority of solvents and that the formation constant of the outer-sphere complex generally is not amenable to direct experimental determination. In the majority of cases the only recourse is to estimate this constant from the theoretical relationship[8]

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

where

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

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Here a represents the center-to-center distance of closest approach of the solvated metal ion and the ligand, and all other symbols have their customary meaning. This equation was derived by Eigen from the ratio of diffusion-controlled association and dissociation rate constants through a consideration of the volume available for the ligand in the complex and by Fuoss on the basis of an electrostatic model of ion pairing. While it is difficult to estimate the uncertainty in the general application of eq 4, its use has led to reasonable results for water[2e] and methanol[9] as solvents.

We report here the results of a stopped-flow investigation of the substitution reactions of nickel(II) ion with pyridine, 2,2′-bipyridine, 1,10-phenanthroline, and 2,2′,2″-terpyridine, mainly in acetonitrile and dimethyl sulfoxide as solvents. In addition, measurements were made with terpyridine in methanol and ethylene glycol and with bipyridine in the following solvent mixtures: methanol–acetonitrile, ethanol–water, and *tert*-butyl alcohol–water. Finally, in order to ensure internal consistency, we repeated measurements previously made by other workers in aqueous solution. In all cases the activation parameters were determined. Recently, Bennetto and Caldin[6b,10] reported results for several of the systems also studied by us; for those systems the experimental data will be compared and for dimethyl sulfoxide as solvent a substantially different interpretation will be presented.

Experimental Section

Solvents. Acetonitrile (Fisher Scientific Co. Certified ACS grade) was purified by distillation from calcium hydride (Fisher Purified grade) after pretreatment as described elsewhere.[11] Dimethyl sulfoxide (J. T. Baker Chemical Co. Analyzed reagent) was distilled *in vacuo* at 35°, first alone and then from calcium hydride. The water content of the products, as determined by Karl Fischer titration, was 10^{-3} M for acetonitrile and 4×10^{-3} M for dimethyl sulfoxide. Methanol (Baker Spectrophotometric grade) and ethanol (U. S. Industrial Chemicals Co. Reagent Quality) were dried over 3-Å molecular sieves (Linde Division, Union Carbide Corp.). Ethylene glycol (Baker Analyzed reagent) was purified as described elsewhere.[12] *tert*-Butyl alcohol (Baker Analyzed reagent) was used without further purification. Water was either deionized or doubly distilled; the two products gave the same results.

Reagents. Nickel(II) was introduced as the perchlorate. For dimethyl sulfoxide as solvent, it was the corresponding hexasolvate.[13] *Caution!* Although we have never experienced explosions with perchlorates in organic solvents, other workers have reported accidents; due precautions against this possibility must be taken. For acetonitrile, methanol, and ethylene glycol as solvents, nickel(II) perchlorate either was prepared *in situ* from equivalent amounts of anhydrous nickel(II) bromide (K & K Laboratories) and silver perchlorate (G. F. Smith Chemical Co.) or was introduced as the monohydrate obtained by heating the recrystallized hexahydrate (G. F. Smith) *in vacuo* at 90 ± 5°. The two preparations gave the same results, provided the product prepared *in situ* contained less than 10^{-6} M bromide.[14] All nickel solutions were standardized by EDTA titration (after dilution with water where appropriate), using an ammonia–ammonium chloride buffer of pH 10 and Erio T as indicator. Pyridine (Malinckrodt Chemical Works Analytical reagent) was used without further purification. Three samples of 2,2′-bipyridine (Fisher Reagent grade, mp 70.0–70.3°, and the K & K product, both before and after recrystallization) gave the same results. The monohydrate of 1,10-phenanthroline (Fisher Certified reagent, mp 99.1–99.4°) gave the same results as the anhydrous form (mp 117°) obtained by recrystallization from water containing the minimum amount of ethanol to effect dissolution, followed by heating *in vacuo* at 35 ± 3°. 2,2′,2″-Terpyridine (Baker, mp 88–91°) was used without further purification.

Instrumentation and Experimental Procedure. All nonaqueous solutions were prepared and dispensed in glove bags filled with dry nitrogen, using glassware that had been dried *in vacuo* at 50° for several days. All other standard procedures for handling nonaqueous solutions were followed.

Visible and ultraviolet spectra were recorded with Cary Model 14 and Perkin–Elmer Model 124 spectrophotometers, the latter equipped with temperature control. Kinetic measurements generally were made at the wavelength of maximum absorption of the complex. These wavelengths are not very solvent sensitive and are 256–268 nm for pyridine, 305–310 nm for bipyridine, 334–338 nm for terpyridine, and 270–275 nm for phenanthroline. However, in the case of pyridine in dimethyl sulfoxide, the complex is relatively unstable and it was preferred to make measurements at 295 nm, where only the complex absorbs.

Kinetic measurements were made with a Durrum Instrument Co. (Palo Alto, Calif.) Model D-110 stopped-flow spectrophotometer equipped with a Kel-F flow system. We have shown elsewhere[15] that when this instrument is thermostated at other than ambient temperatures, a temperature gradient exists in the Kel-F valve block, which has poor thermal conductivity. This problem can be circumvented by dispensing sufficient volumes of reactant solutions (0.41 ml per channel with the 0.20-ml cuvette and 0.34 ml with the 0.06-ml cuvette) to ensure that all of the solution under observation in the cuvette has originated directly from the drive syringes, where the temperature is the same as in the thermostat liquid. Temperatures in the thermostat bath and in the cuvette were controlled to within ±0.1°. Kinetic measurements were made under pseudo-first-order conditions with the total ligand concentration (after mixing) kept constant, usually at 2.5×10^{-5} M, and the nickel concentration varied through three or four values, typically from *ca.* 1 to 4×10^{-3} M. Varying the concentration of bipyridine in acetonitrile from 1.25 to 5.0×10^{-5} M produced no significant change in rate constant; hence, it was assumed that extrapolation of observed pseudo-first-order rate constants to zero ligand concentration would be unnecessary for the remaining systems as well. Conductometry showed that in our concentration range nickel(II) perchlorate in acetonitrile is essentially completely dissociated. As would be expected from the trend observed by Pearson and Ellgen with bipyridine in methanol,[9] ionic strength effects appeared to be negligible in our work. Repeated measurements were made on several systems at intervals of months, using different batches of solvents and reactants. Reproducibility of second-order rate constants was generally within ±2%.

Results

Rate constants for ligand substitution at nickel(II) are presented in Table I, and in Table II rate constants and activation parameters for ligand substitution are compared with those for solvent exchange. In the calculation of the formation constant of the outer-sphere complex (K_{12}) from eq 4 the following values for the distance of closest approach (a, Å) were estimated from interatomic distances and configurations of the solvent molecules:[16] water, 5; methanol and ethylene glycol, 6; dimethyl sulfoxide, 7; acetonitrile, 7.5.

Thermodynamic Properties of Systems Studied. On the basis of the limited experimental information available, certain rough predictions can be made of the relevant thermodynamic properties of the nonaqueous systems studied here. From what is known about trends in polarographic and other properties it seems likely that nickel(II) ion is solvated more strongly in dimethyl sulfoxide,[17] but more weakly in metha-

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(14) Halide ions (and probably many other anions as well) strongly accelerate the reaction of nickel(II) with ligands such as 2,2′,2″-terpyridine in certain nonaqueous solvents. For example, we found that the second-order rate constant for the reaction of terpyridine with $NiBrS_5^+$ in acetonitrile (S) at 25° is 200 times greater than that with NiS_6^{2+}. We will discuss these results elsewhere.

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Table I. Rate Constants for Ligand Substitution at Nickel(II) at Various Temperatures

Solvent	Ligand	Rate constant × 10^{-3},[a] l. mol^{-1} sec^{-1}			
		15°	25°	35°	45°
Water	Bipyridine	1.07[b]	2.26	4.13	8.0
	Terpyridine	0.71	1.49	3.03	
	Phenanthroline	1.98	4.14	7.8	
Methanol	Bipyridine		0.094		
	Terpyridine	0.0190	0.0457	0.125	0.326
Ethylene glycol	Terpyridine	0.0047	0.0096	0.0209	0.0482[c]
Acetonitrile	Pyridine	0.310	0.83	1.88	3.81
	Bipyridine	2.72	4.11	5.9	8.8
	Terpyridine	1.38	2.20	3.87	5.9
	Phenanthroline	37.8[d]	49.7	70	
Dimethyl sulfoxide	Pyridine		*Ca.* 2		
	Terpyridine		0.0251	0.053	0.117[e]
	Phenanthroline		0.348	0.59	0.90

[a] Reproducibility is ±2%; one additional significant figure given. [b] Additional value: 0.50 at 5°. [c] Additional value: 0.103 at 55°. [d] Additional value: 27.1 at 5°. [e] Additional value: 0.284 at 55°.

nol[18] and particularly in acetonitrile,[19] than in water. The four ligands used here are relatively weak proton acceptors. Their pK_a values in water at 25° are as follows:[20] pyridine, 5.17; bipyridine, 4.35; terpyridine, *ca.* 4.3; phenanthroline, 4.86. In acetonitrile the pK_a value of pyridine is 12.3, and in dimethyl sulfoxide it is 3.4.[21] Since the autoprotolysis constants of acetonitrile and dimethyl sulfoxide are of the order of 10^{-30}, it is certain that none of the ligands used will be protonated by the pure solvents; however, acidic impurities must be absent, as they have been shown to be after distillation from calcium hydride. Protonation of the ligands by water, methanol, and ethylene glycol also will be insignificant. This simplifies interpretation of the kinetic results.[22]

The log K_1 values for the formation of the 1:1 complexes of nickel(II) ion with these ligands in water at 25° are as follows:[22] pyridine, 2.1; bipyridine, 7.1; terpyridine, 10.7; phenanthroline, 8.8. The stepwise formation constants of the higher complexes have similar values.[20] Hence, at the concentrations of reactants used here and by previous workers,[10a,22] essentially only the 1:1 complex is produced and its formation is virtually complete in aqueous solution. For the nonaqueous solvents corresponding thermodynamic information is lacking, but the kinetic data discussed below indicate that in all cases only the 1:1 complex is produced and that, with the exception of phenanthroline and particularly pyridine in dimethyl sulfoxide, its formation is essentially complete.

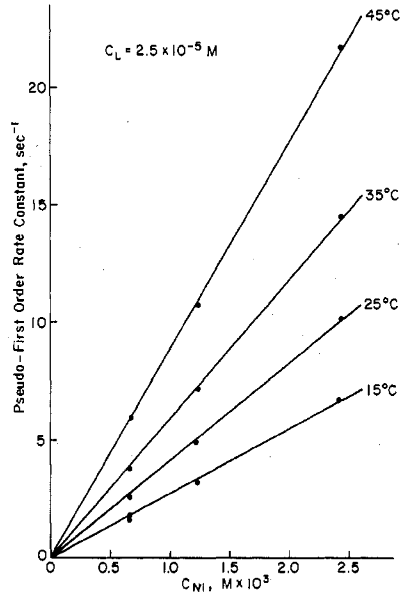

Figure 1. Pseudo-first-order rate constants for the reaction of nickel(II) with 2,2′-bipyridine in acetonitrile as solvent.

Kinetic Results. Kinetic data for pyridine in acetonitrile and dimethyl sulfoxide, for terpyridine in methanol, ethylene glycol, and acetonitrile, and for phenanthroline in acetonitrile and dimethyl sulfoxide have not been reported before. The remaining data can be compared with those of previous workers.[10,22] In the majority of cases agreement is reasonable. A significant exception is bipyridine in acetonitrile. Our pseudo-first-order plots, the slopes of which give the second-order rate constants (k_1) at various temperatures, are given in Figure 1. At all temperatures the plots (a) are linear and (b) pass through the origin, indicating that (a) only one complex is formed and that (b) its formation is essentially complete, as expected. However, Bennetto and Caldin obtained large intercepts in such plots, and these increased with increasing temperature.[10] It is possible that this behavior was caused by the presence of basic salts, because the source of nickel was the hydrated perchlorate which had been heated to a temperature above that (near 105°) at which such thermal decomposition becomes significant.[23] However, for the two systems already indicated we did obtain intercepts in the pseudo-first-order plots, as shown for the case of phenanthroline in dimethyl sulfoxide in Figure 2. In view of the relatively strong solvation of nickel(II) ion by dimethyl sulfoxide, it is not too surprising that this reaction is incomplete, but the greater stability of the bipyridine complex[10] is unexpected. As illustrated by Pearson and Ellgen for the reaction of nickel(II) ion with thiocyanate in water-methanol mixtures,[9a] the slope of such a plot gives the rate constant for the formation of the complex, $k_{1,f}$, while the intercept gives the rate constant for its dissociation, $k_{1,d}$. Results obtained from such plots are summarized in Table III.

In Figure 3 the activation parameters for the reaction of nickel(II) ion with bipyridine in water-ethanol and water-

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Table II. Comparison of Rate Constants and Activation Parameters for Ligand Substitution at Nickel(II) with Those for Solvent Exchange

Solvent	Ligand	No.	k_s or $k_1 = K_{12}k_{23}$ [a]	$R = (4/3)k_1/K_{12}k_s$ [a]	$\Delta H^{\ddagger}$ [b]	$\Delta\Delta H^{\ddagger}$ [b]	$\Delta S^{\ddagger}$ [c]	$\Delta\Delta S^{\ddagger}$ [c]
Water	Water	1	3.0×10^4	*d*	10.8	*d*	−2	*d*
	Pyridine[e]	2	*Ca.* 4×10^3	*Ca.* 0.6	*Ca.* 11	*Ca.* 0	*Ca.* −5	*Ca.* −3
	Bipyridine	3	2.26×10^3	0.33	11.7 ± 0.2	+0.9	−4	−2
	Terpyridine	4	1.49×10^3	0.22	12.3 ± 0.1	+1.5	−3	−1
	Phenanthroline	5	4.14×10^3	0.61	11.5 ± 0.3	+0.7	−4	−2
Methanol	Methanol	6	1.0×10^3	*d*	15.8	*d*	+8	*d*
	Bipyridine	7	9.4×10	0.25				
	Terpyridine	8	4.6×10	0.12	16.8 ± 0.5	+1.0	+5	−3
	Phenanthroline	9	2.4×10^2 [f]	0.65				
Ethylene glycol	Ethylene glycol	10	4×10^3	*d*		*d*		*d*
	Terpyridine	11	9.6	0.006	14.0 ± 0.4		−7	
Acetonitrile	Acetonitrile	12	2.8×10^3	*d*	11.7	*d*	−4	*d*
	Pyridine	13	8.3×10^2	0.39	14.7 ± 0.4	+3.0	+4	+8
	Bipyridine	14	4.1×10^3	1.9	6.5 ± 0.2	−5.2	−20	−16
	Terpyridine	15	2.2×10^3	1.0	8.4 ± 0.3	−3.3	−15	−11
	Phenanthroline	16	5.0×10^4	23	4.7 ± 0.2	−7.0	−21	−17
Dimethyl sulfoxide	Dimethyl sulfoxide	17	7.5×10^3(?)	*d*	8(?)	*d*	−14(?)	*d*
	Pyridine	18	*Ca.* 2×10^3	*Ca.* 0.5	*Ca.* 4	*Ca.* −4	*Ca.* −30	*Ca.* −16
	Bipyridine[g]	19	6.9×10	0.02	12.6 ± 0.1	+5	−8	+6
	Terpyridine	20	2.5×10	0.006	15.0 ± 0.7	+7	−2	+12
	Phenanthroline	21	3.5×10^2	0.08	8.3 ± 0.3	0	−19	−5

[a] Units: sec^{-1} at 25° for k_s, l. mol sec^{-1} at 25° for k_1. Values of k_s selected from ref 6. [b] $\Delta\Delta H^{\ddagger} = \Delta H_1^{\ddagger} - \Delta H_s^{\ddagger}$, kcal mol^{-1}. [c] $\Delta\Delta S^{\ddagger} = \Delta S_1^{\ddagger} - \Delta S_s^{\ddagger}$, cal mol^{-1} deg^{-1}. [d] Not applicable. [e] From R. H. Holyer, C. D. Hubbard, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, 4, 929 (1965). [f] Approximated from data in ref 9a by assuming the ionic strength effect is the same as for bipyridine. [g] From ref 10a.

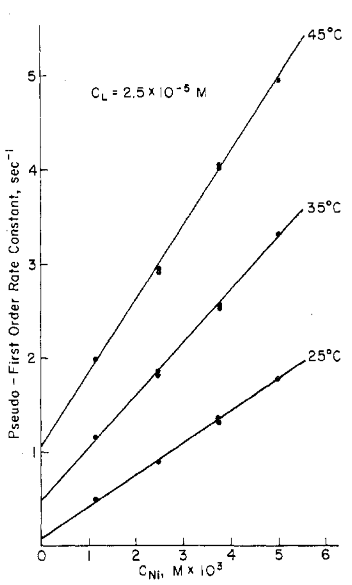

Figure 2. Pseudo-first-order rate constants for the reaction of nickel(II) with 1,10-phenanthroline in dimethyl sulfoxide as solvent.

Table III. Rate and Equilibrium Constants for Weak 1:1 Complexes of Nickel(II) in Dimethyl Sulfoxide as Solvent

Ligand	Temp, °C	$k_{1,f}$, l. mol^{-1} sec^{-1}	$k_{1,d}$, sec^{-1}	K_f,[a] l. mol^{-1}
Pyridine[b]	20	2×10^3	7×10	3×10
	30	3×10^3	2×10^2	1.5×10
Phenanthroline	30	4.8×10^2	3×10^{-1}	1.6×10^3
	35	5.9×10^2	5×10^{-1}	1.2×10^3 [c]
	45	9.0×10^2	1.0	9×10^2

[a] $K_f = k_{1,f}/k_{1,d}$. [b] Preliminary values with relatively high uncertainty. [c] Value from direct spectrophotometric determination: 1.5×10^3.

tert-butyl alcohol mixtures are compared with those in pure water.

Discussion

Among the most significant results in Table II are the following. (1) Rate constants and activation parameters for ligand substitution depend strongly on the nature of the solvent and, in acetonitrile and dimethyl sulfoxide, on the nature of the ligand as well. (2) The value of R (at 25°) for pyridine seems reasonably "normal" in acetonitrile and in dimethyl sulfoxide, as it is in water. (3) In contrast to the situation in water and methanol, values of R for the multidentate ligands are significantly smaller than unity in dimethyl sulfoxide. (4) In sharp contrast to the situation in dimethyl sulfoxide, the properties of multidentate ligands in acetonitrile generally deviate from those in water and methanol in the opposite direction. The value of R for phenanthroline is much greater than unity, and $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ values for all multidentate ligands are significantly negative. (5) Values of R, $\Delta\Delta H^{\ddagger}$, and $\Delta\Delta S^{\ddagger}$ vary by as much as factors of 4.5×10^3, 14 kcal mol^{-1}, and 29 cal deg^{-1} mol^{-1}, respectively.

The *solvent dependence* of rate constants and activation parameters, restricted mainly to bipyridine as ligand, has been discussed in an admittedly speculative but a splendid thought-provoking presentation by Bennetto and Caldin.[6b,10] Assuming in effect that in all solvents $k_{34}/k_{32} \gg 1$ and also that K_{12} has a constant value near 0.1 l. mol^{-1} in all solvents and defining a quantity $n = k_1/K_{12}k_s$,[24] their main conclusions were the following. (1) The properties of aqueous solutions

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[24] Our ratio R (eq 3) differs from n only in that a statistical factor is included and K_{12} is allowed to vary with the solvent.

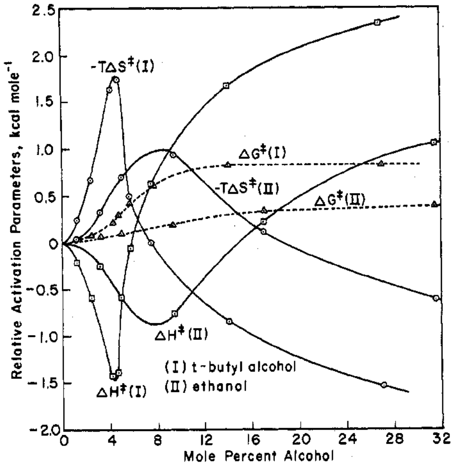

Figure 3. Activation parameters for the reaction of nickel(II) with 2,2′-bipyridine in water-ethanol and water-*tert*-butyl alcohol mixtures, normalized with respect to those in pure water (298° K).

(n near unity, $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ small) are not general. (2) Values of n and $\Delta\Delta H^{\ddagger}$ can be correlated with certain properties of the solvent reflecting the "stiffness" and the "openness" of its structure, such as its enthalpy of vaporization and its fluidity. (3) After correcting for ligand field stabilization, a linear relationship between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ is found for both solvent exchange and ligand substitution at various divalent metal ions in a number of solvents. (4) The above findings can be interpreted in terms of a structural model in which a disordered region separates the primary solvation sphere of the metal ion from the bulk solvent. The first two conclusions can now be examined for additional ligands. Conclusion 1 is strengthened by the new data. As far as conclusion 2 is concerned (replacing the quantity n by the ratio R of eq 3), the types of correlations noted for bipyridine also apply for terpyridine and phenanthroline: R shows a general decreasing and $\Delta\Delta H^{\ddagger}$ an increasing trend with increasing enthalpy of vaporization and decreasing fluidity of the solvent, but the correlations are rather rough. Furthermore, the two correlations are not independent, because a similar approximate relationship exists between the enthalpy of vaporization and the fluidity of these solvents. However, the most significant new information is that the correlations for pyridine show the opposite trend from those of the multidentate ligands, indicating that structural features of the solvent affect the two classes of ligands quite differently. Finally, conclusion 3 is generally supported by the new data, as shown in Figure 4. Uncertainties in the significance of such isokinetic relationships have been discussed in detail by Leffler and Grunwald.[25] The general correlation illustrated by Figure 4 meets all criteria for significance, although several individual systems are not accommodated particularly well. There is remarkably little variation in $\Delta G^{\ddagger}$, with extensive compensation of the large variations in $\Delta H^{\ddagger}$ by those in $-T\Delta S^{\ddagger}$. This behavior is characteristic of many sets of reactions in which solvation changes play an important role; in such cases the slope of the isokinetic plot often lies between 300 and 400°K,[25] as it does here. Very recently Hoffmann[26] has reported a similar isokinetic relationship for a series of metal ions reacting with a single ligand in methanol as solvent; this is an important observation.

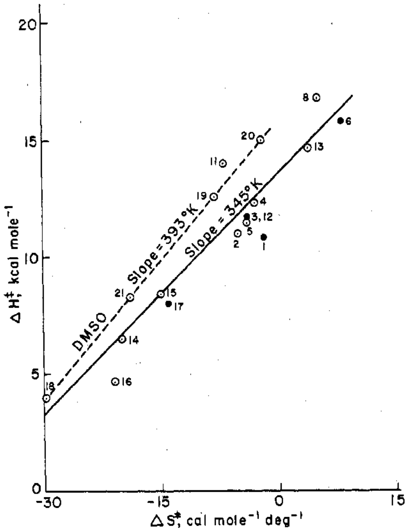

Figure 4. Isokinetic plots for reactions of nickel(II). Numbers refer to Table II. Closed circles represent solvent exchange; open circles, ligand substitution. Solid line is linear least-squares fit to all data; dashed line is restricted to ligand substitution in dimethyl sulfoxide.

In Bennetto and Caldin's interpretation of the above correlations structural features of the solvent occupy a pivotal position. In particular, it is assumed as a working hypothesis that the Frank-Wen model for aqueous solutions,[27] for which strong experimental support exists, can be extended to the nonaqueous solutions under consideration. In this model the primary solvation sphere of the metal ion is separated from the bulk solvent by a disordered region which is the result of competition between ion-solvent and solvent-solvent interactions. Particular solvent molecules may spend little time in this disordered region, where they are characterized by high energy and high entropy. The effective thickness of the disordered region of this dynamic model should be related on the one hand to the enthalpy of vaporization of the solvent and on the other to what may be termed the "structural" components of the enthalpy and entropy of activation. Consequently, cooperativity in the liquid is important, and "the solvent effect on rates mirrors the rhythm of molecular reorganization of the liquid."[6b]

We will now briefly consider what is known about the structure of acetonitrile and dimethyl sulfoxide and speculate about the probability that an intermediate disordered region can be responsible for the observed kinetic effects. It should be stressed at the outset that our knowledge about the structure of these liquids, and particularly about the influence of solutes on their structure, is very limited. Nevertheless, it does seem certain that these dipolar aprotic solvents have little hydrogen-bonded structure but that they do possess considerable order as a result of dipole association (dipole moments at 25°: acetonitrile, 3.37 D; dimethyl sulfoxide, 4.11 D). However, the actual geometrical features of the order in these solvents are much less certain. For acetonitrile most of the evidence is consistent with considerable dimerization, either in an antiparallel or in a skewed-T configuration, with an enthalpy of association of perhaps 8 kcal mol^{-1} at 25°.[28] For dimethyl sulfoxide a variety of properties, such as its very high entropy of vaporization, indicate that the liquid is strongly ordered. Order persists even in relatively dilute solu-

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(25) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 315.

(26) H. Hoffman, *Proc. Int. Conf. Coord. Chem.*, **14**, 206 (1972).

(27) H. S. Frank and W. Y. Wen, *Discuss. Faraday Soc.*, **24**, 133 (1957).

(28) J. F. Coetzee and W. R. Sharpe, *J. Soln. Chem.*, **1**, 77 (1972).

tions in benzene and carbon tetrachloride, as shown by the cryoscopic and infrared spectral properties of these solutions. However, as for acetonitrile, geometrical features are not unambiguously established, although most of the evidence is consistent with the existence of chainlike aggregates produced by S-O dipole alignment.[17a] Finally, there is little doubt that liquid dimethyl sulfoxide is much more ordered than acetonitrile. The main question now is how the order existing in these solvents will be modified by the presence of solutes. An estimate of absolute ionic entropies by Criss, *et al.*,[29] gave, quite reasonably, the least negative values for those solvents considered to have the greatest degree of internal order. Interpolating within the series of solvents considered by Criss, *et al.*, we expect that solute extropies will decrease in the order water ≫ methanol, dimethyl sulfoxide > dimethylformamide > acetonitrile. How far along this sequence creation of an intermediate disordered region by solutes remains significant is the crucial question which cannot be answered with certainty at this time and which undoubtedly deserves future attention. However, it seems likely that in solvents possessing no extended three-dimensional structure the disruptive effect of solutes will be much less significant than that demonstrated for water. For example, unlike in water, structure breaking by the larger alkali metal and halide ions appears to be unimportant in *N*-methylacetamide, which has a chainlike hydrogen-bonded structure.[30] Particularly in the case of acetonitrile it seems questionable to us that the primary solvation sphere of nickel(II) ion (radius ~7 Å) necessarily would be incompatible with the dimerization characteristic of the bulk solvent, and incompatibility is a requisite for a disordered region. In summary, we feel that, while general structural features of acetonitrile and dimethyl sulfoxide undoubtedly affect the properties of the systems studied here, the results are not accommodated convincingly within the restricted and somewhat tenuous framework of a disordered region model for these two solvents. This is particularly true for the dramatic *ligand dependence* of the activation parameters, which may be rationalized more easily in terms of steric effects. In contrast, as pointed out below, results obtained in water-rich alcohol-water mixtures appear to be accommodated adequately by Bennetto and Caldin's structural model.

Considering first the results for dimethyl sulfoxide, in Figure 5 Arrhenius plots for different ligands are extrapolated to higher temperatures. Particularly for pyridine it is not profitable to extend measurements to temperatures much higher than those included here because of the high rate coupled with the incompleteness of the reaction, so that the extrapolation is particularly precarious. Nevertheless, it does appear that near 120° nickel(II) ion in dimethyl sulfoxide loses its ability to discriminate among the four ligands. As the temperature is lowered, the increasing differentiation among ligands must reflect the net effect of a number of interrelated processes including strengthening of nickel-solvent bonds, increasing dispersion and other short-range interactions between ligand and solvent, and increasing order in the bulk solvent and probably in the outer sphere as well. Furthermore, it is likely that the ring-closure step (eq 2, process III) will be strongly influenced by these factors. In the solid state the rings of bipyridine are coplanar but in the trans position,[31] and this also may be the case in solution. However, in its chelates the rings must be in the cis position. Hence, a solvent-dependent barrier to ring closure (and opening) is likely to exist in the case of bipyridine and particularly terpyridine, but it should be less pronounced with the rigid phenanthroline. The results in Figure 5 are consistent with these expectations.

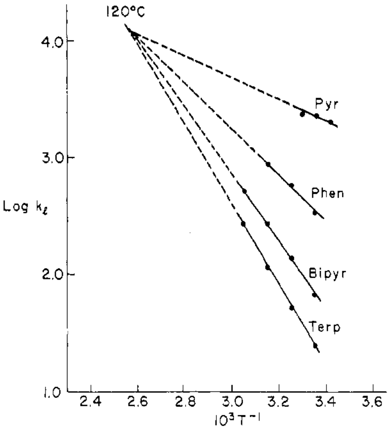

Figure 5. Arrhenius plots for the reaction of nickel(II) with pyridine, 1,10-phenanthroline, 2,2′-bipyridine, and 2,2′,2″-terpyridine in dimethyl sulfoxide. Data for bipyridine are from ref 10a.

We now assume that substitution by pyridine is "normal" in the sense that it proceeds by an I_d mechanism. This assumption may appear to be of questionable validity in view of the large values of $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ given in Table II. However, the activation parameters for pyridine substitution as well as those for solvent exchange have considerable uncertainty. Furthermore, rate constants determined by Dickert and Hoffmann by pressure-jump relaxation for two other unidentate ligands, chloride and thiocyanate ions, are consistent with normal substitution;[32] we have verified their results for thiocyanate by stopped-flow measurements.[33] From the results in Table III a tentative dissection of observed rate constants for the formation and dissociation of the phenanthroline complex now will be carried out, as has been done by Wilkins for several bidentate ligands in aqueous solution.[2e,22a] For phenanthroline at 30° the observed rate constants are given by

$$k_{1,f} = \frac{K_{12}k_{23}k_{34}}{k_{32} + k_{34}} = 4.8 \times 10^2 \tag{5}$$

$$k_{1,d} = \frac{k_{32}k_{43}}{k_{32} + k_{34}} = 3 \times 10^{-1} \tag{6}$$

Assuming as a *first approximation* that the values of $K_{12}k_{23}$ and k_{32} are adequately represented by those of $k_{1,f}$ and $k_{1,d}$ for pyridine, it follows that $k_{34} \approx 40$ and $k_{34}/k_{32} \approx {}^1/_5$, illustrating the influence of the ring-closure step. Furthermore, $k_{43} \approx 4 \times 10^{-1}$, so that $K_{34} = k_{34}/k_{43} \approx 10^2$. Similarly, for bipyridine at 30°, $k_{34}/k_{32} \approx {}^1/_{30}$ (as compared to ${}^{70}/_1$ in water[22a]), and for terpyridine $k'_{34}/k_{32} \approx {}^1/_{80}$, where k'_{34} is an effective overall rate constant for closure of both rings. According to this analysis, the lower stability of the phenanthroline complex in dimethyl sulfoxide as compared to that in water is the result mainly of the fact that k_{34} is smaller while k_{43} is larger in dimethyl sulfoxide than in water. This cannot be attributed solely to an increased barrier to rotation of

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(29) C. M. Criss, R. P. Held, and E. Luksha, *J. Phys. Chem.*, **72**, 2970 (1968).

(30) R. H. Wood, R. K. Wicker, II, and R. W. Kreis, *J. Phys. Chem.*, **75**, 2313, 2319 (1971).

(31) W. W. Brandt, F. P. Dwyer, and E. C. Gyarfas, *Chem. Rev.*, **54**, 959 (1954).

(32) F. Dickert and H. Hoffmann, *Ber. Bunsenges. Phys. Chem.*, **75**, 1320 (1971).

(33) J. F. Coetzee and E. Hsu, to be submitted for publication.

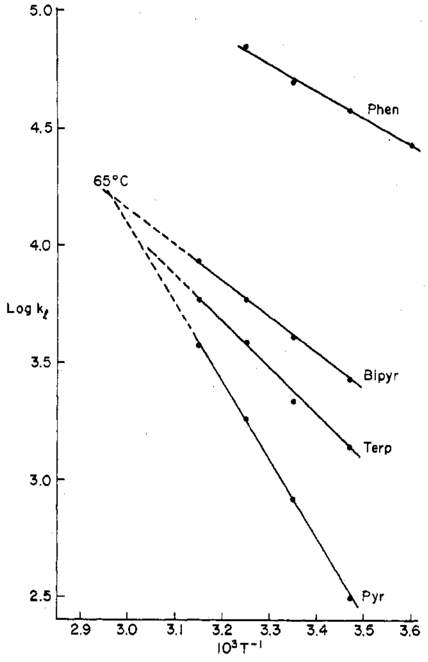

Figure 6. Arrhenius plots for ligand substitution reactions of nickel(II) in acetonitrile.

the ligand (as a whole) in dimethyl sulfoxide, because that would decrease k_{34} and k_{43} equally. It appears that the statistical advantage associated with chelate formation in water[2b] somehow is radically diminished in dimethyl sulfoxide. As stated above, this analysis is only a first approximation. A serious uncertainty at this time is that steric inhibition to first bond formation may be quite different for pyridine and phenanthroline. Further studies with other unidentate ligands having different steric requirements are necessary.

Turning next to the corresponding data for acetonitrile, a substantially different picture emerges. While Figure 6 indicates that, as for dimethyl sulfoxide, there exists a temperature at which nickel(II) ion loses its ability to discriminate among pyridine, bipyridine, and terpyridine, phenanthroline does not fit this picture at all. Also, and unexpectedly, the $\Delta H^{\ddagger}$ value for pyridine is much higher and its $\Delta S^{\ddagger}$ value is more positive than the corresponding values for the multidentate ligands. Here also, further work, particularly with other unidentate ligands having different steric requirements, will be necessary before much can be said about what constitutes "normal" substitution in acetonitrile. The $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ values for the multidentate ligands are significantly negative. One possibility that should be considered is that phenanthroline in particular undergoes a specific interaction with the polarized acetonitrile molecules in the primary solvation shell of nickel(II), in a manner analogous to the "internal conjugate base mechanism" proposed to explain the abnormally high reaction rate of ethylenediamine in aqueous solution.[34] However, evidence to the contrary is that, while cobalt(II) produces significant shifts in the C≡N and C–C infrared stretching frequencies of acetonitrile, its perturbation does not extend to the C–H bonds.[28,35] One can also speculate that the "intrinsic" properties of phenanthroline are more evident in acetonitrile than in water. Phenanthroline forms a stable solid monohydrate involving bonding by both hydrogen atoms of the water molecule,[36] and it is conceivable that such hydrogen bonding in solution may increase the activation barrier in its reactions. The observed increase in the rate constant for the reaction of phenanthroline with nickel(II) when the acidity of the solution is increased[37] would be consistent with this admittedly speculative proposition.

Finally, the results obtained in solvent mixtures will be discussed briefly. With increasing methanol content of methanol-acetonitrile mixtures, the rate constant for the reaction of nickel(II) with bipyridine decreases monotonically while $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ increase, with substantial compensation of *changes* in $\Delta H^{\ddagger}$ by those in $-T\Delta S^{\ddagger}$. All observations are consistent with gradual replacement of acetonitrile by methanol in the primary solvation sphere of nickel(II). Since the results exhibit no particularly interesting features and are essentially the same as those described by Bennetto,[10b] they will not be discussed further. Alcohol-water mixtures exhibit more interesting features, as illustrated in Figure 3. Analogous results have been reported by Bennetto and Caldin for methanol-water mixtures.[10a] With increasing molecular size of the alcohol, the extrema in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ (normalized with respect to corresponding values in pure water) become larger and sharper and occur at progressively lower alcohol content, *viz.*, at 25 mol % methanol, 9% ethanol, and 4.5% *tert*-butyl alcohol. Over the whole range of solvent compositions studied compensation of changes in $\Delta H^{\ddagger}$ by those in $-T\Delta S^{\ddagger}$ is substantial. The extrema in Figure 3 cannot be attributed to dramatic changes in solvation of nickel(II). For example, in 25 mol % methanol only *ca.* 15% of the nickel is in the form $Ni(H_2O)_5CH_3OH^{2+}$, while the rest is still present as the hexahydrate.[18] It is likely that at the extrema for ethanol and particularly *tert*-butyl alcohol the primary solvation sphere contains only water. Furthermore, the extrema occur at essentially the same solvent compositions where other properties, such as the partial molal heats of solution of a variety of salts, exhibit striking maxima.[38] Strong experimental support exists for the hypothesis that when increasing amounts of alcohols are added to water, the water structure is first progressively stiffened until a maximum is reached near the compositions indicated;[10a,38] further addition of alcohol then causes progressive breakdown of water structure. In agreement with Bennetto and Caldin we believe that the initial progressive decrease in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ is consistent with a transition state characterized by passage of a solvent molecule from the disordered region adjacent to the primary solvation sphere into a medium which is both stiffer and more ordered than pure water itself. However, it should be stressed that, while this simple model adequately accounts for the properties of water-rich solvent mixtures, it fails to account for substantial differences in the behavior of bipyridine and ammonia in methanol-rich mixtures.[18,39] In such media the rate constant for ammonia passes through a maximum, attributed[18] to increased lability of methanol in the dominant nickel species, which is $Ni(H_2O)_5CH_3OH^{2+}$. Since

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(34) D. B. Rorabacher, *Inorg. Chem.*, **5**, 1891 (1966).

(35) It was pointed out by a referee that the π-orbital interactions between nickel ion and acetonitrile in the inner sphere and between the same acetonitrile and phenanthroline in the outer sphere may lead to charge delocalization which could have the combined effect of increasing both K_{12} and k_s. The result would be similar to that of the internal conjugate base effect but would not depend on a specific interaction with the hydrogen atoms of coordinated acetonitrile.

(36) J. S. Fritz, F. W. Cagle, Jr., and G. F. Smith, *J. Amer. Chem. Soc.*, **71**, 2480 (1949).

(37) D. W. Margerum, R. I. Bystroff, and C. V. Banks, *J. Amer. Chem. Soc.*, **78**, 4211 (1956).

(38) E. M. Arnett and D. R. McKelvey, *J. Amer. Chem. Soc.*, **87**, 1393 (1965).

(39) F. R. Shu and D. B. Rorabacher, *Inorg. Chem.*, **11**, 1496 (1972).

bipyridine exhibits no increase in rate in such media,[10a] it is reasonable to assume with Shu and Rorabacher[35] that the behavior of this ligand is complicated by steric factors. We conclude that in alcohol-water mixtures the composition of the inner sphere, the steric requirements of the ligand, and the structure of the solvent all play a significant role.

Registry No. Ni, 7440-02-0; water, 7732-18-5; methanol, 67-56-1; ethylene glycol, 107-21-1; acetonitrile, 75-05-8; pyridine, 110-86-1; bipyridine, 366-18-7; terpyridine, 1148-79-4; phenanthroline, 66-71-7; dimethyl sulfoxide, 75-18-3.

Contribution from the Department of Inorganic and Physical Chemistry,
Indian Institute of Science, Bangalore-12, India

Ambidentate Coordination of Isonitrosoacetylacetone Imines in Their Nickel(II) and Palladium(II) Complexes[1]

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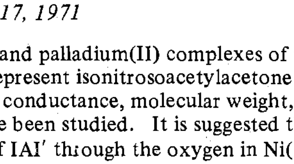
Nickel(II) and palladium(II) complexes of the types Ni(R–IAI)(IAI′), Pd(IAI)(IAI′), and $Pd(R–IAI)_2$, where IAI and IAI′ represent isonitrosoacetylacetone imine and R–IAI represents its *N*-alkyl derivative, have been prepared. The molar conductance, molecular weight, magnetic moment, and ir, pmr, and electronic spectra of these complexes have been studied. It is suggested that the isonitroso group of R–IAI coordinates through the nitrogen and that of IAI′ through the oxygen in Ni(R–IAI)(IAI′). In $Pd(R–IAI)_2$ the isonitroso groups of both ligands coordinate through nitrogen while Pd(IAI)(IAI′) has a structure similar to that of Ni(R–IAI)(IAI′). The amine-exchange reactions of nickel(II) and palladium(II) complexes are discussed and compared on the basis of their structures.

Introduction

Isonitrosoacetylacetone imine (HIAI, 4-imino-2,3-pentanedione 3-oxime) is expected to behave as a versatile ambidentate ligand as it has four donor atoms of which only two can bond to a single metal ion. Bis(isonitrosoacetylacetone imino)metal(II) (metal = Ni or Pd) has been prepared by different methods[2] and different structures have been assigned to these complexes.[2-4] The present paper deals with the preparation and structural characterization of a series of nickel(II) and palladium(II) complexes with isonitrosoacetylacetone imine and its *N*-alkyl derivatives. When the present work on nickel(II) complexes was completed, Lacey, *et al.*,[5] proposed structure Ia for bis(isonitrosoacetylacetone imino)nickel(II). In this structure, IAI represents isonitrosoacetylacetone imine with an N-coordinated isonitroso group and IAI′ that with an O-coordinated isonitroso group.



I

Ia, M = Ni, R = H
b, M = Ni, R = alkyl group
c, M = Pd, R = H

Experimental Section

Materials Used. Isonitrosoacetylacetone was prepared by the method of Wolff, *et al.*,[6] and crystallized from cyclohexane. Bis(isonitrosoacetylacetone imino)nickel(II) was prepared by the procedure described by Taylor and Ewbank[2a] and crystallized from a 1:1 mixture of chloroform and ethanol. Except benzylamine, *n*-propylamine, and ethylenediamine, all other amines were aqueous solutions. Palladium chloride was obtained from Arora-Mathey Ltd., Calcutta. Chloroform, benzene, and acetone were Analar grade reagents.

Method and Apparatus. Molecular weights of the complexes were determined in benzene by the freezing point method. Conductivity measurements were carried out in acetone using a Siemen's conductivity bridge. The magnetic susceptibilities of the nickel(II) complexes were determined at room temperature by the Gouy method using $Hg[Co(NCS)_4]$ as a calibrant. Infrared spectra of the complexes in Nujol mull and in chloroform were recorded on a Carl-Zeiss UR-10 spectrophotometer fitted with LiF, NaCl, and KBr prisms. The electronic spectra of the complexes in chloroform solution were recorded on a Unicam 700 A recording spectrophotometer. The proton magnetic resonance spectra of the complexes in $CDCl_3$ were recorded on a Varian HA-100 spectrometer, using precalibrated paper and tetramethylsilane as the internal standard.

Preparation of the Complexes. (1) (*N*-Methylisonitrosoacetylacetone imino)(isonitrosoacetylacetone imino)nickel(II), Ni(Me-IAI)(IAI′). Methylamine (5 ml, 33% solution, ~0.05 mol) was added to a suspension of Ni(IAI)(IAI′) (2 g, ~0.0065 mol) in a mixture of 70 ml of alcohol and 50 ml of chloroform and refluxed over a water bath for 1 hr, when the suspension dissolved. The solution was cooled and filtered, and the filtrate was evaporated under vacuum to a small volume (10–15 ml), when crystals were obtained. The crystals were filtered off, washed with small amounts of alcohol, and recrystallized from alcohol; yield 83%.

(2) (*N*-Ethylisonitrosoacetylacetone imino)(isonitrosoacetylacetone imino)nickel(II), Ni(Et–IAI)(IAI′). Ethylamine (5 ml, 50% solution, ~0.05 mol) and Ni(IAI)(IAI′) (2 g, ~0.0065 mol) in a mixture of 70 ml of alcohol and 50 ml of chloroform were refluxed over a water bath for 5 hr. The rest of the procedure was the same as in section (1). The complex was recrystallized from alcohol; yield 72%.

(3) (*N*-*n*-Propylisonitrosoacetylacetone imino)(isonitrosoacetylacetone imino)nickel(II), Ni(*n*-Pr–IAI)(IAI′). *n*-Propylamine (5 ml, ~0.061 mol) and Ni(IAI)(IAI′) (2 g, ~0.0065 mol) in a

(1) Part of the work dealing with nickel(II) complexes has been abstracted from the Ph.D. thesis of K. S. B., Indian Institute of Science, 1970.

(2) (a) T. W. J. Taylor and E. K. Ewbank, *J. Chem. Soc.*, 2818 (1926); (b) C. Djordjevic, J. Lewis, and R. S. Nyholm, *ibid.*, 4778 (1962).

(3) A. V. Ablov and V. N. Zubarev, *Russ. J. Inorg. Chem.*, 13, 1563 (1968).

(4) K. G. Das, D. N. Sen, and N. Thankarajan, *Tetrahedron Lett.*, 869 (1968).

(5) M. J. Lacey, C. G. Macdonald, J. S. Shannon, and P. J. Collins, *Aust. J. Chem.*, **23**, 2279 (1970).

(6) L. Wolff, P. Bock, G. Lorentz, and P. Trappe, *Justus Liebigs Ann. Chem.*, **325**, 134 (1902).