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## Binary and Ternary Complex Formation of Nickel(II) in Methanol. Further Evidence for Outer-Sphere Stabilization and Other Factors Contributing to Ligand Substitution Kinetics in Nonaqueous Solvents

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The rate constants of the reactions NiS<sub>6</sub><sup>2+</sup> + Y and NiX<sub>n</sub><sup>+</sup> + Y in S = methanol at 25°C have been determined by stopped-flow measurements for X = chloride, bromide, iodide, and thiocyanate with Y = 4-phenylpyridine, 2,2'-bipyridine, 1,10-phenanthroline, and 2,2',2''-terpyridine. The presence of X in the inner sphere accelerates the reaction with Y by factors ranging from 60 for X = Cl with Y = 4-phenylpyridine to ca. 2 for X = Cl with Y = phenanthroline and for X = I with Y = bipyridine or terpyridine. Some of the results could be compared with those in acetonitrile; accelerating effects are smaller in methanol by factors that correlate well with the free energies of transfer of X<sup>-</sup> between the two solvents. Evidence is presented for extra stabilization of the outer-sphere complex of phenanthroline. The Fuoss equation for outer-sphere complexation holds for simple inorganic ligands but not for pyridine-type ligands. Probable factors contributing to ligand substitution kinetics in nonaqueous solvents are indicated.

In the preceding paper<sup>2</sup> we have summarized evidence for "extra" stabilization of the outer-sphere complexes of nickel(II) ion in acetonitrile as solvent with pyridine-type ligands, particularly phenanthrolines. The evidence comes from three sources: the abnormally high rate constants and low enthalpies of activation for reactions of phenanthrolines,<sup>3</sup> the kinetic effect of electron-withdrawing and electron-donating substituents in the 5 and 6 positions of 1,10-phenanthroline,<sup>3</sup> and the effect of anionic substituents in the inner coordination sphere of nickel(II).<sup>2</sup> The extra stabilization of the outer-sphere complexes is thought to arise from π-orbital and/or electrostatic interaction of ligand molecules present in the outer sphere with the polarized acetonitrile molecules of the inner sphere. It therefore would be useful to determine whether outer-sphere stabilization is limited to solvents in which such π-orbital interactions can occur. It also would be instructive to establish how the influence of anionic inner-sphere substituents in the aprotic solvent acetonitrile compares with that in a protic solvent in which competitive hydrogen bonding of the anions by the solvent occurs. We have chosen methanol for this purpose. Water is not suitable for such comparisons, because the complexes NiX<sup>+</sup> with simple anions as X<sup>-</sup> are too unstable in aqueous solution.<sup>2</sup> Furthermore, methanol and acetonitrile are nearly isodielectric and appear to have donor strengths toward nickel(II) ion that are not widely different, so that it may be possible to relate differences in inner-sphere effects of X in the two solvents to differences in solvation of X<sup>-</sup>.

We report here rate constants for the reactions of Ni<sup>2+</sup> and NiX<sup>+</sup> (for X = chloride, bromide, iodide, and thiocyanate) with Y = 4-phenylpyridine, 2,2'-bipyridine, 1,10-phenanthroline, and 2,2',2''-terpyridine in methanol as solvent and compare some of the results with corresponding data for acetonitrile. We also examine other evidence indicating which factors contribute to the wide spectrum of kinetic behavior observed so far in nonaqueous solvents.

### Experimental Section

The complex ions NiX<sup>+</sup> were generated in situ by addition of MX to an excess of nickel(II) perchlorate monohydrate in methanol as solvent, where M was Et<sub>4</sub>N for X = Cl with Y = phenanthroline; in all other cases M was Na. Absolute methanol (Baker Analyzed reagent) was used without further purification after it was established that it gave the same results as methanol distilled from magnesium metal. The water content, measured with a Photovolt Aquatest II Karl Fischer titrator, was 8 × 10<sup>-3</sup> M. Kinetic measurements generally were made at the wavelengths of maximum absorption of the complexes, which are similar to those in acetonitrile,<sup>4</sup> except that reactions with phenanthroline were monitored at 292 nm where there is a greater difference between the absorbances of the complex and the free ligand. Experimental problems were less severe than in acetonitrile.<sup>2</sup> In particular, unlike in acetonitrile, reaction rates of NiX<sup>+</sup> were sufficiently low to allow the use of a range of concentrations of NiX<sup>+</sup> adequately high to ensure pseudo-first-order conditions with respect to NiX<sup>+</sup> (as well as Ni<sup>2+</sup>). Typically, solutions after mixing contained total (analytical) concentrations of Ni and X in the ranges (2–10) × 10<sup>-3</sup> and (2.5–7.5) × 10<sup>-4</sup> M, respectively, with that of Y held constant at 2.5 × 10<sup>-5</sup> M. Consequently, the limiting eq 13 of

Table I. Comparison of Rate Constants for Ligand Substitution at Nickel(II) Ion with That for Solvent Exchange in Methanol at 25°C

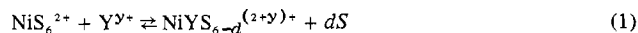
Ligand, Y	$I^a$	$\log k_1^b$	$\log R^c$
4-Phenylpyridine <sup>d</sup>	<0.06	2.1	-0.5
Bipyridine <sup>d</sup>	<0.03	2.0	-0.6
Bipyridine <sup>e</sup>	0.200	2.1 <sub>5</sub>	-0.4
	0.100	2.0 <sub>8</sub>	-0.5
	0.060	2.0 <sub>0</sub>	-0.6
Phenanthroline <sup>d</sup>	<0.03	2.8	+0.2
Terpyridine <sup>d</sup>	<0.03	1.6	-1.0
Thiocyanate <sup>e</sup>	0.300	3.6 <sub>5</sub>	+0.1
	0.100	3.8 <sub>7</sub>	0
	0.050	4.0 <sub>3</sub>	0
Thiocyanate <sup>f</sup>	0	5.2 <sup>g</sup>	+0.1
NiSCN <sup>+</sup> → Ni(SCN) <sub>2</sub>	0	5.1 <sup>g</sup>	<i>h</i>
Selenocyanate <sup>e</sup>	0.100	3.7 <sub>2</sub>	-0.2
Maleonitrile dithiolate <sup>e</sup>	0.100	5.3 <sub>0</sub>	+0.3
Dithiooxalate <sup>e</sup>	0.100	5.4 <sub>0</sub>	+0.4
	0.050	5.7 <sub>3</sub>	+0.1

<sup>a</sup> Ionic strength, *M*. <sup>b</sup> Rate constant for ligand substitution resulting in formation of 1:1 complex (except where noted otherwise), in  $M^{-1} \text{ sec}^{-1}$ . <sup>c</sup> See eq 2 and ref 2. Value of  $\log k_s$  used is 3.0, from ref 5; values of  $K_{12}$  were calculated from eq 3 in ref 2, with  $a = 6 \text{ \AA}$ . <sup>d</sup> This work; for experimental details, see Table II, footnote b. <sup>e</sup> From ref 6. <sup>f</sup> From ref 7. <sup>g</sup> Rate constant for dissociation of complex also determined; for 1:1 and 1:2 complexes, values are  $3 \times 10^{-1}$  and  $1 \times 10^2 \text{ sec}^{-1}$ , respectively. <sup>h</sup> Value of  $k_s$  is not available; however, the accelerating effect of coordinated thiocyanate is illustrated by the fact that  $\log k_{23} = 4.1$ , as compared to 3.0 for the formation of the 1:1 complex.

ref 2 applied and any possible rapid regeneration of NiX<sup>+</sup> from NiXY<sup>+</sup>, as discussed in ref 2, would have been irrelevant.

## Results and Discussion

**Binary Complex Formation in Methanol.** Rate constants for the overall substitution reaction



for a variety of ligands with charge numbers  $\gamma = 0, 1-,$  and  $2-$  and dentate numbers  $d = 1, 2,$  and  $3$  in  $\text{S} = \text{methanol}$  are listed in Table I. Also given are values of the dimensionless ratio  $R$  given by

$$R = (4/3)k_1/K_{12}k_s \quad (2)$$

where  $k_1$  and  $k_s$  are the rate constants for ligand substitution and solvent exchange, respectively, and  $K_{12}$  is the equilibrium constant of the outer-sphere complex postulated as a steady-state intermediate in an  $I_d$  pathway.<sup>2</sup> The parameter  $R$  should have a value near unity if the substitution mechanism follows an  $I_d$  pathway in which the rate-determining step is solvent exchange and if specific interactions between the inner and outer spheres do not occur.

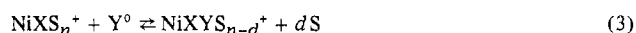
For the majority of the entries in Table I, including those for ligands of different charge type and solutions of different ionic strength,  $R$  indeed is not very different from unity. With the exceptions of phenanthroline and terpyridine, there is little sign of ligand specificity, and this provides compelling evidence against a D (limiting  $S_N1$ ) mechanism. The more detailed data presented here generally support the conclusions reached by Pearson and Ellgen in 1967.<sup>6</sup> Predominantly similar behavior was observed in several other ligand substitution reactions in methanol, viz., by Hoffmann et al. in the reactions of manganese(II), iron(II), and cobalt(II) ions with chloride ion and of magnesium ion with trifluoroacetate ion,<sup>8</sup> and by Petrucci et al. in the reaction of copper(II) ion with perchlorate ion.<sup>9</sup>

We will defer until later in our discussion consideration of the significantly fast reaction of nickel(II) ion with phenanthroline, other than to note here that it is slowed down markedly in the presence of sodium ion. This behavior is

similar to that observed by Sanduja and Smith in *ethanol* and for which association of phenanthroline with sodium ion was suggested as a possible cause.<sup>10</sup> We found that, in methanol, the value of  $\log k_1$  decreases from 2.87 to 2.70 when 0.2 *M* sodium perchlorate is added. The latter value is significantly higher than that (2.54) found by Pearson and Ellgen<sup>6</sup> under the same conditions. We are unable to account for the discrepancy. As a cross-check on our reactants, we repeated Sanduja and Smith's measurements in ethanol<sup>10</sup> and found  $\log k_1 = 3.56$ , in reasonable agreement with their value of 3.49. The effect of added water (in relatively low concentrations) was modest; e.g., with 0.2 *M* sodium perchlorate present, 0.3 *M* water increased the rate by a factor of only 1.3. The effect of water was very similar to that observed by Pearson and Ellgen<sup>6</sup> and Bennetto and Caldin<sup>11</sup> for bipyridine as ligand.

The relatively slow reaction of nickel(II) ion with terpyridine is an example of a rapidly expanding class of reactions in which certain multidentate ligands experience some sort of steric inhibition of reactivity, possibly during first-bond formation<sup>12,13</sup> and/or during ring closure.<sup>4,12</sup> Examples are the reactions of manganese(II) ion with terpyridine<sup>12</sup> and of several metal ions with *m*-benzenedisulfonate ion<sup>14</sup> in methanol, and particularly those of nickel(II) ion with bipyridine, phenanthroline, and terpyridine in dimethyl sulfoxide.<sup>4</sup>

**Ternary Complex Formation in Methanol.** In Table II, rate constants are given for the overall substitution reaction



for  $\text{X} = \text{Cl}, \text{Br}, \text{I},$  and  $\text{SCN}$  with various uncharged ligands  $\text{Y}$  in  $\text{S} = \text{methanol}$ . Table II also gives a comparison with corresponding data in  $\text{S} = \text{acetonitrile}$ .<sup>2</sup> As in acetonitrile, the presence of  $\text{X}$  in the inner sphere accelerates the reaction with  $\text{Y}$ , but to a much smaller degree than in acetonitrile. The major factor responsible for this difference is that the Ni-X bond is stronger in acetonitrile than in methanol because the former solvent competes less for  $\text{X}$ , so that bound  $\text{X}$  reduces the effective positive charge on nickel and thereby stabilizes  $\text{S}$  in  $\text{NiXS}_n^+$ , to a greater extent in acetonitrile than in methanol. Furthermore, preferential solvation of bound  $\text{X}$  by methanol would be expected to parallel that of free  $\text{X}^-$  and to be greatest for "hard" anions, which are good hydrogen-bond acceptors. Preferential solvation of free  $\text{X}^-$  by methanol is given by the free energies of transfer from methanol to acetonitrile:<sup>15</sup> chloride (5.7 kcal mol<sup>-1</sup>) > bromide (4.9) > iodide (2.9), becoming less significant for the "soft" anion thiocyanate (1.6). It is noteworthy that the values of  $N_{\text{AN}}/N_{\text{M}}$  in Table II follow this same order.

**Factors Contributing to Ligand Substitution Kinetics in Methanol and Other Solvents.** We have attributed the accelerating influence of anionic inner-sphere substituents in acetonitrile to the net effect of two opposing factors: solvent labilization and outer-sphere destabilization.<sup>2</sup> It will now be shown that both factors are important in methanol as well.

There is evidence for enhanced stability of certain outer-sphere complexes,  $\text{MS}_6^{2+}\text{Y}$ , particularly those of  $\text{Y} = \text{phenanthroline}$ , in methanol. In Table III, rate constants for substitution by phenanthroline, bipyridine, and terpyridine in various solvents are compared with "norms" available for unperturbed  $I_d$  substitution: the rate constant for solvent exchange and that for substitution by 4-phenylpyridine, a ligand which exhibits reasonably "normal" behavior in several solvents. More thorough comparisons will be possible when all activation parameters become available, provided the gross uncertainties in the values for solvent exchange<sup>3,4,11</sup> can be resolved. Guided by previous findings in acetonitrile<sup>3</sup> and dimethyl sulfoxide,<sup>4</sup> which represent the two extremes in solvent effects uncovered so far, we will assume as a working hypothesis that in all four solvents listed in Table III the rate constants for the multidentate ligands may reflect the *net effect*

Table II. Accelerating Effect of Anionic Inner-Sphere Substituents (X) on Rates of Reactions of Nickel(II) with Various Incoming Ligands (Y) in Methanol at 25°C and Comparison with Corresponding Data for Acetonitrile

Y	X	Methanol			Acetonitrile <sup>a</sup>			
		log $k_{Ni}$ <sup>b</sup>	log $k_{NiX}$ <sup>c</sup>	log $N^d$	log $k_{Ni}$	log $k_{NiX}$	log $N^d$	log ( $N_{AN}/N_M$ )
4-Phenylpyridine	Cl	2.1	3.9	1.8				
	Br		3.3	1.2				
	I		2.8	0.7				
	SCN		2.9	0.8				
Bipyridine	Cl	2.0	3.1	1.1	3.61	6.3	2.7	1.6
	Br		2.5	0.5				
	I		2.3	0.3				
	SCN		3.0	1.0				
Phenanthroline	Cl	2.8	3.1	0.3	4.70	6.6	1.9	1.6
	Terpyridine	1.6	2.8	1.2	3.38	6.3	2.9	1.7
Terpyridine	Br		2.2	0.6		5.7	2.3	1.7
	I		1.8	0.2		4.8	1.4	1.2
	SCN		2.8	1.2		5.5	2.1	0.9
	NO <sub>3</sub>					4.4	1.0	

<sup>a</sup> Data from ref 2. <sup>b</sup> Measured at  $C_Y = 2.5 \times 10^{-5} M$  and several values of  $C_{Ni}$  in the range of  $(1-4) \times 10^{-2} M$  for Y = 4-phenylpyridine (which forms a weak complex) and of  $(2-10) \times 10^{-3} M$  for the other incoming ligands. Values obtained in the absence and in the presence of X were in close agreement, the largest discrepancy occurring with Y = bipyridine for which values were 1.9, and 2.0, respectively. <sup>c</sup> Measured at several  $C_{Ni}$  values in the ranges given above, with  $C_{MX} = 2.5, 5.0,$  and  $7.5 \times 10^{-4} M$ , and  $C_Y = 2.5 \times 10^{-5} M$ ; M is Na, except for Y = phenanthroline, where it is  $(C_2H_5)_4N$  (see text). <sup>d</sup>  $N = k_{NiX}/k_{Ni}$ .

Table III. Comparison of Rate Constants for Substitution by Phenanthroline, Bipyridine, and Terpyridine in Various Solvents with Rate Constants for Solvent Exchange and for Substitution by 4-Phenylpyridine<sup>a</sup>

Ligand	Water <sup>b</sup>	Methanol		Dimethyl sulfoxide <sup>e</sup>	Acetonitrile <sup>f</sup>
		Ni <sup>c</sup>	Mn <sup>d</sup>		
4-Phenylpyridine	3.6, <sup>g</sup> -0.3 <sup>g</sup>	2.1, -0.5		3.2, -0.5	3.0, -0.3
Phenanthroline	3.5, -0.4	2.8, +0.2	5.0, -0.1	2.6, -1.1	4.7, +1.4
Bipyridine	3.2, -0.7	2.0, -0.6	4.2, -0.9	1.8, -1.9	3.6, +0.3
Terpyridine	3.1, -0.8	1.6, -1.0	3.7, -1.4	1.4, -2.3	3.3, 0.0

<sup>a</sup> All data refer to substitution at the nickel(II) ion, except those in column 4 which are for the manganese(II) ion. For each ligand-solvent combination, the first entry represents log  $k_1$  while the second is log  $R$ , where  $R = (4/3)k_1/K_{12}k_s$ ; see text. Temperature is 25°C. <sup>b</sup> From ref 16. <sup>c</sup> This work. <sup>d</sup> From ref 12. <sup>e</sup> From ref 4 and 17. <sup>f</sup> From ref 3. <sup>g</sup> Ligand is pyridine.

of two opposing factors: enhanced stabilization of outer-sphere complexes and steric inhibition of coordination. In all cases, the order of rate constants is phenanthroline > bipyridine > terpyridine, covering a range of  $10^{0.4}$  in water and  $10^{1.3 \pm 0.1}$  in all three nonaqueous solvents. For the multidentate ligands in dimethyl sulfoxide, rate constants are so low that steric inhibition of coordination appears to be the dominant effect. For bipyridine and terpyridine, such inhibition may involve both first- and subsequent-bond formation, while for the rigid phenanthroline molecule it probably results from the requirement that the two donor atoms must coordinate essentially simultaneously. However, even for dimethyl sulfoxide, some degree of enhanced stabilization of the outer-sphere complexes, particularly that of phenanthroline, cannot be ruled out. For methanol, the rate constants for the reactions of both nickel(II) and manganese(II) ions with bipyridine and especially terpyridine also are low and indicative of inhibition of coordination. The trend in the rate constants for these two ligands and phenanthroline is very similar in dimethyl sulfoxide and methanol. Hence, it seems likely that, also in methanol, phenanthroline must experience at least some degree of inhibition of coordination, in the absence of which its already high rate constants would have been even higher. We conclude that, in methanol as solvent, the outer-sphere complexes of nickel(II) and manganese(II) ions with phenanthroline in particular possess stabilities greater than those predicted by the Fuoss relationship (eq 3 of ref 2).

This conclusion is supported by two additional lines of evidence. First, Table II shows that in methanol, as in acetonitrile, the accelerating effect of X = Cl is much smaller for Y = phenanthroline than for the other incoming ligands. The general order of decreasing acceleration produced by a given X in methanol is 4-phenylpyridine > bipyridine, terpyridine >> phenanthroline; this is the same as the order of increasing stability of the outer-sphere complexes,  $NiS_6^{2+}Y$ , deduced from other considerations for S = acetonitrile.<sup>3</sup> In other words, introduction of X into the inner sphere has the greatest destabilizing effect on the most stable outer-sphere complexes, which is what would be expected on the basis of our simple polarization model for outer-sphere complexation.<sup>3</sup> Second, for the case of X = Cl, NMR data for solvent exchange are available,<sup>18</sup> so that our conclusions can be tested further. While introduction of X into the inner sphere accelerates solvent exchange by a factor of 200, it accelerates the reactions with Y = 4-phenylpyridine, bipyridine, terpyridine, and phenanthroline by factors of only 60, 13, 16, and 2, respectively, numbers that are consistent with a decrease in the equilibrium constant for outer-sphere complexation by factors of 3, 15, 13, and 100, respectively.

There is, therefore, considerable evidence that the Fuoss relationship (eq 3 in ref 2), which accounts well for the rate constants of simple inorganic and nonaromatic organic ligands (Table I), cannot predict the kinetics of pyridine-type ligands, except when a fortuitous cancellation of errors occurs, as with phenanthroline. If the reaction follows an I<sub>d</sub> pathway and if, for multidentate ligands, ring closure is rapid, the following relationship should apply<sup>2</sup>

$$k_1/k_s = fK_{12} \quad (4)$$

In Table IV, experimental results are compared with the predictions of eq 4 for a value of the statistical factor  $f$  of  $3/4$ . It may be entirely reasonable to reconcile the predicted value of  $k_1/k_s$  with the experimental value for the reaction of  $Ni^{2+}$  with 4-phenylpyridine by choosing instead  $f = 1/4$ , but for the reaction of  $NiCl^+$  with the same ligand, one then either would have to choose  $f = 1/12$ , which is equivalent to suggesting that bond formation is inhibited by serious steric problems, or else would have to reject the predicted value of  $K_{12}$ . The values of  $k_1/k_s$  for  $NiCl^+$  reflect the inhibition of multiple-bond formation much more clearly than do the corresponding values for  $Ni^{2+}$  which include contributions from inner-sphere-outer-sphere interactions and therefore are more complex quantities than the Fuoss treatment is intended to represent.

Table IV. Experimental Values of the Ratio  $k_1/k_s$  for the Reactions of  $\text{NiS}_6^{2+}$  and  $\text{NiClS}_5^+$  with Various Incoming Ligands Y in S = Methanol at 25°C

Y	log ( $k_1/k_s$ )	
	$\text{NiS}_6^{2+}$	$\text{NiClS}_5^+$
4-Phenylpyridine	-0.9	-1.4
Phenanthroline	-0.2	-2.2
Bipyridine	-1.0	-2.1
Terpyridine	-1.4	-2.5
All Y <sup>a</sup>	-0.4	-0.4

<sup>a</sup> Value predicted by eq 3 of ref 2 for the following conditions: solvent exchange is rate limiting and no interaction occurs between the inner and outer coordination spheres.

The conclusions reached here have implications for the general theory of ligand substitution kinetics proposed by Benetto and Caldin<sup>11,19</sup> to account for correlations observed between the kinetic parameters ( $k_1/k_s$ ) and ( $\Delta H^\ddagger_1 - \Delta H^\ddagger_s$ ) on the one hand and quantities related to solvent structure, such as its enthalpy of vaporization and its fluidity, on the other. The correlations involved eight solvents, including water, methanol, dimethyl sulfoxide, and acetonitrile, but were restricted to bipyridine (mainly) and terpyridine, and, subsequently,<sup>20</sup> to the bidentate ligand pyridine-2-azo-*p*-dimethylaniline. In order to account for the proposed influence of solvent structure, an elegant theory was developed in which passage of a solvent molecule from the disordered region surrounding the solvation sphere into the bulk solvent is thought to contribute to the kinetics to the extent that the ligand modifies local solvent structure. We have given a preliminary critique of the theory elsewhere.<sup>4</sup> As a probe into the solvent dependence of ligand substitution kinetics, a ligand such as bipyridine presents serious complications, such as its severe steric requirements, both in first-bond formation<sup>13</sup> and in ring closure,<sup>4,12</sup> and its polarity and aromatic character. It has been found subsequently that simple inorganic ligands, and even unidentate ligands such as pyridine or 4-phenylpyridine, show little correlation with solvent structure,<sup>3,4,21,22</sup> but the unidentate (not the multidentate) ligands do show a correlation with the ligand strength of the solvent.<sup>22</sup> Furthermore, it was recently shown by Langford that solvent exchange is insensitive to bulk solvent structure when the entering group, leaving group, and nonlabile ligands all are kept invariant.<sup>23</sup> This led Langford to suggest that Benetto and Caldin's correlations

apply to the outer-sphere complexation step. However, the evidence presented in this paper has shown that other factors also must be considered. The observed correlations reflect the complex interplay of such factors as the size and ligand strength of solvent molecules present in the inner sphere, the structure of the solvent in the outer sphere and in the bulk medium, and the steric requirements, polarity, and aromaticity of the ligand, various combinations of which affect outer-sphere complexation, first-bond formation, and ring closure.

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**Registry No.**  $\text{Ni}(\text{MeOH})_6^{2+}$ , 18443-63-5;  $\text{NiCl}(\text{MeOH})_5^+$ , 24445-82-7;  $\text{NiBr}(\text{MeOH})_5^+$ , 25999-77-3;  $\text{NiI}(\text{MeOH})_5^+$ , 25999-78-4;  $\text{Ni}(\text{SCN})(\text{MeOH})_5^+$ , 41119-86-2; 4-phenylpyridine, 939-23-1; 2,2'-bipyridine, 366-18-7; 1,10-phenanthroline, 66-71-7; 2,2',2''-terpyridine, 1148-79-4.

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## N-Alkylation of Macrocyclic Secondary Amine Complexes of Nickel(II)

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The utility of deprotonation-alkylation reaction sequences in macrocyclic amine-nickel complexes for the synthesis of new *N*-alkyl complexes is outlined. Extensive use is made of DMSO as solvent with KOH and  $\text{CH}_3\text{S}(\text{O})\text{CH}_2\text{Na}$  as bases in these reactions. Special consideration is given to stereochemical aspects of the synthetic method. Fast proton transfer between acid and conjugate base strongly affects the stereoselectivity of the alkylation reactions in certain cases. Because of the strongly basic nature of the amide species produced in the deprotonation reaction only alkylating agents without  $\beta$  hydrogens have been studied. Chemical reactions of the new complexes are described; these include both metal and ligand oxidation and ligand protonation. The kinetic stability of the *N*-alkylated complexes increases with increased *N*-substitution. Spectral studies suggest that the ligand field strength steadily decreases for a given ligand system as the number of *N*-alkyl groups is increased.

### Introduction

Although macrocyclic amine ligands and their metal complexes have been the subject of extensive investigation over the past 14 years, only recently have these ligands incorporated tertiary amine donors. As a part of our study of the redox

chemistry of Ni(III) complexes of macrocyclic amine ligands we required a complex of a saturated ligand without amine protons.<sup>1</sup> Only a few examples of macrocyclic ligands with tertiary donors were known when we began our investigation.<sup>2</sup> None of these met our needs, either because the chelate ring