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Influence of Anionic Inner-Sphere Substituents on the Kinetics of Ternary Complex Formation of Nickel(II) in Acetonitrile as Solvent. Opposing Effects of Solvent Labilization and Outer-Sphere Destabilization[1]

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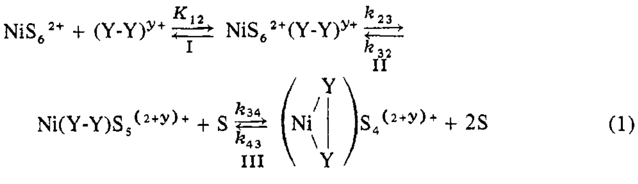
The ratio N of the rate constants of the two reactions (A) $NiXS_n^+ + Y$ and (B) $NiS_6^{2+} + Y$ in S = acetonitrile has been determined by stopped-flow measurements for X = chloride, bromide, iodide, thiocyanate, and nitrate, with Y = 2,2',2''-terpyridine and (in the case of X = chloride) with 2,2'-bipyridine and 1,10-phenanthroline as well. The inner-sphere substituents X all produce substantial accelerating effects, the value of N with Y = terpyridine at 25° varying from 10 for nitrate to 800 for chloride. With Y = phenanthroline, the accelerating effect of chloride is much smaller ($N = 80$). As shown before, the rate of reaction B is notably sensitive to the nature of Y, and, particulary with Y = phenanthroline, it is much higher than predicted by the value of the outer-sphere equilibrium constant calculated from electrostatics. We have attributed this fact to "extra" stabilization of the outer-sphere complex by interaction of the ligand with the polarized acetonitrile molecules of NiS_6^{2+}. This view is now supported by the fact that the rate of reaction A is much less sensitive to the nature of Y than is the case for reaction B, which is consistent with the weaker polarization of S in $NiXS_n^+$ than in NiS_6^{2+}. Consequently, the accelerating influence of anionic inner-sphere substituents is attributed to the net effect of solvent labilization and outer-sphere destabilization.

The reactions of nickel(II) ion with many (not all) ligands in aqueous as well as nonaqueous solutions are consistent with a dissociative interchange (I$_d$) mechanism in which solvent exchange constitutes the rate-determining step. The details of the reaction scheme may be illustrated as in eq 1 for the



$$NiS_6{}^{2+} + (Y\text{-}Y)^{y+} \underset{I}{\overset{K_{12}}{\rightleftarrows}} NiS_6{}^{2+}(Y\text{-}Y)^{y+} \underset{\underset{II}{k_{32}}}{\overset{k_{23}}{\rightleftarrows}}$$

$$Ni(Y\text{-}Y)S_5{}^{(2+y)+} + S \underset{\underset{III}{k_{43}}}{\overset{k_{34}}{\rightleftarrows}} \left(Ni\begin{matrix}Y\\ |\\ Y\end{matrix}\right)S_4{}^{(2+y)+} + 2S \qquad (1)$$

case of a bidentate ligand $(Y\text{-}Y)^{y+}$ in a solvent S. Process I (outer-sphere complexation) is diffusion controlled and therefore rapid, and process III (ring closure) usually, but not always, is also rapid. Hence, process II (solvent exchange) represents the rate-determining step. Usually the concentration of the outer-sphere complex is small as compared to that of free ligand, in which case the observed rate constant for ligand substitution, k_l, is given by the relation[2] $k_l = K_{12}k_{23}$. Evidence in support of this reaction scheme has been summarized for water,[2] dimethyl sulfoxide,[3-7] acetonitrile,[4,8,9] and several other solvents.[4] Such evidence comes mainly from a comparison of rate constants and activation parameters for ligand substitution with the corresponding quantities for solvent exchange. For example, k_{23} should be related to the rate constant for solvent exchange, k_s, through a statistical factor f representing the probability that the ligand will occupy a particular coordination site vacated by a solvent molecule, so that $k_{23} = fk_s$. It is convenient to consider a dimensionless ratio R given by

$$R = k_l/K_{12}fk_s \qquad (2)$$

which should have a value near unity if the I$_d$ mechanism applies. For the statistical factor f a value of $^3/_4$ has been proposed.[10] The equilibrium constant for the outer-sphere complex, K_{12}, usuallly cannot be evaluated experimentally and must be estimated through the theoretical relationship from electrostatics[11,12]

$$K_{12} = \frac{4\pi N a_1{}^3}{3 \times 10^3} e^{-U a_2/kT} \qquad (3a)$$

where

$$U(a_2) = \frac{z_1 z_2 e^2}{\epsilon a_2} - \frac{z_1 z_2 e^2 \kappa}{\epsilon(1 + \kappa a_2)} \qquad (3b)$$

Here, a_1 represents the center-to-center distance of closest approach of the solvated metal ion and the *reaction site* on the ligand, a_2 is the corresponding distance between the two *charge sites* for the case of a charged ligand, and κ is the Debye–Hückel function of the ionic strength, I, given by

$$\kappa^2 = 8 \times 10^{-3}\pi N^2 e^2(\epsilon RT)^{-1}I^{1/2} \qquad (3c)$$

where ϵ is the dielectric constant of the medium. Other symbols have their customary meaning. Uncertainties in the application of eq 3 have been discussed.[12] Of particular significance to the results presented in this and the next paper is the fact that the equation cannot apply if specific interactions occur between the inner and outer coordination spheres.

It has been found that in *aqueous solution* reactions of nickel(II) with a number of incoming ligands Y^{y+} are influenced to varying degrees by ligands X^{x+} already present in the inner coordination sphere of nickel. (For simplicity, dentate numbers of Y and X are omitted henceforth.) We shall be concerned with a comparison of the rate-determining steps

$$NiS_6{}^{2+}Y^{y+} \underset{}{\overset{k_{23}}{\rightleftarrows}} NiYS_5{}^{(2+y)+} + S \tag{4}$$

$$NiXS_n{}^{(2+x)+}Y^{y+} \overset{k_{23}}{\rightleftarrows} NiXYS_{n-1}{}^{(2+x+y)+} + S \tag{5}$$

For aqueous solutions, the surprising result emerges that, while the ratio *N* of the observed overall rate constant $k_l = K_{12}k_{23}$ of the species $NiXS_n{}^{(2+x)+}$ to that of $NiS_6{}^{2+}$ does depend on the nature and number of nitrogen donor atoms in X, it is not very sensitive to the charge numbers *x* and *y*. With ligands such as 2,2'-bipyridine, 1,10-phenanthroline, and 2,2',2''-terpyridine as X, the value of *N* generally is not much greater than unity. Results obtained with such ligands have been reviewed recently by Wilkins[2] and by Gutmann.[13] However, with a variety of aliphatic polyamines, particularly with tris(2-aminoethyl)amine, as X, a marked acceleration was obtained with Y = ammonia.[14] A parallel increase was observed in the water-exchange rate with X = ammonia or ethylenediamine and Y = S = water, increasing monotonically with the number of nitrogen atoms coordinated.[15] It appears that the increase in *N* must be the result of labilization of remaining coordinated water by X.

In a thorough investigation of the influence in aqueous solution of the charge numbers *x* and *y*, Hague and Kinley[16] measured rate constants and activation parameters for the formation and dissociation of ternary complexes NiXY, with X = polytriphosphate, iminodiacetate, nitrilotriacetate, ethylenediamine-*N*,*N'*-diacetate, diethylenetriamine, triethylenetetramine, and 2,2',2''-triaminotriethylamine and with Y = 5-nitrosalicylate dianion. Here also, the number of nitrogen donor atoms in X has a marked effect on *N* as well as on the activation parameters, but variation of the overall charge $(x + y)$ from 2+ to 3− has surprisingly little effect. The results were accounted for in terms of an I_d mechanism but with the important proviso that the *local* (rather than the overall) charge on nickel is considered, particularly in the calculation of the equilibrium constant K_{12} for the outer-sphere complex.

The influence of simple anionic ligands as X is quite modest. With the monoanion of 4-(2-pyridylazo)resorcinol as Y, the substitution rate increases in the order F^- ($<H_2O$) $<$ CH_3COO^- $<$ OH^- $<$ N_3^-, *N* varying from 0.6 for F^- to 6 for N_3^-.[17] This order of rates is also that of the electron-donor abilities of X and was logically attributed to labilization of remaining coordinated water.[13,17] There is also some direct evidence that such ligands actually labilize coordinated water. For example, the exchange rate of water at nickel(II) is 3 times higher in 7 *M* lithium chloride than in 6.5 *M* lithium perchlorate.[15,18]

We have reported elsewhere[6] the preliminary observation that the accelerating effect of halide ions is orders of magnitude greater in *acetonitrile* than in water. We now report detailed stopped-flow data for X = chloride, bromide, iodide, thiocyanate, and nitrate, with Y = 2,2',2''-terpyridine and (in the case of X = chloride) with 2,2'-bipyridine and 1,10-phenanthroline as well. Hoffmann has reported a similar accelerating effect with X = Y = nitrate, trifluoroacetate, and *p*-toluenesulfonate ions,[8] as well as thiocyanate ion.[20] Also, large increases in solvent-exchange rate have been observed by Lincoln and West[21] with ter- and quadridentate ligands as X. Complexes were found with nonequivalent exchange sites. For example, in the complex $NiXS_2{}^{2+}$ with X = 2,2',2''-triaminotriethylamine, one acetonitrile molecule exchanges about 100 times and the other 1000 times more rapidly than in $NiS_6{}^{2+}$. Apart from these examples, there is still a paucity of data on the influence of inner-sphere substituents on ternary complex formation in nonaqueous solvents.

Table I. Stepwise Equilibrium Constants for Formation of NiX^+ and NiX_2 Complexes in Various Solvents at 20°C

X	Solvent	log K_1	log K_2	Ref
SCN	Water	1.8		20
	Methanol	5.2	3.1	20
	Acetonitrile	5.5	4.3	20
	Dimethylformamide	3.9	2.4	20
	Dimethyl sulfoxide	3	1.5	20
Cl	Dimethyl sulfoxide	2.7		3
NO_3	Acetonitrile	4.4	3.1	8
ClO_4	Acetonitrile	1.6[a]		22, 23

[a] $T = 25°C$.

Experimental Section

The complex ions NiX^+ were generated in situ by addition of MX to an excess of nickel(II) perchlorate monohydrate in acetonitrile as solvent, where MX represents Et_4NCl, Et_4NBr, NaI, Bu_4NI, NaSCN, $LiNO_3$, Bu_4NNO_3, $Et_4NOOCCH_3$, and $Et_4NOOCC_6H_5$. Quaternary ammonium salts were Eastman White Label products. Kinetic measurements were made with a Durrum Instrument Co. stopped-flow spectrophotometer equipped with a Kel-F flow system. Reactions were monitored at the wavelengths of maximum absorption of the complexes NiY^{2+} reported elsewhere.[6] Most other experimental details were the same as described before;[6] those changes necessitated by the generally high reaction rates of NiX^+ are illustrated in the tables of experimental results.

Results and Discussion

In all cases measurements were made on solutions containing not only NiX^+ but also excess free nickel(II) ion in order to minimize possible problems due to incomplete conversion of X^- into NiX^+ and/or formation of NiX_2. Only a few equilibrium constants are available for these complexes in acetonitrile or any other solvent, and the values are given in Table I. In addition, for X = Cl in acetonitrile, $K_2/K_1 \approx 1$, but the individual values could not be determined.[24] From what is known about relative free energies of solvation of nickel(II) ion[6] and anions[25] in acetonitrile and dimethyl sulfoxide, we estimate $K_1 \approx 10^5$ for X = Cl in acetonitrile.

Since all solutions contained excess "free" nickel(II) ion, Y will react along two parallel pathways. Writing for simplicity only the overall reactions and omitting solvent molecules present in the inner sphere, these pathways may be represented as eq 6a and 6b. Our purpose is to compare the rate constants

$$\begin{tikzcd}
Ni^{2+} + X^- + Y \arrow[r, shift left, "k_{ab}"] \arrow[d, shift right, "k_{ac}"'] & NiY^{2+} + X^- \arrow[l, shift left, "k_{ba}"] \arrow[d, shift right, "k_{bd}"'] & (6a) \\
NiX^+ + Y \arrow[u, shift right, "k_{ca}"'] \arrow[r, shift left, "k_{cd}"] & NiXY^+ \arrow[l, shift left, "k_{dc}"] \arrow[u, shift right, "k_{db}"'] & (6b)
\end{tikzcd}$$

k_{ab} and k_{cd}. Values of log k_{ab} have been reported before[6] and vary from 2.9 to 4.7 for Y = pyridine and phenanthroline, respectively. Values of log k_{ac} and log k_{ca} are known for X = SCN and NO_3 only; these are log k_{ac} = 5.0 and 5.3 and log k_{ca} = −0.5 and +0.9 for SCN and NO_3, respectively.[8,20] It is likely that the presence of Y in the inner sphere will cause labilization of other substituents (S and X), so that $k_{bd} > k_{ac}$ and $k_{db} > k_{ca}$. Hence, it is likely that the two pathways are always in rapid equilibrium; anyway, under our experimental conditions (see Tables I–III) the equilibrium $Ni^{2+} + X^- \rightleftarrows NiX^+$ lies far to the right for X = SCN and NO_3, and probably for Cl, Br, and I as well.

Figure 1 shows that, for X = SCN and Y = terpyridine, the absorption spectrum of $NiXY^+$ is so similar to the sum of those of NiX^+ and NiY^{2+} that it was not feasible to measure the rate of the overall reaction

$$NiXY^+ + Ni^{2+}(\text{excess}) \rightleftarrows NiX^+ + NiY^{2+} \tag{6c}$$

We assumed that the same would be true for other combinations of X and Y. In all cases the sum of the concentrations of $NiXY^+$ and NiY^{2+} was monitored.

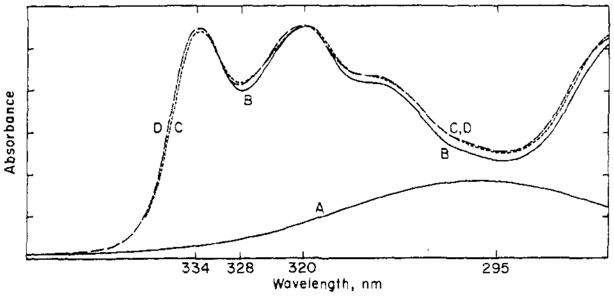


Figure 1. Ultraviolet spectra of nickel(II) complexes with X = SCN and Y = 2,2′,2″-terpyridine in acetonitrile at 25°C: A, 1.25×10^{-3} *M* NiX^+; B, 1.5×10^{-4} *M* NiY^{2+}; C, 1.5×10^{-4} *M* $NiXY^+$; D, 1.5×10^{-4} *M* $NiXY^+ + 3.0 \times 10^{-4}$ *M* Ni^{2+}. Absorbance for B, C, and D at 334 and 320 nm is 2.20 (path length 1 cm). Absorbance values: at 328 nm, A, 0.18; B, 1.61; C and D, 1.65; at 295 nm, A, 0.74; B, 0.92; C and D, 1.00. The spectra do not allow measurement of the rate of reaction 6c.

In a typical experiment, the total (analytical) concentrations of nickel, inner-sphere substituent (X), and incoming ligand (Y) were of the order of 10^{-3}, 10^{-4}, and 10^{-5} *M*, respectively. That of nickel will be related to concentrations at time zero and time *t* as in

$$C_{Ni} = [Ni^{2+}]_0 + [NiX^+]_0 = [Ni^{2+}]_t + [NiX^+]_t + [NiXY^+]_t + [NiY^{2+}]_t \qquad (7)$$

while those of X and Y will be given by the corresponding mole balances as in

$$C_X = [X^-]_0 + [NiX^+]_0 \approx [NiX^+]_0 = [NiX^+]_t + [NiXY^+]_t \qquad (8)$$

$$C_Y = [Y]_0 = [Y]_t + [NiY^{2+}]_t + [NiXY^+]_t \qquad (9)$$

In the general case, the rate of formation of NiY^{2+} plus $NiXY^+$ will be given by

$$dx/dt = k_{Ni}([Ni^{2+}]_0 - a - c)(C_Y - x) + k_{NiX}([NiX^+]_0 - b + c)(C_Y - x) \qquad (10)$$

where k_{Ni} and k_{NiX} now replace k_{ab} and k_{cd}, respectively, *x* is the total contration of NiY^{2+} and $NiXY^+$ produced at time *t*, *a* and *c* are the concentrations of Ni^{2+} consumed in reactions 6a and 6c, respectively, and *b* is that of NiX^+ consumed in reaction 6b. It follows that $x = a + b$. Only reduced forms of eq 10 will be considered. In all cases, $[Ni^{2+}]_0 \gg a + c$. Furthermore, for many systems given in Tables II and III, $k_{NiX}[NiX^+]_{0,t} \gg k_{Ni}[Ni^{2+}]_{0,t}$, so that $a \ll b \sim x$ and eq 10 becomes

$$dx/dt = \{k_{Ni}[Ni^{2+}]_0 + k_{NiX}([NiX^+]_0 - x + c)\}\{C_Y - x\} \qquad (11)$$

Two limiting cases will now be considered. If the rate of the overall reaction 6c is so low that $c \ll x$, then eq 11 reduces to

$$dx/dt = \{k_{Ni}[Ni^{2+}]_0 + k_{NiX}([NiX^+]_0 - x)\}\{C_Y - x\} \qquad (12)$$

On the other hand, if it is so high that $c \approx x$, it follows that

$$dx/dt = (k_{Ni}[Ni^{2+}]_0 + k_{NiX}[NiX^+]_0)(C_Y - x) \qquad (13)$$

Here, NiX^+ acts essentially as a catalyst present at virtually constant concentration during most of the reaction. Obviously, eq 13 also applies at sufficiently high values of $[NiX^+]_0$ so that pseudo-first-order conditions apply with respect to NiX^+ as well as Ni^{2+}.

Table II. Influence of Anions (X) on the Rate of Reaction of Nickel(II) with 2,2′,2″-Terpyridine (Y) in Acetonitrile at 25°C

X	10^5-C_X,[a] *M*	log k_{NiX} (apparent) (*k* in M^{-1} sec^{-1})	X	10^5-C_X,[a] *M*	log k_{NiX} (apparent) (*k* in M^{-1} sec^{-1})
Chloride	1.25	6.24	Thiocyanate	5.00	5.4
(Et_4NCl)	2.50	6.20	(NaSCN)	10.0	5.3
	5.00	6.13		20.0	5.15
	12.5	6.0		40.0	5.06
	25.0	5.9		10.0[c]	5.37
	2.50[b]	6.13		40.0[c]	5.10
	2.50[c]	6.15		10.0[f]	5.5 (?)
	2.50[d]	6.29		40.0[f]	5.12
Bromide	1.25	5.7	Nitrate	50.0	4.32
(Et_4NBr)	2.50	5.68	($LiNO_3$)	75.0	4.26
	5.00	5.63		25.0[c]	4.38
	8.5	5.65		50.0[c]	4.40
	10.0	5.65		75.0[c]	4.26
	20.0	5.5		25.0[d]	4.40
Iodide	5.00[e]	4.9		50.0[d]	4.34
(NaI or	10.0[e]	4.85		75.0[d]	4.23
Bu_4NI)	20.0[e]	4.86		25.0[f]	4.40
	20.0	4.84		50.0[f]	4.30
				75.0[f]	4.20
			Nitrate	25.0[c]	4.36
			(Bu_4NNO_3)	50.0[c]	4.34
				75.0[c]	4.38
				100.0[c]	4.40

[a] $C_Y = 2.5 \times 10^{-5}$ *M* in all cases; $C_{Ni} = 1.25 \times 10^{-3}$ *M* except where noted otherwise. [b] $C_{Ni} = 0.61 \times 10^{-3}$ *M*. [c] $C_{Ni} = 2.50 \times 10^{-3}$ *M*. [d] $C_{Ni} = 3.75 \times 10^{-3}$ *M*. [e] $C_{Ni} = 1.32 \times 10^{-3}$ *M*. [f] $C_{Ni} = 5.00 \times 10^{-3}$ *M*.

Table III. Influence of Chloride Ion (X) on Rates of Reaction of Nickel(II) with Various Ligands (Y) at Different Temperatures in Acetonitrile

Ligand	Temp, °C	$10^5C_{Cl^-}$,[a] *M*	log k_{NiX} (apparent) (*k* in M^{-1} sec^{-1})
Bipyridine	15	10.0	5.74
	25	2.50	6.16
		5.00	6.01
		10.0	5.91
		20.0	5.77
	35	10.0	6.12
	45	10.0	6.23
Phenanthroline	25	5.00	6.32
		10.0	6.20
Terpyridine	15	1.25	6.06
		2.50	5.97
		5.00	5.87
		6.25	5.87
	25	See Table II	
	35	1.25	6.51
		2.50	6.41
		5.00	6.37

[a] $C_Y = 2.5 \times 10^{-5}$ *M*; $C_{Ni} = 1.25 \times 10^{-3}$ *M*.

Experimental data are listed in Table II for X = chloride, bromide, iodide, thiocyanate, and nitrate, with Y = 2,2′,2″-terpyridine, at 25°C, and in Table III for X = chloride, with Y = 2,2′-bipyridine, 1,10-phenanthroline, and 2,2′,2″-terpyridine, at different temperatures. Rate constants listed were obtained from eq 13, which generally accounted well for the experimental data, even when C_X was not much larger than C_Y. Extreme examples are the first entries for X = Cl and Br, for which $C_X = C_Y/2$; here, eq 13 still holds at $t > t_{1/2}$, consistent with rapid regeneration of NiX^+. Admittedly, the assumed kinetics illustrated in eq 6 are complicated and the satisfactory fit of the data at low values of C_X is a necessary, but not a sufficient, criterion for the uniqueness of the assumed rate law. Nevertheless, Table II shows that, for all anions,

Table IV. Preferred Values of Rate Constants and of the Acceleration Number N for the Reaction of Monoanion Complexes of Nickel(II) (NiX^+) with Various Incoming Ligands (Y) in Acetonitrile at 25°C

X	Y	$\log k_{NiX}$[a]	$\log k_{Ni}$[a]	$\log N$[b]
Chloride	Bipyridine	6.3	3.61	2.7
	Phenanthroline	6.6	4.70	1.9
	Terpyridine	6.3	3.38	2.9
Bromide	Terpyridine	5.7	3.38	2.3
Iodide	Terpyridine	4.8	3.38	1.4
Thiocyanate	Terpyridine	5.5	3.38	2.1
Nitrate	Terpyridine	4.4	3.38	1.0
Acetate	Terpyridine	4.4 (?)[c]	3.38	1.0 (?)[c]
Benzoate	Terpyridine	4.5 (?)[c]	3.38	1.1 (?)[c]

[a] Units of k: M^{-1} sec^{-1}. Values for "free" nickel(II) ion taken from ref 6, except that with Y = terpyridine the value that is most consistent with all present data is 3.38, rather than 3.34, as previously reported. Values for NiX^+ have been extrapolated to $C_X = 0$. [b] $N = k_{NiX}/k_{Ni}$. [c] These values seem much too low and are reported here only to illustrate complications encountered with acetate and benzoate ions; see text.

it was possible to make at least some measurements at sufficiently high values of C_X so that approximate pseudo-first-order conditions applied with respect to NiX^+; in such cases, the speculative element in our argument concerning the rapid regeneration of NiX^+ does not arise.

Values of k_{NiX} listed in Tables II and III generally exhibit definite negative trends with C_X. Trends with C_{Ni} are small and usually positive. Those with C_X are particularly large for X = Cl and SCN and also for nitrate when it is introduced as lithium nitrate. Formation of higher complexes, such as NiX_2, would be expected to cause trends with C_X and C_{Ni} in the opposite direction from those obtained. However, the observed trends would occur if formation of NiX^+ were incomplete (eq 8). The overall reaction generating NiX^+ may be represented as

$$NiClO_4^+ + MX \rightleftarrows NiX^+ + MClO_4 \qquad (14)$$

ignoring association of NiX^+ and ClO_4^-, which is likely to be trivial. The equilibrium constant of reaction 14 can be calculated in the cases of X = SCN and NO_3 for which the association constants of all four spcies indicated are available. What is known or predictable about the association constants of $NiClO_4^+$ and other NiX^+ complexes already has been indicated. Other relevant association constants (derived from the Fuoss–Onsager conductance equation) are the following:[26,27] NaI, 0; Bu_4NI, 3; NaSCN, 87; $LiNO_3$, 2.4×10^3; Bu_4NNO_3, 7; Et_4NClO_4, 0; Bu_4NClO_4, 0; $NaClO_4$, 10; $LiClO_4$, 4. On the basis of trends exhibited by tetraalkylammonium halides in acetonitrile, we estimate the following association constants: Et_4NCl, ca. 20; Et_4NBr, ca. 10. The above numbers predict that formation of $NiNO_3^+$ should be essentially complete for Bu_4NNO_3 but not at the higher concentrations of $LiNO_3$ listed in Table II. For the latter salt, the observed trends in the apparent rate constant with C_{NO_3} are in fair quantitative agreement with these predictions. The virtual absence of corresponding trends with C_{Ni} is roughly consistent with the opposing influence of (a) the common ion effect of Ni^{2+} on the formation of $NiNO_3^+$, and (b) the strong dependence of the concentration of $NiClO_4^+$ ion pairs on the total concentration of $Ni(ClO_4)_2$, as well as the expected effect of ionic strength on the four association constants contributing to the overall equilibrium constant of reaction 14. Similar considerations apply to X = SCN and Cl. However, for X = Br and I, trends in the apparent rate constant with C_X are small and consistent with virtually complete formation of NiX^+.

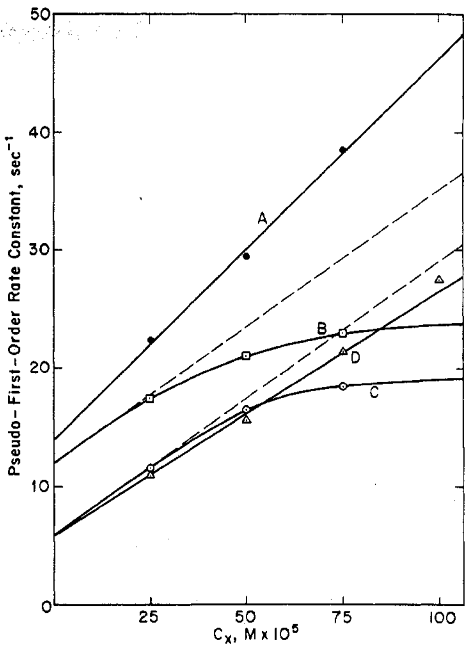


Figure 2. Pseudo-first-order kinetic plots for Y = 2,2′,2″-terpyridine: A, MX is tetraethylammonium benzoate, $C_{Ni} = 2.5 \times 10^{-3}$ M; B, MX is lithium nitrate, $C_{Ni} = 5.0 \times 10^{-3}$ M; C, MX is lithium nitrate, $C_{Ni} = 2.5 \times 10^{-3}$ M; D, MX is tetrabutylammonium nitrate, $C_{Ni} = 2.5 \times 10^{-3}$ M.

In Table IV preferred values of rate constants are given. These numbers were obtained by extrapolating apparent rate constants to $C_X = 0$. In spite of the greater uncertainty in the preferred rate constants for chloride and thiocyanate, the relationship between these numbers and those for bromide and iodide seems reasonable.

A special case is presented by the results obtained with X = acetate and benzoate. The results for benzoate are compared with those for lithium nitrate and tetrabutylammonium nitrate in Figure 2. For X = NO_3, eq 13 holds. The slope of line D and the limiting slopes of lines B and C are equal to k_{NiX}, and the intercepts are equal to $k_{Ni}[Ni^{2+}]_0$. However, for X = benzoate (line A), the intercept is twice as large as predicted by eq 13. Similar results were obtained with X = acetate, and these are given in more detail in Figure 3. For both acetate and benzoate the following rate equation is obeyed

$$dx/dt = [k_{Ni}(C_{Ni} - C_X) + \lambda + k_{NiX}C_X][C_Y - x] \qquad (15)$$

where λ is a constant. For the upper part of Figure 3, the slope of the lines is equal to k_{Ni} and the intercepts are equal to $(k_{NiX}C_X + \lambda)$. For the lower part of the figure, the slope of the line is equal to k_{NiX}, while the intercept is equal to λ. This behavior would be expected if all solutions contained a *constant* concentration of an additional reacting species, conceivably $NiOHClO_4$ present in saturated solution. It was in fact noticed that the more concentrated solutions developed a slight turbidity. In principle, the value of k_{NiX} derived from this procedure should not be seriously compromised by this additional complication, but the values actually obtained and listed in Table IV seem anomalously low and will not be considered further.

The literature contains only limited data on the accelerating effect of inner-sphere substituents at nickel(II) in nonaqueous solvents, and these are summarized in Table V. Also included are our preliminary NMR data for solvent exchange with X = Br and NO_3.[29] (With X = Cl and SCN there are solubility problems.) Comparison of substituent effects on the rate-determining steps for incoming ligands of different charge types requires correction of observed overall rate constants for differences in the equilibrium constants of the outer-sphere

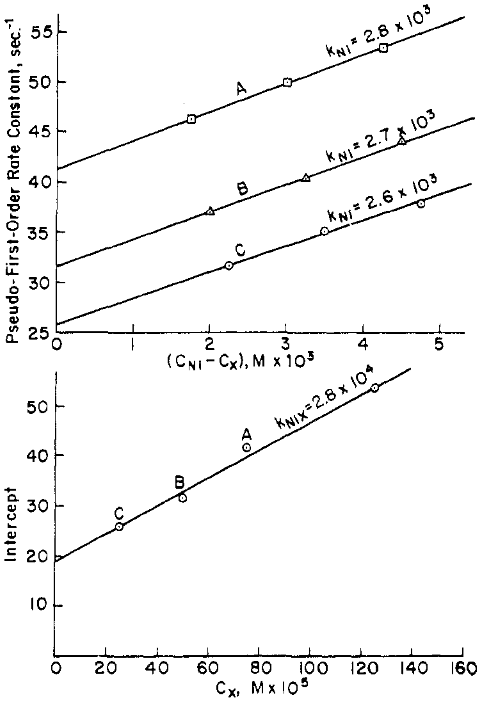


Figure 3. Pseudo-first-order kinetic plots for X = acetate, Y = 2,2′,2″-terpyridine: upper half, C_{Ni} varied, C_X kept constant at 7.5, 5.0, and 2.5 × 10^{-4} M for A, B, and C, respectively; lower half, see eq 15.

Table V. Additional Values[a] for the Accelerating Effect of Anionic Inner-Sphere Substituents (X) in the Reaction of Nickel(II) with Various Incoming Ligands (Y) in Different Solvents

Solvent	X	Y	T, °C	log N_{23}[b]	Ref
Dimethyl sulfoxide	Thiocyanate	Thiocyanate ion	20	1.0	20
Methanol	Chloride	Methanol	25	2.3	28
	Thiocyanate	Thiocyanate ion	25	1.3	20
Acetonitrile	Bromide	Acetonitrile	25	3.0	29
	Nitrate	Acetonitrile	25	1.1	29
	Nitrate	Nitrate ion	20	1.6	8
	Thiocyanate	Thiocyanate ion	20	2.0	20
	Trifluoroacetate	Trifluoroacetate ion	20	2.5	8
	p-Toluenesulfonate	*p*-Toluenesulfonate ion	20	2.0	8

[a] Also see Table IV. [b] $N_{23} = N(K_{12,Ni}/K_{12,NiX})$, where $N = k_{NiX}/k_{Ni}$, and K_{12} has been calculated from eq 3. Note that when Y is uncharged, as in Table IV, $N_{23} = N$.

complexes. For the examples listed in Table V this correction was based on eq 3, using values of a reported before.[6] For X = Br, solvent exchange (Y = S) is accelerated by a factor of 1 × 10^3, while with Y = terpyridine (Table IV) the reaction is accelerated by a factor of only 2 × 10^2. For X = NO_3, the acceleration numbers are 13 for Y = S, 10 for Y = terpyridine, and ca. 40 for Y = NO_3, the last number including the uncertainty introduced by eq 3. For X = SCN, the acceleration number is 1 × 10^2 for Y = terpyridine as well as thiocyanate ion. The most significant implication of the data in Tables IV and V will now be considered.

Ligand substitution reactions at NiS_6^{2+} in acetonitrile as solvent are characterized by a marked sensitivity of rate constants and activation parameters to the nature of the ligand.[6,9] At one extreme of the wide spectrum of ligand behavior is pyridine, for which the rate constant and activation parameters are consistent with the classical I_d mechanism in which the value of the equilibrium constant for the outer-sphere complex appears to be adequately represented by eq 3. At the other extreme is phenanthroline, for which the rate constant at 25°C is 60 times greater and the enthalpy of activation is 10 kcal mol^{-1} smaller than those of pyridine. Bipyridine and terpyridine exhibit intermediate behavior. From the influence of electron-withdrawing and -donating substituents in the 5 and 6 positions of 1,10-phenanthroline, and from other evidence, we have concluded that bipyridine, terpyridine, and particularly phenanthroline form outer-sphere complexes of much greater stability than predicted by eq 3. Such "extra" stabilization may be the result of π-orbital and/or electrostatic interaction of ligand molecules present in the outer sphere with the polarized acetonitrile molecules of the inner sphere.[9] If this interpretation is correct, one would expect less "extra" stabilization of the outer-sphere complexes of NiX^+ than of those of Ni^{2+}. The results in Table IV are consistent with this expectation. Whereas the order of k_{Ni} values in Table IV is phenanthroline > bipyridine > terpyridine, the accelerating effects produced by chloride follow the opposite order, so that $NiCl^+$ does not exhibit the marked discrimination among ligands shown by Ni^{2+}. These results reinforce our belief[9] that the strong ligand dependence of the substitution kinetics of Ni^{2+} in acetonitrile is caused mainly by differences in outer-sphere stabilities. Furthermore, the acceleration in rate produced by X must then be the net effect of two opposing factors: solvent labilization and outer-sphere destabilization.[30] For example, the results for X = Br in Tables IV and V are interpreted to mean that, whereas this inner-sphere substituent accelerates solvent exchange by a factor of 10^3, it reduces the equilibrium constant of the outer-sphere complex with terpyridine by a factor of 5.

In view of the uncertainties in k_{NiCl} values, as already discussed, only approximate values for the activation parameters can be calculated from the data in Table III. These are the following: $\Delta H^{\ddagger} \approx 6$ and 9 kcal mol^{-1} and $\Delta S^{\ddagger} \approx -10$ and 0 cal mol^{-1} deg^{-1} for bipyridine and terpyridine, respectively. Corresponding values for Ni^{2+} are 6.5 ± 0.2 and 8.4 ± 0.3 kcal mol^{-1} and −20 and −15 cal mol^{-1} deg^{-1}, respectively.[6] Hence, with both incoming ligands, the difference in the reaction rates of $NiCl^+$ and Ni^{2+} is determined mainly by the difference in the entropy of activation. These results are not inconsistent with our general interpretation of substituent effects. While solvent labilization probably will be accompanied by a decrease in $\Delta H^{\ddagger}$ (exceptions to this expected correlation have been found in aqueous solution[15]), outer-sphere destabilization should increase both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, so that substitution of X into the inner sphere should increase $\Delta S^{\ddagger}$ but may have little effect on $\Delta H^{\ddagger}$, as observed. Less speculative interpretation of these results will be possible only when more detailed NMR data for solvent exchange at NiX^+ become available.

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Registry No. $NiCl(CH_3CN)_5^+$, 57428-18-9; $NiBr(CH_3CN)_5^+$, 57428-19-0; $NiI(CH_3CN)_5^+$, 57458-87-4; $Ni(SCN)(CH_3CN)_5^+$, 57428-20-3; $Ni(NO_3)(CH_3CN)_5^+$, 57428-21-4; $Ni(CH_3CO_2)(CH_3CN)_5^+$, 57428-22-5; $Ni(PhCO_2)(CH_3CN)_5^+$, 57428-23-6; 2,2′-bipyridine, 366-18-7; 1,10-phenanthroline, 66-71-7; 2,2′,2″-terpyridine, 1148-79-4; $Ni(CH_3CN)_6^{2+}$, 15554-59-3.

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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_6^{2+} + Y and $NiXS_n^+$ + 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^- 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[2] 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,[3] the kinetic effect of electron-withdrawing and electron-donating substituents in the 5 and 6 positions of 1,10-phenanthroline,[3] and the effect of anionic substituents in the inner coordination sphere of nickel(II).[2] 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^+ with simple anions as X^- are too unstable in aqueous solution.[2] 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^-.

We report here rate constants for the reactions of Ni^{2+} and NiX^+ (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^+ were generated in situ by addition of MX to an excess of nickel(II) perchlorate monohydrate in methanol as solvent, where M was Et_4N 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^{-3} *M*. Kinetic measurements generally were made at the wavelengths of maximum absorption of the complexes, which are similar to those in acetonitrile,[4] 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.[2] In particular, unlike in acetonitrile, reaction rates of NiX^+ were sufficiently low to allow the use of a range of concentrations of NiX^+ adequately high to ensure pseudo-first-order conditions with respect to NiX^+ (as well as Ni^{2+}). Typically, solutions after mixing contained total (analytical) concentrations of Ni and X in the ranges $(2-10) \times 10^{-3}$ and $(2.5-7.5) \times 10^{-4}$ *M*, respectively, with that of Y held constant at 2.5×10^{-5} *M*. Consequently, the limiting eq 13 of