INFLUENCE OF SOLVENT PROPERTIES ON LIGAND SUBSTITUTION MECHANISMS OF LABILE COMPLEXES
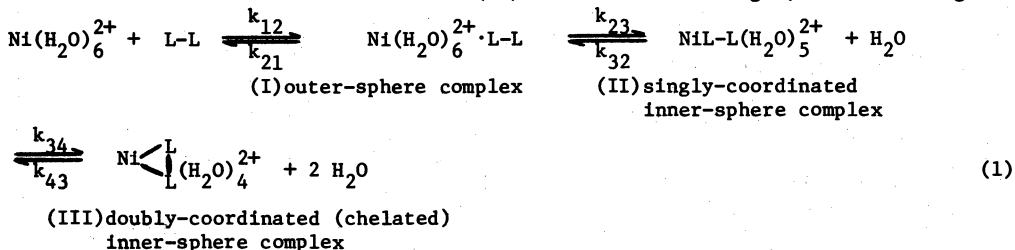
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Abstract - The kinetics of substitution reactions at such metal ions as nickel(II) are relatively insensitive to the nature of the ligand in aqueous solution, but exhibit a marked ligand dependence in certain nonaqueous solvents. While the kinetics of simple unidentate ligands are consistent with a dissociative interchange mechanism, as in water, ligands such as bipyridine and phenanthroline react either "too slow" or "too fast" in certain solvents. It is shown that reaction by the flexible ligand bipyridine requires that the two rings be in the cis position, so that the two donor atoms will coordinate essentially simultaneously. The deviations from simple substitution are attributed to the combined effect of the stability of the outer-sphere complex and the orientation of the ligand in the outer sphere. Both factors are influenced by the donor strength of the solvent, the thickness and openness of the inner sphere, and competition between the ligand and solvent in the outer sphere.

INTRODUCTION

In aqueous solution, the rate constants and activation parameters for many ligand substitution reactions at metal ions depend only slightly on the nature of the ligand and are similar to the corresponding quantities for solvent exchange. In such cases, the reaction is best represented by a dissociative interchange (I_d) mechanism, i.e., an interchange or concerted process characterized by a dissociative mode of activation (Ref. 1-3). The mechanism can be illustrated as follows for the reaction of nickel(II) ion with an uncharged, bidentate ligand:

$$Ni(H_2O)_6^{2+} + L-L \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} Ni(H_2O)_6^{2+} \cdot L-L \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} NiL-L(H_2O)_5^{2+} + H_2O$$

$$\text{(I) outer-sphere complex} \qquad \text{(II) singly-coordinated}$$
$$\text{inner-sphere complex}$$

$$\underset{k_{43}}{\overset{k_{34}}{\rightleftharpoons}} Ni\underset{L}{\overset{L}{<}}(H_2O)_4^{2+} + 2 H_2O \qquad (1)$$

$$\text{(III) doubly-coordinated (chelated)}$$
$$\text{inner-sphere complex}$$

Formation of the outer-sphere complex (process I) is diffusion controlled and therefore rapid, and, with few exceptions (Ref. 2 & 4), ring closure (process III) is also rapid. Process II is therefore the rate-determining step for most ligands reacting by an I_d mechanism, irrespective of their dentate numbers. The complete rate equations can be found elsewhere (Ref. 2 & 5); only the simplest but most common case will be considered here. Provided (i) a large excess of nickel(II) ion is used, (ii) both intermediates are present at steady-state concentrations, and (iii) the concentration of the outer-sphere complex is much smaller than that of free ligand, the rate equation reduces to

$$d[NiL_2^{2+}]/dt = k_{\ell,f}[Ni^{2+}][L-L] - k_{\ell,d}[NiL_2^{2+}] \qquad (2)$$

where

$$k_{\ell,f} = K_{12}k_{23} \qquad (3)$$

and

$$k_{\ell,d} = k_{32}(k_{43}/k_{34}) = k_{32}/K_{34} \qquad (4)$$

Here, $k_{\ell,f}$ (in 1 mol^{-1} sec^{-1}) and $k_{\ell,d}$ (in sec^{-1}) are the overall second-order and first-order rate constants for ligand substitution resulting in formation and dissociation, respectively,

of the inner-sphere complex. The equilibrium constant, K_{12}, represents the ratio k_{12}/k_{21} and therefore is the formation constant of the outer-sphere complex. For a unidentate ligand, Eq. 3 remains the same but Eq. 4 simplifies to $k_{\ell,d} = k_{32}$. It is convenient to write Eq. 2 in the form

$$k_{obs} = k_{\ell,f}[Ni^{2+}] + k_{\ell,d} \qquad (5)$$

where k_{obs} (in sec^{-1}) is the experimentally observed pseudo-first-order rate constant. Hence, a plot of k_{obs} vs. $[Ni^{2+}]$ should be linear with a slope and intercept equal to $k_{\ell,f}$ and $k_{\ell,d}$, respectively.

As shown in Eq. 1, the rate-determining step (process II) in an I_d mechanism involves loss of a solvent molecule from the inner coordination sphere of the metal ion. Hence, the rate constant for this process (k_{23}) should be related to that for solvent exchange (k_s) as $k_{23} = fk_s$, where f is the probability that the ligand will enter a particular coordination site vacated by a solvent molecule. Hence, for an I_d mechanism the following relationship should apply:

$$k_{\ell,f} = fK_{12}k_s \qquad (6)$$

However, assignment of a mechanism is complicated by the fact that evaluation of both f and K_{12} is uncertain; difficulties have been discussed recently (Ref. 5-7). For f, we shall use a value of 3/4 (Ref. 8), but other authors have preferred different values. As far as K_{12} is concerned, if the outer-sphere and inner-sphere complexes are both present in sufficiently high concentrations, both K_{12} and k_{23} in principle can be measured, e.g., by relaxation methods. However, this condition rarely exists. The only examples for nickel(II) ion are with sulfate and methylphosphate ions as ligands, for which separate experimental values for K_{12} and k_{23} were obtained by ultrasonic absorption (Ref. 9) and temperature-jump (Ref. 10) relaxation, respectively. In all other cases, the only recourse is to estimate values of K_{12} from the following theoretical relation (Ref. 6, 11-13):

$$K_{12} = \frac{4\pi Na_1^3}{3 \times 10^3}e^{-U(a_2)/kT} \qquad (7a)$$

where

$$U(a_2) = \frac{z_1 z_2 e^2}{\varepsilon a_2} - \frac{z_1 z_2 e^2 \kappa}{\varepsilon(1 + \kappa a_2)} \qquad (7b)$$

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

$$\kappa^2 = 8 \times 10^{-3}\pi N^2 e^2(\varepsilon RT)^{-1}I^{1/2} \qquad (7c)$$

where ε is the dielectric constant of the medium. Other symbols have their customary meaning. It should be noted that Eq. 7 does not allow for specific interactions between the inner and outer spheres, nor does it allow for ion-dipole or any other interactions between the metal ion and the ligand when the latter is uncharged. We shall return to this important limitation.

In testing for an I_d mechanism, it is convenient to write Eq. 6 in the form

$$R_1 = (4/3)k_{\ell,f}/K_{12}k_s \qquad (8)$$

where the dimensionless ratio R_1 should have a value near unity. Furthermore, the enthalpy of activation for ligand substitution should be related to that for solvent exchange as follows:

$$\Delta H_{\ell,f}^{\ddagger} = \Delta H_s^{\ddagger} + \Delta H_{12}^0 \qquad (9)$$

where ΔH_{12}^0 is the standard enthalpy of formation of the outer-sphere complex and usually (not always) will be negligible. An analogous expression applies to the entropy of activation. Unfortunately, rate constants and activation parameters for solvent exchange, particularly the latter quantities, are frequently uncertain. This makes the application of Eq. 9 tenuous and also adds to the uncertainities already incorporated in Eq. 8. Nevertheless, these criteria for an I_d mechanism are met reasonably well by a large number of labile complexes in aqueous solution (Ref. 1-3, 14). Typical examples are shown in Table 1.

<u>Note:</u> In Table 1 and all other tables, data are for a temperature of 25°C, except where
        indicated otherwise. Units of $\Delta H^{\ddagger}$ are kcal mol^{-1}, where 1 cal = 4.18 J, and those of

TABLE 1. Rate constants and activation parameters for "normal" ligand substitution reactions of nickel(II) ion in aqueous solution

Ligand	I	$\log k_{\ell,f}$	$\log R_1$	$\Delta H^{\ddagger}_{\ell,f}$	$\Delta S^{\ddagger}_{\ell,f}$	$\log k_{\ell,d}$	$\Delta H^{\ddagger}_{\ell,d}$	$\Delta S^{\ddagger}_{\ell,d}$	Ref.
Water	0.3-0.8	4.5[a]		14[a]	+ 9[a]				15
Ammonia	0.1	3.6	-0.3	10	- 6	0.8	13	-10	16,17
Pyridine	0.3	3.6	-0.3	11	- 5	1.6	15	+ 2	17,18
Bipyridine	<0.015	3.2	-0.7	13	0	-4.3	23	0	18-20
Phenanthroline	<0.03	3.5	-0.4	13	+ 1	-5.0	24	- 1	18-20
Terpyridine	<0.01	3.1	-0.8	14	+ 3	-7.6	24	-14	18,19
Hydrogen oxalate, HL	0.1	3.7	-0.9	14	+ 7	3.2[b]			21
Oxalate, L^{2-}	0.1	4.9	-0.7	14	+12	0.6			21

[a] Refers to solvent exchange.

[b] In this case, units of $k_{\ell,d}$ are $\ell\ mol^{-1}\ sec^{-1}$.

For most of the ligands listed in Table 1, Eq. 9 applies well. Values of R_1 calculated from Eq. 7 (assuming a = 5 Å) and Eq. 8 are reasonably similar for ligands of three charge types. The mean value of R_1 is 0.25, which could mean that the proper value of f is smaller than that assumed, or, as the foregoing dicussion has shown, it could mean any of several other things. The final conclusion is that the data in Table 1 are represented reasonably well by a simple I_d mechanism, although some degree of ligand specificity remains unexplained.

In the reaction scheme given in Eq. 1, a direct and crucial role is attributed to the solvent. Consequently, variation of the solvent would be highly desirable. Pioneering work in which this was done was carried out by Pearson and Ellgen (22) and Bennetto and Caldin (23). During the past few years considerable additional information has accumulated on the solvent dependence of ligand substitution kinetics of labile metal complexes, and it has been reviewed recently (Ref. 5). The principal finding has been that the apparently straightforward behavior of aqueous solutions is not general. While the results generally can be accomodated within the framework of a dissociative interchange mechanism, the solvent may influence all three steps of the reaction scheme given in Eq. 1, often in a complex manner. A broad spectrum of solvent effects already has been uncovered, with water occupying an intermediate position. The extremes of the spectrum will be examined in this paper.

SOLVENT PROPERTIES AND SOLVENT-EXCHANGE PARAMETERS OF NICKEL(II) ION

Selected solvent properties are listed in Table 2 and solvent-exchange parameters of nickel(II) ion, derived from NMR line-broadening data, are shown in Table 3. While values of rate constants for a given system at 25°C obtained by different authors generally are in fair agreement, values of activation parameters frequently fluctuate widely. In such cases, assignment of a mechanism for ligand substitution is compromised.

SOLVENT EFFECTS ON SUBSTITUTION KINETICS OF BIPYRIDINE AND SIMILAR LIGANDS

In 1968 and particularly in 1971, Caldin et al. (23) presented evidence showing that the simple I_d mechanism, as described in the Introduction, cannot fully accomodate the kinetics of ligand substitution reactions in nonaqueous solvents. Rate constants and activation parameters were reported for the reactions of nickel(II) and cobalt(II) ions with 2,2'-bipyridine and 2,2',2"-terpyridine in a variety of solvents. Results obtained subsequently by Bennetto (46) with the bidentate ligand pyridine-2-azo-p-dimethylaniline (PADA) in the same solvents exhibit, with some exceptions, the same trends. In addition, solvent exchange parameters for several divalent metal ions in a variety of solvents were considered. Results for the formation of the mono-complex of nickel(II) ion with bipyridine, as well as relevant solvent properties, are shown in Table 4. As criteria for "normal" substitution Bennetto and Caldin (23, 47) considered a quantity n which is equal to the quantity R_1 of Eq. 8 with the restrictions that, in Eq. 6, f = 1 and K_{12} = 0.1 1 mol^{-1} for all solvents. They also considered the quantities $\Delta\Delta H^{\dagger} = \Delta H_{\ell,f}^{\dagger} - \Delta H_s^{\dagger}$ and $\Delta\Delta S^{\dagger} = \Delta S_{\ell,f}^{\dagger} - \Delta S_s^{\dagger}$ (cf. Eq. 9). Table 4 shows that n, $\Delta\Delta H^{\dagger}$ and $\Delta\Delta S^{\dagger}$ cover a wide range of values. Bennetto and Caldin drew the following conclusions. 1. The kinetic properties of aqueous solutions are not general. 2. Values of n and $\Delta\Delta H^{\dagger}$ 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. The slope of the plot of $\Delta\Delta H^{\dagger}$ vs. ΔH_{vap} is between 2 and 3, suggesting that several solvent molecules are involved. 4. After correcting for ligand field stabilization, a single linear (isokinetic) relationship between $\Delta H^{\dagger}$ and $\Delta S^{\dagger}$ is found for solvent exchange as well as ligand substitution at various divalent metal ions in a number of solvents, as shown in Fig. 1. Reactions obeying an isokinetic relationship typically proceed by the same mechanism. In this case, it is significant that ligand substitution and solvent exchange obey the same isokinetic relationship. The large variations in $\Delta H^{\dagger}$ are so effectively compensated by corresponding variations in $T\Delta S^{\dagger}$ that there is little change in $\Delta G^{\dagger}$. This behavior is typical of sets of reactions in which solvation changes play an important role.

Bennetto and Caldin proposed that these correlations could be interpreted in terms of a general structural model in which passage of a solvent molecule from the disordered region surrounding the solvation sphere of the metal ion into the bulk solvent contributes to the kinetics to the extent that the ligand modifies local solvent structure. We have discussed some of the implications of this hypothesis elsewhere (Ref. 5 & 19). Ligands such as PADA and especially bipyridine present complications, e.g., their severe steric requirements and their aromaticity and polarity. Simpler ligands are required to establish "norms" for substitution reactions. In subsequent sections, we shall describe the behavior of such ligands and attempt to identify which steps in the reaction mechanism are responsible for the correlations observed by Bennetto and Caldin. It will be most instructive to focus our attention on two solvents at or near the extremes in the correlations noted, viz., dimethylsulfoxide and acetonitrile.

TABLE 2. Solvent properties and parameters

Property	Water	Methanol	Ethanol	2-Propanol	Ethylene glycol	Dimethyl-formamide	Dimethyl-sulfoxide	Aceto-nitrile	Propylene carbonate
Freezing temperature, °C	0	-97.8	-114.1	-88.0	-12.4	-61	18.45	-45.7	-49
Boiling temperature (1 atm.), °C	100	64.5	78.3	82.3	197.4	153	189	81.6	242
Vapor pressure, torr	23.7	120	60	45	0.14	3.5	0.5	92	
ΔH of vaporization, kcal mol^{-1} -at normal bt (1 atm.)	9.7	8.4	9.3	9.5	11.8	10.0	10.7	7.1	
-at 25°C	10.5	9.0	10.1	10.9	13.8	11.4	12.6	7.7	
ΔS of vaporization, cal mol^{-1} K^{-1} at normal bt	26.05	24.96			25.1	23.46	23.16	20.06	
Fluidity, g ml^{-1} cP^{-1}	1.12	1.43	0.73	0.37	0.061	1.19	0.55	2.27	0.47
Relative permittivity	78.5	32.6	24.6	19.9	37.7	36.7	46.6	36.0	64.4
Dipole moment, D	1.85	1.68	1.7	1.7	2	3.8	4.3	4.1	
Refractive index, n_D^{20}	1.333	1.3288	1.3614	1.3772	1.4317	1.4306	1.4787	1.344	1.4209
Donor number	33(?)	19(?)				26.6	29.8	14.1	14.7

Note: For temperature-dependent properties, temperature is 25°C except where noted otherwise. Data are mainly from Ref. 23-26.

Table 3. Rate constants and activation parameters for solvent exchange at
          nickel(II) ion in various solvents

Solvent	Method	log k_s	$\Delta H_s^{\ddagger}$	$\Delta S_s^{\ddagger}$	Ref.
Water	O-17	4.4	11.6	+ 0.6	27
	O-17	4.5	10.8	- 1.7	28
	O-17	4.5	13.9	+ 8.7	15
	O-17	4.5	12.1	+ 2.9	29
	O-17	4.6	10.3	- 5.2	30
Methanol	H-1	3.0	15.8	+ 8.0	31
Ethanol	H-1	4.0	10.8	- 4	32
Acetonitrile	H-1	3.6	10.9	- 8.8	33
	H-1	3.4	11.7	- 3.6	34
	H-1	4.1	11.8	- 0.2	35
	H-1	3.4	15	+11	36
	N-14	3.3	16.4	+12.0	37
Dimethylsulfoxide	H-1	3.9	8	-14	38
	H-1	4.0	7.3	-16	39
	H-1	3.7	12.1	- 1.3	40
	H-1	3.5	13.0	+ 3.2	41
	H-1	3.9	6.2	-20	42
	H-1	4.0	12.3	+ 1.2	43
Dimethylformamide	H-1	3.6	15	+ 8	44
	O-17	3.9	9.4	- 9.1	45

ABNORMALLY SLOW REACTIONS IN DIMETHYLSULFOXIDE AND OTHER STRONG-DONOR SOLVENTS

Results obtained mainly by Moore (48), Coetzee (19, 49) and Hoffmann (50), and summarized in
Table 5, established that the "norm" for substitution by unidentate ligands at nickel(II) ion
in dimethylsulfoxide is a simple I_d mechanism. It is particularly significant that the ratio
of the rate constant for thiocyanate or chloride ion to that for pyridine or 4-phenylpyridine
is represented well by the ratio of the K_{12}-values (27/0.86 ∿ 30) calculated from Eq. 7 (as-
suming a = 7Å), so that estimated k_{23} - values are virtually constant. Furthermore, although
solvent exchange parameters for dimethylsulfoxide are particularly uncertain (see Table 3),
it is reassuring that the k_{23} - values for the first four ligands listed in Table 5 correspond
to a log k_s - value of 3.5 which falls within the range of the NMR data.

In sharp contrast, the kinetic properties of certain multidentate ligands deviate from the
norm, as shown in Table 6. While the rate constants for the aminopyridines, which are prob-
ably bidentate even in the strong-donor solvent dimethylsulfoxide, are very similar to the
norm established by unidentate ligands, the activation parameters do reflect a significant
degree of ligand specificity. Furthermore, the rate constants for phenanthroline, bipyridine
and terpyridine are smaller than the norm and decrease in the above order. Coetzee (5, 19)
and Moore (53) have suggested two different kinds of steric inhibition of coordination as
being responsible for these low rates. The first possibility considered (Ref. 5 & 19) was
that for bipyridine and terpyridine the principal steric barrier involves the ring-closure
step(s). In the solid state the rings of bipyridine are coplanar but in the trans configura-
tion (Ref. 54), and even in solution bipyridine and terpyridine exist preferentially in the
trans and trans-trans configuration, respectively (Ref. 55). Since in the chelate the rings

TABLE 4. Correlation of rate constants and activation parameters for the reaction between nickel(II) ion and bipyridine with certain solvent properties

| Solvent	ρ/η	ΔH_{vap}	$\log k_s$	$\Delta H_s^{\ddagger}$	$\Delta S_s^{\ddagger}$	$\log k_{\ell,f}^{\ddagger}$	$\Delta H_{\ell,f}^{\ddagger}$	$\Delta S_{\ell,f}^{\ddagger}$	$\log n$	$\Delta\Delta H^{\ddagger}$	$\Delta\Delta S^{\ddagger}$
Water	1.12	10.5	4.5	10.8	– 2	3.20	12.6	– 2	-0.3	+1.8	0
Deuterium oxide	1.00	10.8	4.5	10.8	––	3.04	14.0	+ 2	-0.5	+3	––
Methanol	1.43	9.0	3.0	15.8	+ 8	1.92	17.0	+ 7	-0.1	+1.2	– 1
Ethylene glycol	0.061	13.8	3.6	––	––	1.52	16.8	+ 5	-1.1	––	––
Dimethylformamide	1.19	11.4	3.9	9.4	– 9	2.73	12.7	– 3	-0.2	+3.3	+ 6
Dimethylsulfoxide	0.55	12.6	3.9	8	-14	1.84	12.6	– 8	-1.1	+5	+ 6
Dimethylmethylphosphonate	0.58	13.3	4.4	7.5	-11	2.32	13.9	– 1	-1.1	+6.4	+10
Acetonitrile	2.27	7.7	3.4	11.7	– 4	3.67	6.6	-20	+1.3	-5.1	-16

Note: Data are from Bennetto and Caldin (23).
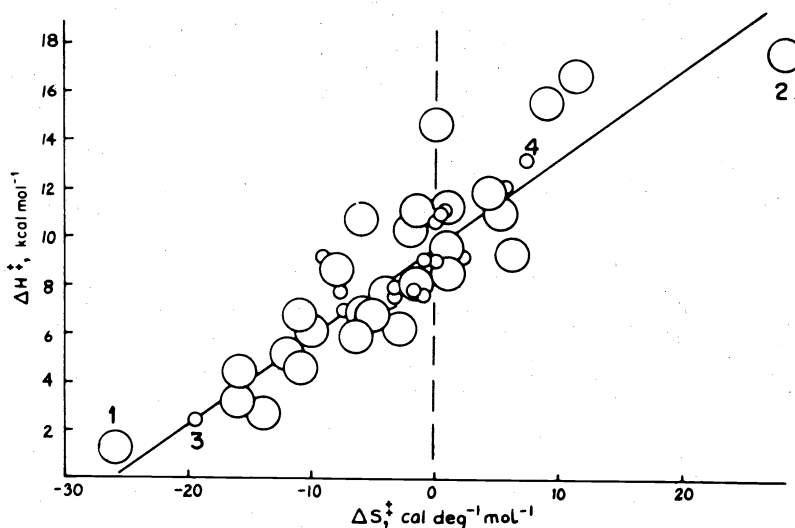
Fig. 1. Isokinetic plot for substitution reactions of bivalent metal ions. Large
circles: solvent exchange; small circles: substitution by uncharged ligands. Num-
bered entries are: 1, Mn^{2+} in DMF; 2, Mg^{2+} in EtOH; 3, Ni^{2+} + bipyridine in CH_3CN;
and 4, Ni^{2+} + bipyridine in MeOH. Based on plot given by Bennetto and Caldin (23),
by permission.

TABLE 5. Evaluation of rate constants k_{23} for the conversion of outer-sphere into
inner-sphere complexes of nickel(II) with unidentate ligands in dimethyl-
sulfoxide as solvent

Ligand	T,°C	log $k_{\ell,f}$	Ref.	log k_{23}
Pyridine	25	3.4	19	3.5
	20	3.3	19	3.4
4-Phenylpyridine	25	3.21	48	3.3
Thiocyanate	25	5.0	49	3.5
	20	4.9	49	3.4
	20	4.9	50,51	3.4
Chloride	20	4.8	50	3.3
Dithiocarbamates	25	4.2-4.4	52	2.7-2.9

must be in the cis position, the structure of the solvent was thought to present a barrier to
rotation of the free end of the ligand in the singly-coordinated intermediate and hence to
ring closure. The second possibility considered (Ref. 53) was that coordination of the first
donor atom is hindered by interference between the adjacent hydrogen atom on the flanking
trans pyridine ring and the bulky dimethylsulfoxide molecules present in the inner sphere. We
have now established (Ref. 56) that neither explanation is quite correct. If first-bond for-
mation by 2,2'-bipyridine occurs while the second pyridine ring is in the trans configuration,
then this step in the reaction mechanism should be closely simulated by the behavior of 2-
phenylpyridine. This compound is a feeble ligand that does not react significantly with
nickel(II) ion in dimethylsulfoxide, in water, or even in the weaker donors 2-propanol and
acetonitrile. However, it does react in the very weak donors sulfolane and propylene carbo-
nate. In the latter solvent, its rate constant is 2 1 mol^{-1} sec^{-1}, which is exceptionally
low compared to those of 4-phenylpyridine (2 x 10^5) and 2,2'-bipyridine (also 2 x 10^5). It
is clear that, even in propylene carbonate, formation of the complex is subject to severe
steric hindrance. However, these steric problems do not result in particularly fast dissoci-
ation of the complex, since the equilibrium constant for its formation is of the order of

TABLE 6. Comparison of rate constants and activation parameters for reactions of nickel(II) ion with uncharged ligands in dimethylsulfoxide with corresponding quantities for solvent exchange

Ligand	$\log k_s$ or $\log k_{\ell,f}$	$\log R_1$	$\Delta H_s^{\dagger}$ or $\Delta H_{\ell,f}^{\dagger}$	$\Delta S_s^{\dagger}$ or $\Delta S_{\ell,f}^{\dagger}$	Ref.
Dimethylsulfoxide	3.9		a	a	
4-Phenylpyridine	3.21	-0.5	9	-13	48
Bipyridine	1.84	-1.9	13	- 8	23,47
Phenanthroline	2.6	-1.1	11	- 8	5
Terpyridine	1.41	-2.3	12	-12	23,47
	1.40	-2.3	15	- 2	19
2-(Aminomethyl)pyridine	3.64	-0.1	9	-11	53
2-(2-Aminoethyl)pyridine	3.65	-0.1	12	0	53
2-(Aminomethyl)-6-methylpyridine	3.73	0	14	+ 7	53
2-[(Methylamino)methyl]pyridine	3.33	-0.4	9	-14	53

a
Uncertain; see Table 3.

10^3 l mol^{-1}, so that $k_{\ell,d}$ (which is equal to k_{32}; see Eq. 1) is of the order of 10^{-3} sec^{-1}. Now, when increasing amounts of dimethylsulfoxide are added to a solution of nickel(II) perchlorate in propylene carbonate, the formation rates of both the 2-phenylpyridine and the bipyridine complexes are strongly affected. Results are shown in Fig. 2, which also contains
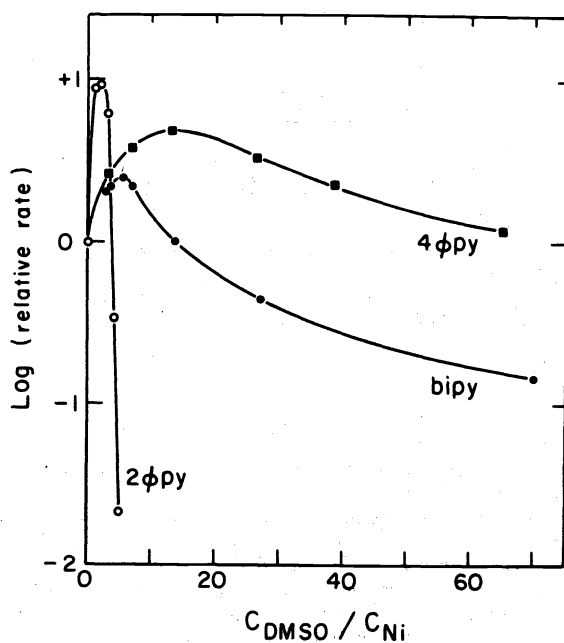

Fig. 2. Effect of added dimethylsulfoxide on rates of reaction of nickel(II) ion with 2-phenylpyridine, 4-phenylpyridine and 2,2'-bipyridine in propylene carbonate as solvent. For the first ligand (L), C_L = 5 x 10^{-5}, C_{Ni} = 10 x 10^{-3} M; for the other two ligands, C_L = 2.5 x 10^{-5}, C_{Ni} = 1 x 10^{-3} M. Initial rates have been normalized.

corresponding data for 4-phenylpyridine. For this latter compound, which serves as a refer-
ence ligand, the initial increase in rate is similar to that observed for many other systems
and is caused by increasing labilization of propylene carbonate by dimethylsulfoxide until
five dimethylsulfoxide molecules have entered the inner sphere. This apparently happens when
$C_{DMSO}/C_{Ni} \equiv R_C \sim 10$. Introduction of a sixth dimethylsulfoxide molecule apparently presents
some difficulty, probably because the inner sphere becomes crowded, and so further addition
of dimethylsulfoxide beyond $R_C \sim 10$ results in only a gradual decrease in rate. For bipy-
ridine the maximum rate occurs at a lower value of R_C (5 or 6), when the inner sphere very
likely contains four dimethylsulfoxide molecules. Now, it is significant that for 2-phenyl-
pyridine the maximum occurs at a much lower value of R_C (1 or 2). In fact, for 2-phenylpyri-
dine the rate becomes much lower than that in pure propylene carbonate long before the inner
sphere can possibly contain more than two or three dimethylsulfoxide molecules. Consequently,
the decrease in rate is more reasonably attributed to a lowering of the effective positive
charge of nickel(II) ion by the strong donor dimethylsulfoxide than to the large size of the
dimethylsulfoxide molecules. This conclusion is substantiated by the fact that addition of
acetonitrile, which actually alleviates steric crowding in the inner sphere, affects the
reaction rate of 2-phenylpyridine in propylene carbonate in a manner qualitatively similar
to the effect of dimethylsulfoxide. Quantitatively, the influence of acetonitrile is less
marked than that of dimethylsulfoxide, in keeping with its lower donor strength.

When dimethylsulfoxide is added to propylene carbonate in concentrations higher than those
shown in Fig. 2, it continues to decrease the reaction rates of both 4-phenylpyridine and
bipyridine over the entire range of solvent compositions, as shown in Fig. 3. Up to $\underline{ca}$.
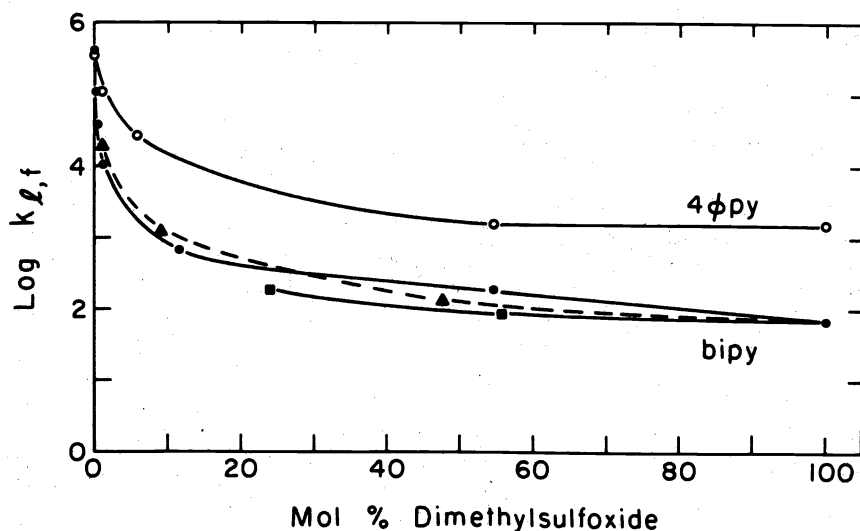

Fig. 3. Effect of added diluents (D) on rates of reaction of nickel(II) ion with
ligands (L) in dimethylsulfoxide as solvent. Open circles: D = propylene carbon-
ate, L = 4-phenylpyridine; closed circles: D = propylene carbonate, L = 2,2'-
bipyridine; squares: D = benzene, L = bipyridine; triangles: D = methylene
chloride, L = bipyridine.

10 mol-% added the decrease is much larger for the latter ligand than for the former, but
between 10 and 100 mol -% the decrease is the same for the two ligands and it remains vir-
tually the same when propylene carbonate is replaced with methylene chloride or benzene.

Our interpretation of the kinetic properties of bipyridine, 2-phenylpyridine and 4-phenyl-
pyridine in propylene carbonate and its mixtures with dimethylsulfoxide is as follows. 1.
Under all conditions, the principal mode of attack by bipyridine is with its two rings in the
cis position, so that its two donor atoms must coordinate essentially simultaneously. Forma-
tion of only one bond while the uncoordinated ring is substantially out of the cis position is
severely limited by steric hindrance. Furthermore, it is likely that this requirement holds
for all solvents. The rigid molecule phenanthroline already has its donor atoms fixed in
the cis position and therefore should generally react faster than bipyridine, except in a
solvent that has the ability to stabilize the proper orientation of bipyridine in the outer
sphere, e.g., in water by hydrogen bonding to the inner sphere. Data presented later (see
Table 8) support this hypothesis. 2. Dimethylsulfoxide is a solvent possessing extended
two-dimensional order (Ref. 5) but it has little ability to donate hydrogen bonds. It is
likely that, in the outer sphere, so much solvent order exists that the bulky solvent

molecules interfere with the proper orientation of the bipyridine rings. Furthermore, certain other factors that undoubtedly contribute to proper orientation of the rings in many other solvents must be unimportant in dimethylsulfoxide. For example, ion-dipole interaction will be weak because the effective positive charge of nickel(II) ion will be significantly reduced by the strong-donor solvent, and because the inner sphere is so tightly packed that no significant decrease in the interaction distance from penetration by the incoming ligand is possible. 3. Returning now to Fig. 3, the gradual increase in reaction rates of bipyridine and 4-phenylpyridine in the region from 100 to 10 mol-% dimethylsulfoxide probably should be attributed to outer-sphere stabilization in view of Frankel's observation (57) that the rate of dimethylsulfoxide exchange at $Ni(DMSO)_6^{2+}$ ion does not vary much when "diluents" such as methylene chloride or nitromethane are added in concentrations up to 90 mol-%. The corresponding data in Fig. 3 can be rationalized by suggesting that addition of the diluent gradually replaces dimethylsulfoxide in the outer sphere with diluent molecules which present less steric hindrance to the incoming ligands. 4. Further addition of diluent causes a more rapid increase in rate, particularly for bipyridine. We attribute this to an increase in solvent exchange rate accompanied by a further elimination of dimethylsulfoxide from the outer sphere, so that bipyridine increasingly becomes capable of the proper orientation for coordination.

The mechanism proposed here for the anomalously slow reaction of bipyridine in dimethylsulfoxide contains some elements of mechanisms previously advanced, but with significant differences. We propose that, while solvent structure is indeed important, what is significant is neither the influence of bipyridine on solvent structure (Ref. 23), nor the effect of solvent structure on the ring-closure step (Ref. 19), but rather the influence of the solvent structure in the outer sphere on the proper orientation of the ligand. Furthermore, while steric inhibition of first-bond formation is indeed important (Ref. 53), it is in fact so severe that the ligand can react only when the two rings are in the cis position, so that both bonds will form essentially simultaneously. In all solvents, proper orientation of bipyridine in the outer sphere should become increasingly difficult with increasing donor strength of the solvent and increasing thickness and close packing of the inner sphere, unless specific interaction (e.g., hydrogen bonding) occurs between the ligand and the inner sphere.

ABNORMALLY FAST REACTIONS IN ACETONITRILE AND OTHER WEAK-DONOR SOLVENTS

In acetonitrile, the kinetic properties of unidentate ligands are consistent with a simple I_d mechanism, as in dimethylsulfoxide, but the properties of bipyridine, terpyridine and phenanthroline contrast sharply with those observed in dimethylsulfoxide. Results are summarized in Table 7. Whereas in dimethylsulfoxide these ligands react abnormally slowly, in acetonitrile they react faster and with much lower enthalpies of activation than the norm. This abnormal ease of reaction is most marked with phenanthroline and its 5- and 5,6-derivatives, and we have attributed it to exceptional outer-sphere stabilization (Ref. 7, 19, 58, 61-63) within the framework of the general I_d mechanism represented by Eq. 1; the possibility of an associative mechanism can be ruled out because the sterically less demanding unidentate ligands show no rate enhancement. This conclusion is consistent with our discussion of the slowness of the reactions of these multidentate ligands in dimethylsulfoxide. Acetonitrile is a relatively weak donor and its more or less cylindrical molecule fills little space laterally. Consequently, the ion-dipole interaction between nickel(II) ion and the ligand is strong because the effective positive charge of the ion is high and the interaction distance can be shortened by penetration of the ligand into the inner sphere. The outer-sphere complexes of the phenanthrolines are more stable than those of the unidentate pyridines mainly because ion-dipole interaction is promoted by the presence of two donor atoms located favorably and rigidly in the cis position. For the flexible ligands bipyridine and terpyridine there is the partially-offsetting requirement that only the cis orientation is effective in coordination.

The possibility exists that outer-sphere stabilization is also promoted by interaction of the ligand with the polarized acetonitrile molecules of the inner sphere, but it now seems unnecessary to invoke any specific π-orbital interaction (Ref. 58), because enhanced reactivity of phenanthroline has been observed in other solvents also, as shown in Table 8. It is particularly significant that the reaction rate of phenanthroline relative to the solvent exchange rate and/or the reaction rate of 4-phenylpyridine is the highest in those solvents (acetonitrile and propylene carbonate) in which nickel(II) ion is solvated most weakly and with the most open inner spheres.

The point of view that the outer-sphere complexes of particularly the phenanthrolines possess "extra" stability is supported by two additional lines of evidence. First, the affect of electron-donating and electron-withdrawing substituents in the 5- and 5,6-positions obeys a Hammett correlation, as shown in Fig. 4. Electron-donating substituents increase the electron density on the nitrogen atoms and therefore promote outer-sphere stability, and vice versa. We have discussed the details of the correlation shown in Fig. 4, and have compared substituent effects in acetonitrile with those in water (Ref. 58). The second line

TABLE 7. Comparison of rate constants and activation parameters for ligand
          substitution reactions in acetonitrile with corresponding quantities
          for solvent exchange

Metal Ion	Ligand	$\log k_s$ or $\log k_{\ell,f}$	$\log R_1$	$\Delta H_s^\ddagger$ or $\Delta H_{\ell,f}^\ddagger$	$\Delta S_s^\ddagger$ or $\Delta S_{\ell,f}^\ddagger$
Nickel(II)	Acetonitrile	3.43	–	15	+11
	Thiocyanate ion [a]	5.00	–0.1	17 [b]	+22 [b]
	Nitrate ion [a]	5.28	+0.1	17.5 [b]	–
	Trifluoroacetate ion [a]	5.18	0	–	–
	p-Toluenesulfonate ion [a]	5.11	0	17.0 [b]	–
	Ammonia	3.5	+0.2	–	–
	Pyridine	2.92	–0.4	14.7	+ 4
	4-Phenylpyridine	2.99	–0.3	11.2	– 7
	Isoquinoline	3.09	–0.2	11.9	– 5
	2,2'-Bipyridine	3.61	+0.3	6.5	–20
	2,2',2''-Terpyridine	3.34	0.0	8.4	–15
	1,10-Phenanthroline	4.70	+1.4	4.7	–21
	5-Nitrophenanthroline	4.09	+0.8	5.1	–23
	5-Chlorophenanthroline	4.37	+1.1	6.5	–17
	5-Methylphenanthroline	4.81	+1.5	5.5	–18
	5,6-Dimethyl- phenanthroline	4.86	+1.6	3.5	–25
	2,9-Dimethyl- phenanthroline	2.63	–0.7	10.1	–13
Cobalt(II)	Acetonitrile	5.51	–	11.4	+ 5
	Pyridine	5.06	–0.3	10.5	0
	4-Phenylpyridine	4.98	–0.4	8.7	– 7
	Isoquinoline	5.05	–0.3	7.0	–12
Iron(II)	Acetonitrile	5.74	–	9.7	0
	4-Phenylpyridine	6.3	+0.7	7	– 7

Note: Data are from Ref. 58 except where indicated otherwise. Uncertainty in
       $\Delta H^\ddagger$ is estimated to be $\pm$ 1 kcal mol^{-1}.

[a] Data are from Ref. 59 & 60 for T = 20°C.

[b] Comparison of the values for anionic ligands with those for uncharged ligands
requires correction for the $\Delta H°$ and $\Delta S°$ values for the formation of the outer-
sphere complex (see Eq. 9), viz., 2.2 kcal mol^{-1} and 15.5 cal mol^{-1} K^{-1},
respectively (Ref. 59). This correction leads to the following mean values for
the rate-determining step for the three anionic ligands: $\Delta H_{23}^\ddagger = 15.0 \pm 0.5$,
$\Delta S_{23}^\ddagger = 6.5 \pm 2$.

TABLE 8. Comparison of rate constants for substitution by phenanthroline, bipyridine and terpyridine at nickel(II) ion with rate constants for solvent exchange and for substitution by 4-phenylpyridine

Solvent	D^a	$\log k_s^b$	4-Phenpyr	Phenanthroline	Bipyridine	Terpyridine
Ethylene glycol		3.6			1.5, -1.7, -	1.0, -2.2, -
Dimethylsulfoxide	30	3.9	3.2, -0.5	2.6, -1.1, -0.6	1.8, -1.9, -1.4	1.4, -2.3, -1.8
Dimethylmethyl-phosphonate		4.4			2.3, -2.0, -	
Dimethylformamide	27	3.9			2.7, -1.1, -	
Water	33?	4.5	3.6^c, -0.3	3.5, -0.4, -0.1	3.2, -0.7, -0.4	3.1, -0.8, -0.5
Methanol	19	3.0	2.1, -0.5	2.8, +0.2, +0.7	2.0, -0.6, -0.1	1.6, -1.0, -0.5
Ethanol		4.0	3.8^c, -0.1	4.5, +0.6, +0.7	3.8, -0.1, 0	
2-Propanol			5.2, -	5.9, -, +0.7	5.0, -, -0.2	4.4, -, -0.8
Acetonitrile	14	3.4	3.0, -0.3	4.7, +1.4, +1.7	3.6, +0.3, +0.6	3.3, 0.0, +0.3
Isobutyronitrile			3.9, -	>5, -, >1	3.7, -, -	3.6, -, -0.3
Propylene carbonate	15		5.3, -	7, -, 2	5.4, -, +0.1	5.3, -, 0

Note: For each ligand-solvent combination, the first entry represents $\log k_{\ell,f}$, the second $\log R_1$, and the third $\log R_2$, where $R_1 = (4/3)k_{\ell,f}/K_{12}k_s$ and $R_2 = (k_{\ell,f})_L/(k_{\ell,f})_{L'}$ with L' representing 4-phenylpyridine as reference ligand. Data are from Ref. 63.

a — Donor number; see text.

b — Refers to solvent exchange; has not yet been measured for 2-propanol, isobutyronitrile and propylene carbonate.
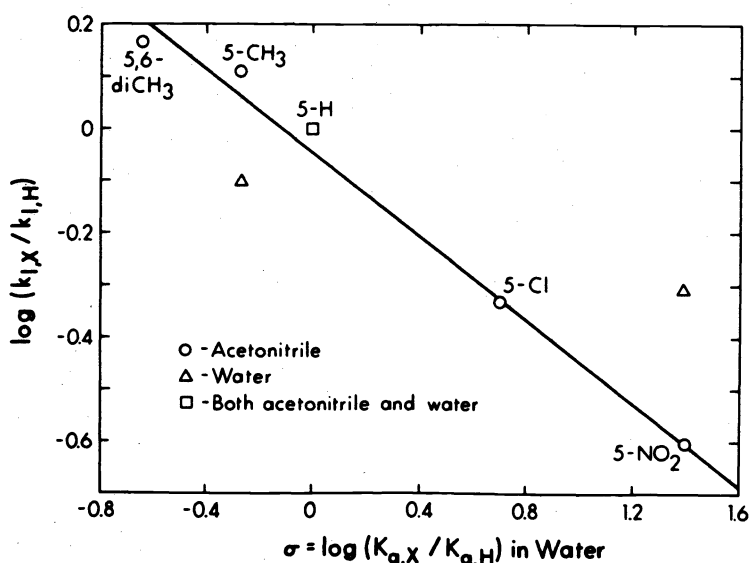
c — Ligand is pyridine.

Fig. 4. Hammett correlation for reactions of substituted phenanthrolines with nickel(II) ion in acetonitrile. Slope = -0.40 ± 0.03. From Chattopadhyay and Coetzee (58).

of evidence supporting the view that the outer-sphere complexes of terpyridine, bipyridine and particularly phenanthroline possess extra stability in acetonitrile comes from the kinetic influence of anionic substituents in the inner coordination sphere of nickel(II) (Ref. 61). If this extra stability is the result of ion-dipole interaction, as proposed, then introduction of an anion into the inner sphere should decrease the outer-sphere stability of all three complexes, but particularly that of phenanthroline. Since introduction of an anion into the inner sphere also produces a second, and larger, effect, viz., labilization of remaining solvent molecules, its kinetic influence should reflect the net effect of solvent labilization and outer-sphere destabilization. That these expectations are fulfilled is evident from the results shown in Table 9 for acetonitrile (Ref. 61) and also for methanol (Ref. 7) as solvents. For both solvents, the "acceleration number", N, is much smaller for phenanthroline than for the other incoming ligands. An additional, and reassuring, result is that the relative acceleration numbers for the two solvents, N_{AN}/N_M, closely parallel the free energies of transfer of the free anions from methanol to acetonitrile, for which the following values have been estimated (Ref. 64): chloride ion (5.7 kcal mol^{-1}) > bromide (4.9) > iodide (2.9) > thiocyanate (1.6). Hence, preferential solvation by methanol occurs with all four anions, and it is most marked with the "hard" anion, chloride ion, which is a good hydrogen bond acceptor. Table 9 shows that preferential solvation by methanol of bound X in NiX^+ parallels its preferential solvation of free X^-, weakening the Ni-X bond more and therefore allowing less solvent labilization in methanol than in acetonitrile in the same order of chloride > bromide > iodide > thiocyanate.

We have attributed both the abnormally fast reaction rates observed in acetonitrile and the abnormally slow rates in dimethylsulfoxide to outer-sphere effects without invoking bulk solvent structure per se. The evidence presented here generally supports the suggestion by Langford (65) who, noting that solvent exchange is insensitive to bulk solvent structure when the entering group, leaving group and nonlabile ligands are all kept invariant, attributed Bennetto and Caldin's correlations to the outer-sphere complexation step.

We shall now briefly return to the question of the validity of predictions based on Eq. 6 and 7. We have seen that such predictions are in reasonable agreement with experimental values of $k_{\ell,f}$ for relatively simple unidentate ligands in a variety of solvents, but that predicted values for certain multidentate ligands in a number of solvents are seriously in error. For phenanthroline and particularly for bipyridine and terpyridine in dimethylsulfoxide, the effective value of f in Eq. 6 is much smaller than that based on a priori considerations. In contrast, for phenanthroline in most other organic solvents studied, the value of K_{12} is significantly larger than that calculated from Eq. 7. A further illustration of the limitations of Eq. 6 and 7 is provided by Table 10 in which observed rate constants are compared with predicted values for NiS_6^{2+} and $NiClS_5^+$ in S = methanol. From our previous discussion it is evident that the good agreement for the reaction of NiS_6^{2+} with phenanthroline is the result of fortuitous cancellation of errors in the calculated value. The rates of reaction of $NiClS_5^+$ with all incoming ligands, but particularly the multidentate ligands, are much lower than predicted. Factors contributing to the stability of the outer-sphere complex of NiS_6^{2+} and the proper orientation of the ligand in it (ion-dipole interaction and hydrogen bonding to the polarized methanol molecules of the inner sphere) are much less effective in

TABLE 9. Accelerating effect of anionic inner-sphere substituents (X) on rates of reactions of nickel(II) with various incoming ligands (Y) in methanol and acetonitrile

Y	X	Methanol			Acetonitrile			
		$\log k_{Ni}$	$\log k_{NiX}$	$\log N^a$	$\log k_{Ni}$	$\log k_{NiX}$	$\log N^a$	$\log (N_{AN}/N_{M})$
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	Cl	1.6	2.8	1.2	3.38	6.3	2.9	1.7
	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$_3$					4.4	1.0	

$^a N = k_{NiX}/k_{Ni}$.

TABLE 10. Experimental values of the ratio $k_{\ell,f}/k_s$ for the reactions of NiS_6^{2+} and $NiClS_5^+$ with various incoming ligands Y in S = methanol

Y	log $(k_{\ell,f}/k_s)$[a]	
	NiS_6^{2+}	$NiClS_5^+$
4-Phenylpyridine	-0.9	-1.4
Phenanthroline	-0.2	-2.2
Bipyridine	-1.0	-2.1
Terpyridine	-1.4	-2.5
(All Y [b]	-0.4	-0.4)

[a] Value of k_s is from Ref. 66.

[b] Value predicted by Eq. 6 and 7 for the following conditions: solvent exchange is rate limiting, and no interaction occurs between the ligand in the outer sphere and either the metal ion or the inner sphere.

the case of $NiClS_5^+$. Introduction of chloride into the inner sphere generates inhibition to coordination similar to that encountered when methanol is replaced by a stronger donor solvent, such as dimethylsulfoxide.

A recurring theme throughout this paper has been the demonstrated or expected influence of the donor strength of the solvent on the kinetics of formation of metal complexes. It should be noted that the correlation between kinetic parameters and donor strength is not a simple one, because the kinetics are also strongly influenced by steric and other factors. A much simpler correlation exists between _dissociation_ kinetics and donor strength, as shown by Hoffmann (67). The best guide to the donor strengths of solvents that is presently available is provided by the donor numbers (Ref. 26 and Table 2), but caution must be exercised that these numbers are not used indiscriminately for purposes for which they were not intended. Donor numbers represent the $-\Delta H°$ values (in kcal mol^{-1}) for the reactions of the donors with antimony pentachloride in 1,2-dichloroethane as solvent. Consequently, they will not necessarily apply to such acceptors as nickel(II) ion. For example, the electronic spectra of nickel(II) ion in acetonitrile-propylene carbonate mixtures show that the former solvent is a much better donor towards nickel than the latter, which is the opposite order of that of the donor numbers. Furthermore, it is difficult to adjust donor numbers to the effective values for pure solvents, particularly for those solvents possessing extensive order. It would be desirable to evaluate the enthalpies and entropies of transfer of nickel(II) and similar ions from one solvent to another, preferably based on the extrathermodynamic assumption (Ref. 64) that the transfer energies of tetraphenylarsonium and tetraphenylborate ions are equal.

SUMMARY

1. In aqueous solution, the kinetics of many reactions between metal ions and ligands of different chemical types depend only slightly on the nature of the ligand and are best represented by a dissociative interchange (I_d) mechanism in which rapid formation of an outer-sphere complex precedes the rate-determining step which is loss of a solvent molecule from the inner-coordination sphere of the metal.

2. In nonaqueous solvents, a broad spectrum of kinetic properties has been observed. While the kinetics of all ligands studied can still be accomodated within the framework of a general I_d mechanism, it is necessary to incorporate additional features to account for the strong ligand dependence observed. While the simple unidentate ligands react in a straight-forward manner, as in water, certain multidentate ligands in certain solvents react either slower or faster than the "norm" established by unidentate ligands. For example, the rate of reaction of 2,2',2"-terpyridine with nickel(II) ion in dimethylsulfoxide at 25°C is 60 times lower than the norm, while that of 5,6-dimethylphenanthroline in acetonitrile is 70 times higher than the norm. Corresponding deviations occur in the activation parameters.

3. We propose that these deviations from the norm originate mainly in the outer sphere. Both the stability of the outer-sphere complex and the orientation of the ligand in the outer sphere are important. Both factors are influenced by (a) the effective positive charge on

the metal ion, which in turn is determined by the donor strength of the solvent, (b) the interaction distance between the ligand and the metal ion, which is determined by the thickness and openness of the inner sphere and the steric requirements of the ligand, and (c) competition between the ligand and solvent in the outer sphere, in which any specific interaction (e.g., hydrogen bonding) of the ligand with the polarized solvent molecules of the inner sphere will be important. The kinetic properties of 2-phenylpyridine show that coordination of a flexible multidentate ligand such as 2,2'-bipyridine can occur only when the two rings are in the cis position, so that both donor atoms will coordinate essentially simultaneously. Formation of just one bond, when the second ring is out of the cis orientation, is subject to severe steric hindrance. One result is that bipyridine reacts more slowly than the rigid ligand 1,10-phenanthroline in all solvents, the difference between the two ligands being the smallest in water, in which the proper orientation of bipyridine undoubtedly is promoted by hydrogen bonding to the inner sphere. In dimethylsulfoxide, which is a strong donor and has bulky molecules, the reactivity of bipyridine and similar ligands is inhibited because factors (a), (b) and (c) are all unfavorable. In acetonitrile and propylene carbonate, which are weak donors and in which the inner spheres are relatively open, the reaction rate of phenanthroline in particlar is strongly promoted.

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