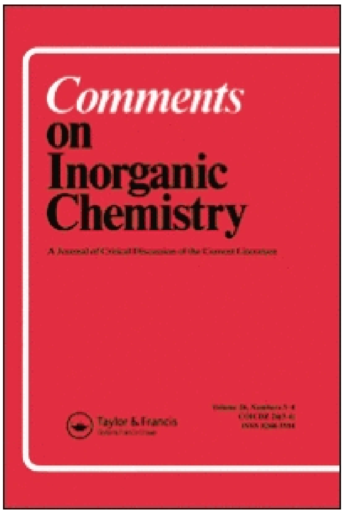

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Mechanisms of Ligand Replacement in Octahedral Nickel(II) Complexes-an Update

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Mechanisms of Ligand Replacement in Octahedral Nickel(II) Complexes—an Update

The present status of the mechanisms of complexing of nickel(II) is discussed. The influence of the entering ligand, and of ligand other than water, coordinated to the nickel is assessed. Results with other solvents are described and a comparison with other metal ions is made.

INTRODUCTION

The first measurements of the rates of reaction of nickel(II) complexes with ligands were carried out in the early 1950's by using alcoholic solutions at $-75°C$.[1] Advantage was thereby taken of the slower rates to use conventional monitoring, an approach which has been successfully exploited in recent years, particularly by biochemists.[2] Nickel(II) has become the labile metal ion system of choice for several reasons. It forms a large number and variety of stable complexes. The rates of formation or dissociation of nickel(II) complexes are rarely too fast for measurement by flow or even in some cases by conventional methods. This author carried out with Dr. Ahmed the first stopped-flow experiments on the acid dissociation of nickel(II) ammine complexes.[3] Quentin Gibson was Professor of Biochemistry at the University of Sheffield, and we were fortunate to have access to his stopped-flow apparatus, the design of which in a modified form is still used in the Dionex commercial model. We were concerned with reactions of the type

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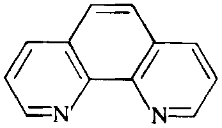
$Ni(H_2O)_6^{2+}$ +  $\rightleftharpoons Ni(H_2O)_4phen^{2+} + 2H_2O \quad k_f, k_d, K.$ (1)

From the study of just a few systems involving neutral ligands, it became apparent that the variation in stability of nickel complexes [K in Eq. (1)] resided mainly in variation of dissociation rate constants (k_d). The formation rate constants ($k_f = Kk_d$) were thus approximately constant for different complexes. The full import of this was shown by Eigen.[4] From an examination with Tamm[5] of the ultrasonics of the nickel–sulfate and other metal–sulfate systems, it was considered that complex formation took place through an intermediate outer-sphere complex which transformed to an inner-sphere complex. Generally, the replacement of water in the $Ni(H_2O)_6^{2+}$ ion* by a unidentate ligand, L^{n-}, could be represented

$$Ni(H_2O)_6^{2+} + L^{n-} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \underset{\text{outer-sphere complex}}{Ni(H_2O)_6 \cdot L^{(2-n)+}} \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \underset{\text{inner-sphere complex}}{Ni(H_2O)_5L^{(2-n)+}} + H_2O. \qquad (2)$$

If the outer-sphere complex is in relatively small concentration and very rapidly formed (both reasonable assumptions) the second-order formation rate constant k_f is

$$k_f = \frac{k_{12}}{k_{21}} k_{23} = K_{12} \cdot k_{23}. \qquad (3)$$

For similarly charged ligands, the outer-sphere complexity constants K_{12} are likely to be similar. Also, since k_{23} is an approximate constant for all systems, being related to the water-exchange rate constant for $Ni(H_2O)_6^{2+}$ ion, the constancy of k_f for a particular ligand type would then be understandable. This mechanism is now termed I_d, indicating a rate-determining $H_2O - L^{n-}$ interchange in the outer-sphere complex.

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*The hexahydrated nature of the nickel(II) ion in solution has been established by NMR peak area techniques[6] and by a neutron scattering technique in concentrated nickel salt solutions.[7]

In addition, it is thought that there is little bonding by the entering ligand or departing H_2O in the I_d transition state (dissociative).[8]

The mechanism represented in (2) was given substantial support as the result of a comprehensive compilation of all kinetic data available up to 1964,[9] and later by a review of octahedral nickel(II) substitution behavior.[10] This account is an update. The rate of complexing of Ni^{2+} ion with some 250 different ligand species has been measured[11] and nickel is still a favorite metal ion for the study of new fast reaction equipment, unusual ligand systems, nonaqueous solvation effects, micellar behavior, and so on. This popularity stems from the established dissociative mechanism† for substitution in nickel(II) in spite of, or perhaps because of, well-intentioned attempts to weaken it!

EXAMINATION OF EQUATION 3

The rate constant k_{23} can be considered to be close to that for H_2O exchange with the species $Ni(H_2O)_6L^{(2-n)+}$ in (2). Apparently, the latter exchange differs little in its kinetic characteristics from that of the free $Ni(H_2O)_6^{2+}$ ion, at least with $L^{n-} = SO_4^{2-}$ (Refs. 5 and 12), $CH_3PO_4^{2-}$ (Ref. 13) and $CH_3CO_2^-$ (Ref. 14), so that k_{23} is identified with k_s in (4):

$$Ni(H_2O)_6^{2+} + H_2{}^*O \underset{k_s}{\overset{k_s}{\rightleftharpoons}} Ni(H_2O)_5(H_2{}^*O)^{2+} + H_2O, \qquad (4)$$

a process which has been thoroughly studied by NMR line broadening methods.[6,15,16] The latest kinetic parameters for (4) and the corresponding values in some other solvents are collected in Table I.[16] Recently a major effort has been directed towards measurement of the effects of pressure on NMR-measured solvent exchange rate constants for a number of metal ions.[16] The sign and magnitude of the values for $\Delta V^{\neq}$ (Table I) are indicative of an I_d (dissociative) mechanism. The low $\Delta V^{\neq}/V_s^{\circ}$ ratio, where V_s° is the partial molar volume of the exchanging solvent, indicates an interchange mechanism rather than a fully disso-

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†This mechanism has been named the Eigen, Eigen–Wilkins, Eigen–Tamm and even Eigen–Wilkins–Tamm mechanism. The name is relatively unimportant, but references to the key papers by Eigen and Tamm[5] and by Eigen and Wilkins[9] would seem appropriate in a mention of the mechanism.

TABLE I
Rate parameters for the solvent exchange on nickel(II)[16]

Species	$k_s^{298^\circ}$ (s^{-1})	$\Delta H^{\neq}$ kJ M^{-1}	$\Delta S^{\neq}$ J $K^{-1}M^{-1}$	$\Delta V^{\neq}$ cm^3M^{-1}	$\Delta V^{\neq}/V_s^\circ$
$Ni(H_2O)_6^{2+}$	3.2×10^4	57	+32	+7.2	0.40
$Ni(CH_3OH)_6^{2+}$	1.0×10^3	66	+34	+11.4	0.28
$Ni(CH_3CN)_6^{2+}$	2.8×10^3	64	+37	+9.6	0.18
$Ni(DMF)_6^{2+}$	3.8×10^3	63	+34	+9.1	0.12

ciative (D) mechanism, when $\Delta V^{\neq}/V_s$ would be near unity. The interpretation of $\Delta V^{\neq}$ values for solvent exchange is relatively straightforward because of the absence of electrostrictive effects.[16,17]

The assessment of an accurate value for the preassociation constant K_{12} in (3) is less easy. The theoretical relationship may be used:

$$K_{12} = \frac{4\pi N_0 a^3}{3000} \exp\left[-U(a)/kT\right], \tag{5}$$

where $U(a)$ is the Coulomb interaction.[18,19] It does not take into account specific interactions within the outer-sphere complex. In certain nickel(II)–ligand systems[5,12–14] it has been possible to determine values for K_{12} and k_{23} separately from relaxation experiments. These are in reasonable agreement with those expected from application of (5) and from the value of k_s, respectively. A value for $K_{12} = 0.1 - 0.2\ M^{-1}$ for neutral ligands can be estimated from (5) (by setting the exponential term equal to unity) as well as from consideration of random collisions.[20]

The second-order rate constants k_f for the formation of nickel(II) complexes with most unidentate ligands can therefore be rationalized quite well in terms of (3).* Table II shows some representative examples.[11,14,22,23] More complete lists are given elsewhere.[11,21] The activation parameters are also generally consistent with those expected on the basis of (3), being close to those for solvent exchange.

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*Strictly, a factor f should also be incorporated with K_{12}, this being the probability that L^{n-} will enter a particular solvent-vacated site. A value 0.75 is often used but is of secondary consideration, considering the problem in assessing K_{12}.

TABLE II

Rate parameters for the reaction of $Ni(H_2O)_6^{2+}$ with unidentate ligands L^{n-} at 25°C

L^{n-}	$10^{-3}k_f$ $M^{-1}s^{-1}$	Remarks	Ref.
$CH_3CO_2^-$	300	P- and T-jump data lead to value $k_{23} = 1.5 \times 10^4 s^{-1}$	14,22
C_5H_5N	3.6	Using $k_{23} = 3 \times 10^4$, $K_{12} = 0.12$	23
NH_3	4.5	Using $k_{23} = 3 \times 10^4$, $K_{12} = 0.15$	11
$(CH_3)_2NH$	0.33	Steric effects, reducing K_{12}	11
$Ru(NH_3)_5pyz^{2+}$	1.1	Suggests 2+ charge delocalized	11

THE FORMATION OF CHELATE COMPLEXES

The kinetics of reaction of nickel(II) has been most investigated with bidentate ligands.[11] If we represent a neutral bidentate ligand by L–L, the inner-sphere complex with one end of the ligand free by $(H_2O)_5Ni\text{-}L\text{-}L^{2+}$ and the final chelated product as $Ni(L_2)^{2+}$, then mechanism (2) for unidentates can be easily extended to Eq. (6) for bidentates. Assuming (6a) is very rapid, and that stationary state conditions obtain for the intermediates, Eq. (7) is obtained.

$$(H_2O)_6Ni^{2+} + L\text{–}L \rightleftharpoons (H_2O)_5Ni(H_2O)L\text{–}L^{2+}, \quad K_{12} \tag{6a}$$

$$(H_2O)_5Ni(H_2O)L\text{–}L^{2+} \rightleftharpoons (H_2O)_5Ni\text{–}L\text{–}L^{2+} + H_2O, \quad k_{23}, k_{32} \tag{6b}$$

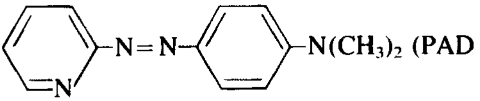
$$(H_2O)_5Ni\text{–}L\text{–}L^{2+} \rightleftharpoons (H_2O)_5Ni\ (L_2)^{2+} + H_2O, \quad k_{34}, k_{43} \tag{6c}$$

$$d[Ni(L_2)]/dt = k_f\,[Ni(H_2O)_6^{2+}]\,[L\text{–}L] - k_d\,[Ni(L_2)],$$

$$k_f = \frac{K_{12}k_{23}k_{34}}{k_{32} + k_{34}} \qquad k_d = \frac{k_{32}k_{43}}{k_{32} + k_{34}}. \tag{7}$$

The factor k_{34}/k_{32} dominates chelate formation.[10] If it is greater than unity then $k_f = K_{12}k_{23}$, first-bond formation (6b) is rate determining and the situation is akin to unidentate ligands. If, however, $k_{34}/k_{32} < 1$, the rate determining step is ring closure and an additional complication is introduced into rationalizing k_f. It is difficult to detect $k_{34} <$

k_{32} except by the examination of k_f together with estimated K_1 and k_{23} values. For a large number of Ni(II)-bidentate ligand systems, it is clear that $1 \geqslant k_{34}/k_{32} \geqslant 0.1$.[6,10,11,21] Observations such as $\Delta V^{\neq}$ for reaction of Ni^{2+} with murexide[24] or PAD[25] being similar to $\Delta V^{\neq}$ for solvent exchange (Table I) are also supportive of a mechanism (6) with $k_{34} \gtrsim k_{32}$. *Direct* evidence for the latter relationship with the Ni^{2+}–PAD system was obtained in some recent ingenious experiments.[26] Photochemical perturbation of the system at equilibrium generates sufficiently high concentrations of $(H_2O)_5Ni–L–L^{2+}$ that a relaxation involving its ring closure (6c) can be observed following the perturbation.


(PAD = L–L).

Armed with the ring closure rate constant and kinetic data for the overall equilibrium (from temperature-jump and flow experiments), it is possible to estimate values for the various rate constants:

$$K_{12}k_{23} = 1.5 \times 10^3 M^{-1}s^{-1}, \qquad k_{32} = 1.4 \times 10^4\ s^{-1},$$

$$k_{34} = 2.9 \times 10^4\ s^{-1}, \qquad k_{43} = 0.3\ s^{-1}.$$

(The stability constant of the unidentate bound PAD ($K_{12}k_{23}/k_{32} = 0.1\ M^{-1}$) does appear disturbingly low.) Obviously, k_f is still dominated by k_{34}, the rate constant for water loss from the metal ion.

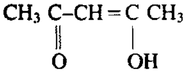
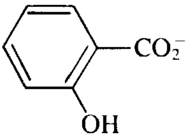
In the formation of complexes with multidentate ligands, the rate determining step is unlikely to be *after* first or second bond formation, because of the small value for k_{43} (breaking open a chelate ring) and the likelihood that $k_{45}/k_{43} > 1$. The formation of the first Ni–N bond is therefore rate limiting in complexation with $trienH^+$ and $tetraenH_2^{2+}$. The kinetic interest with these systems might very well be in the subsequent transformation of isomers (2,3,2-tet = $H_2N(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2$)[27]:

$$\begin{array}{lll} Ni^{2+} + 2,3,2\text{-tet} & \overset{\text{rapid}}{\rightleftharpoons} & \textit{cis}\text{-}Ni(2,3,2\text{-tet})\ (H_2O)_2^{2+}, \\ & & \textit{trans}\text{-}Ni(2,3,2\text{-tet})\ (H_2O)_2^{2+}, \qquad (8) \\ & \overset{\text{slow}}{\rightleftharpoons} & \\ & \underset{\text{rapid}}{\rightleftharpoons} & \text{planar } Ni(2,3,2\text{-tet})^{2+}. \end{array}$$

Many different types of bidentate ligands do not conform well to the behavior expected from Eq.(7). Some of these are shown in Table III.[11,28–31] The high rate constants for reaction of aliphatic diamines has been long recognized and a reasonable explanation offered in terms of an internal conjugate base mechanism.[11] *Lower* than anticipated rate constants are, however, more commonly encountered, and may reside in low k_{34}/k_{32} values. Closing of six-membered chelate rings as in diketones and β-aminoacid complexes (Table III) appears difficult and leads to low k_f values ("sterically-controlled" or "chelation-controlled" substitution[11]). Protonation of a ligand may have a small effect (arising from increased positive charge and a lowered value for K_{12}) or a profound influence on its reactivity towards Ni(II). The need to break internal hydrogen bonds during the formation of a complex, either at the very start or during progress of chelation, will produce low rate constants.[32] The rate constant for reaction of uninegative salicylates[30] with $Ni(H_2O)_6^{2+}$ is as low as 70 $M^{-1}s^{-1}$. Even more remarkably, that for the reaction [31] of H_2DOTA^{2-} is ~10 $M^{-1}s^{-1}$ (Figure 1). With both ligands, the need to rupture strong internal hydrogen bonding is pre-

TABLE III

Rate parameters for the reaction of $Ni(H_2O)_6^{2+}$ with selected bidentate ligands at 25°C

Ligand	$k_f(M^{-1}s^{-1})$	Ref.
$H_2N(CH_2)_2NH_2$	3.5×10^5	28
 $CH_3\,\underset{\underset{O}{\|}}{C}-CH=\underset{\underset{OH}{\mid}}{C}\,CH_3$	19.3	29
$H_2N(CH_2)_2CO_2^-$	4.1×10^4	11
$H_2N(CH_2)CO_2^-$	5.0×10^3	11
	70 $(6.3 \times 10^4)^a$	30
H_2DOTA^{2-}	~10	31

[a] Reaction with $NiOH^+$.

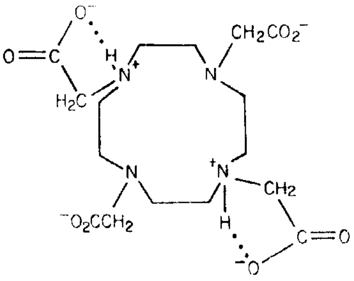
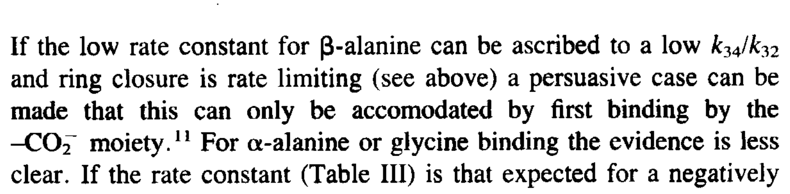


FIGURE 1 H_2DOTA^{2-}

sumably the basis for their low reactivity. The release of the blocking H^+ in salicylates is aided when reaction with $NiOH^+$ is studied, and much nearer normal rate constants are observed[30] (Table III). Incidentally, in few studies has an enhanced effect for the monohydroxonickel(II) species been observed (or needed consideration).

The zwitterionic form of aminoacids is relatively unreactive.[33] The reasons for this have been discussed.[34,35] It is concluded that rate-limiting ring closure is not the cause.[35] One of the problems is in the correct assignment for ionization constants for transient species or (below) the estimation of rate constants for normal behavior. A different approach will almost certainly be necessary to resolve the differences. Aminoacids represent an important class of unsymmetrical ligands where two sequences of chelation are possible[10]:



$$\begin{tikzcd}
 & (H_2O)_5Ni\text{-}NH_2CH_2CO_2^+ \arrow[dr] & \\
(H_2O)_6Ni^{2+} + H_2NCH_2CO_2^- \arrow[ur, leftrightarrow] \arrow[dr, leftrightarrow] & \text{Path A} & (H_2O)_4Nigly^+ \\
 & (H_2O)_5Ni\text{-}OCOCH_2NH_2^+ \arrow[ur] & \\
 & \text{Path B} &
\end{tikzcd} \qquad (9)$$

If the low rate constant for β-alanine can be ascribed to a low k_{34}/k_{32} and ring closure is rate limiting (see above) a persuasive case can be made that this can only be accomodated by first binding by the $-CO_2^-$ moiety.[11] For α-alanine or glycine binding the evidence is less clear. If the rate constant (Table III) is that expected for a negatively charged ligand, this suggests that fruitful attack is from the nitrogen end of the aminoacid.[10] If the rate constant is lower than that anticipated from the operation of an internal conjugate base mechanism, then again path B is more likely, although path A cannot be ruled out.[11] *Again*, surmise will have to be replaced by ingenious experimentation to solve these interesting problems.

EFFECT OF SUBSTITUENTS ON REPLACEMENT RATES

Substituting water in the nickel(II) ion by other ligands will affect the rates and mechanisms of further substitution.[6,10,11,36] Coordinated NH_3 or polyamines appear to have the largest accelerating influence. There is, in fact, a linear correlation between log k_f and the number of nitrogen donor atoms coordinated to the nickel.[11] The effect resides largely in the value for k_{23} ($= k_s$) (Table IV).[11,37,38] Other coordinating groups such as carboxylates in aminoacids and polyaminocarboxylates, heterocycles, pyridine[23] and bipyridine, etc. have much less labilizing influence (Table IV). Eq. (3) or (7) is applicable, but the calculation of K_{12} is difficult since the reacting nickel complex is nonspherical and the distribution of charge in it is nonuniform.[11]

An interesting perturbation of the value of K_{12} is displayed by some aromatic ligands.[10] It is considered[39] that there is a "stacking" interaction of an incoming terpyridine molecule with the complex $Ni(terpy)(H_2O)_3^{2+}$ enhancing the "usual" K_{12} value from ~0.1 to ~4 M^{-1}, and thereby increasing the rate constant for formation of $Ni(terpy)_2^{2+}$. This phenomenon may have analogies in biological systems for positioning substrates. The whole question of the effects of bound ligands on metal ion reactivity towards entering ligands is pertinent to metalloproteins. With the latter, the generally unusual geometry

TABLE IV

Water exchange rate constants (s^{-1}) of a number of nickel(II) complexes[11,37,38]

Complex^{2+}	$10^{-5}k_s$	Complex^{2+}	$10^{-5}k_s$
$Ni(H_2O)_5NH_3$	2.5	$Ni(H_2O)(NH_3)_5$	43
$Ni(H_2O)_4(NH_3)_2$	6.1	$Ni(H_2O)_4bipy$	0.49
$Ni(H_2O)_3dien$[a]	34, 4.4	$Ni(H_2O)_3terpy$	0.52
$Ni(H_2O)_2trien$	5.7	$Ni(H_2O)EDTA^{2-}$	7.2
$Ni(H_2O)tetraen$	112		

[a] Two kinetically different waters (two H_2O's fast, one H_2O slow)

of the metal site and the nature of the local solvent environment may make extrapolation of ideas and rules obtained with simple metal complexes difficult.

SOLVENTS OTHER THAN WATER

Nickel ion has proved the most popular of the labile ions for studies in a variety of solvents. The solvent exchange rate constants k_s,

$$\mathrm{NiS_6^{2+}} + {}^*\mathrm{S} \rightleftharpoons \mathrm{NiS_5{}^*S^{2+}} + \mathrm{S}\ k_s, \tag{10}$$

are surprisingly insensitive to the nature of the solvent (Table I).[21,40] The $\Delta V^{\neq}$ values suggest that the I_d mechanism persists in all solvents so far examined.[16] In net substitution by unidentate ligands, the experimental values of k_f agree quite well with those estimated on the basis of (11)[6,21,40]:

$$k_f = 0.75\ K_{12}k_s. \tag{11}$$

For reaction with bidentate and terdentate ligands, the k_f values calculated from (11) may be larger, smaller and (occasionally!) very similar to those determined experimentally. The ligands thus show much greater specificity than in water.[6,21,40,41] The reasons for this are far from clear. In some solvents (DMF)[25,42] or solvent mixtures (DMSO–H_2O),[43] Eq. (11) is well obeyed. On the other hand, the rate constants in DMSO may be as much as 60 times smaller, and in CH_3CN 70 times larger, than predicted.[21] All possible culprits for this disagreement have been blamed. There is difficulty in assessing a reasonable value for K_{12}.[21] In nonaqueous solvents, it may be incorrect to equate k_{23} with k_s.[40] Finally, it is possible that ring closure may be rate limiting, especially when one considers that the unidentates behave quite well. The overwhelming consensus is still towards an I_d mechanism but it is apparent that the simplicity of behavior in water (which may be more imagined than real) has disappeared in nonaqueous solution.

Striking support[44] for a dissociative mechanism for ligand exchange at octahedral nickel in chlorobenzene is provided by a comparison of the activation parameters for the two processes [Eqs. (12a) and (12b)] (bbh = biacetyl bis(α-hydroxybenzylidene)hydrazone^{2-}):

$$\mathrm{Ni(bbh)L_2} \overset{k_a}{\rightleftharpoons} \mathrm{Ni(bbh)L} + \mathrm{L} \rightleftharpoons \mathrm{Ni(bbh)} + \mathrm{L}, \qquad (12a)$$

octahedral square planar

$$\mathrm{Ni(bbh)L_2} + {}^*\mathrm{L} \rightleftharpoons \mathrm{Ni(bbh)L} * \mathrm{L} + \mathrm{L}. \quad k_{\mathrm{exch}} \qquad (12b)$$

The octahedral to square-planar interconversion was measured by microwave temperature-jump.[45] The data were consistent with the first loss of L being rate determining (k_a). The exchange was measured by ^{14}N-NMR line broadening.[44] The agreement of k_{exch}, $\Delta H^{\neq}_{\mathrm{exch}}$ and $\Delta S^{\neq}_{\mathrm{exch}}$ with the corresponding values for k_a (Table V) for L = py and (poorer) with 2-Mepy are direct evidence for a dissociative mechanism for the ligand exchange.[44]

Attempts are now being made to differentiate solvent effects into those arising from ground state changes and those from activated complex effects, using water-rich mixed solvents.[43,46] This direction, although tedious, must help with the understanding of the solvent role, as is illustrated below.[47]

OTHER METAL IONS

In 1970, we[10] wrote "The values of k_f are appreciably constant for a particular (bivalent) metal ion and are sensibly related to the corresponding k_s, except for the case of Mn(II)." From the values of $\Delta V^{\neq}$ for solvent exchange (Table VI) it is suggested that bivalent first-row

TABLE V
Rate constants and activation parameters for ligand exchange by examination of reactions (12a) and (12b)[44,45]

Reaction	k $\mathrm{s^{-1}}$	$\Delta H^{\neq}$ kJ M^{-1}	$\Delta S^{\neq}$ J $M^{-1}K^{-1}$
(12a), L = py	3.0×10^4	66	63
(12b), L = py[a]	3.0×10^4	62	50
(12a), L = 2-Mepy	4.0×10^5	43	8
(12b), L = 2-Mepy[a]	9.0×10^5	55	56

[a] 20% py or 2-Mepy in C_6H_5Cl; minor effects of solvent change from 100% py or 2-Mepy.

TABLE VI
Rate parameters for water exchange of bivalent metal ions[16]

Species	k_s^{298} (s^{-1})	$\Delta H^{\neq}$ kJ M^{-1}	$\Delta S^{\neq}$ $JK^{-1}M^{-1}$	$\Delta V^{\neq}$ cm^3M^{-1}	$\Delta V^{\neq}/V_s^0$
$V(H_2O)_6^{2+}$	87	62	0	-4.1	-0.23
$Mn(H_2O)_6^{2+}$	2.1×10^7	32	$+6$	-5.4	-0.30
$Fe(H_2O)_6^{2+}$	4.4×10^6	41	$+21$	$+3.8$	$+0.21$
$Co(H_2O)_6^{2+}$	3.2×10^6	47	$+37$	$+6.1$	$+0.34$
$Ni(H_2O)_6^{2+}$	3.2×10^4	57	$+32$	$+7.2$	$+0.40$

transition metal ions show a gradual mechanism changeover along the series, the early members exchanging by an I_a mechanism (negative $\Delta V^{\neq}$), iron by an I mechanism, and cobalt and nickel by I_d mechanism (positive $\Delta V^{\neq}$).[16] The changeover is best documented for aqueous solution but is duplicated in CH_3OH and CH_3CN solvents.[16] However, attention has been drawn[47] to the fact that the partial molar volumes (V^0) of Mn^{2+}, Fe^{2+}, Co^{2+} and Ni^{2+} aquated ions being respectively, -17.4, -25.3, -25.4 and -28.4 $cm^3 M^{-1}$, this leads to partial molar volumes of the activated complex ($V^0 + \Delta V^{\neq}$) of -22.8, -21.5, -19.3 and -21.3 $cm^3 M^{-1}$, respectively, i.e., appreciably constant. Thus, significantly, the trends in $\Delta V^{\neq}$ in the Mn^{2+}–Ni^{2+} series reside in changes in the *initial state*, and the activated complexes resemble each other closely.[47] Obviously, the last word on the detailed mechanism of solvent exchange with solvated metal ions has not been written.

Nevertheless, we have reached the comfortable state where a knowledge of the water exchange rate for a metal ion allows us to make a fair estimate of the rate of constant for its ligand binding, even where there is evidence for associative character to the substitution.[11] We can

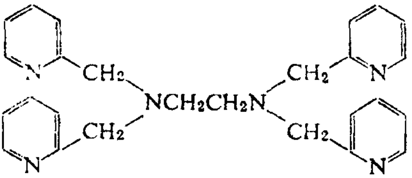


FIGURE 2 TPEN

TABLE VII
Rate constants ($M^{-1}s^{-1}$, 25°C, $I = 0.3M$) for reactions of LH^+ and L[49]

Metal ion	LH^+	L	$-\log k_{LH^+}/k_s$
Zn^{2+}	7.5×10^5	—	2.8
Mn^{2+}	3.7×10^4	—	2.7
Fe^{2+}	1.9×10^4	—	2.4
Co^{2+}	1.3×10^4	8.5×10^4	2.4
Ni^{2+}	6.0×10^2	2.1×10^3	1.7

illustrate this with recently obtained stopped-flow data for the rates of reaction of five transition metal ions with the powerful ligand TPEN (Figure 2).[48] The results (Table VII) show that there is an almost constant ratio for $k\ (LH^+)/k(H_2O)$ exchange. The rate constants for reaction of Ni^{2+} with LH^+ and L are close to those for enH^+ and NH_3[11] and suggest that water exchange on the metal ion plays a dominant role in the substitution even with this multidentate ligand.[49]

CONCLUSIONS AND FUTURE DIRECTIONS

It is gratifying that a number of ideas developed some years ago remain approximately correct. The last decade has seen increasing interest in redox, rather than substitution, reactions involving the labile transition metal ions. This is occasioned by the lively interest in electron-transfer metalloproteins and the strongly developed theoretical ideas.[50] The same interest in ligand binding to metallosites has not yet developed, and may have to await studies of substitution of metal ions with coordination numbers other than regular octahedron, as well as results in nonaqueous solution. There is an increasing interest in the study of complexing in micellar systems and in the presence of different cationic and anionic polyelectrolytes.[51] Nickel(II)–ligand systems are often used to probe the specific interactions present in these solutions.[52] The variety of sites presented by many ligands of biological interest (e.g., nucleotides) can be explored by kinetic studies, complementing thermodynamic data.[53] Finally, the detailed mechanism of complexing by the macrocycle ligands needs elucidating, possibly with fresh approaches.[54]

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