sequence like (38) and (39) but involving CO_2 rather than O_2 is also a possibility.

This application of recent laboratory negative ion reaction measurements to the D-region ion chemistry involves the full utilization of present laboratory capability. Reactions of several "nonsimple" ions, O_2^-, O_4^-, CO_3^-, CO_4^-, and NO_2, are required and these ions need to be allowed to react with the "difficult" neutrals O and O_3. It is only in the past few years (since 1967) that such laboratory measurements have been achieved.

Gas-Phase Organic Chemistry

An important application of the flowing afterglow technique to negative ion studies which is not discussed in this review is the application to gas-phase organic reactions. Two postdoctoral fellows working in our laboratory, D. K. Bohme and L. B. Young, have amply demonstrated the value of this approach (ref 14 and other papers submitted for publication). Quantitative reaction rate constants can be readily obtained for such ions as O^-, OH^-, $C_3H_3^-$, $C_4H_7^-$, CH_3O^-, $(CH_3)_2CHO^-$, $C_6H_5^-$, $C_6H_5C(CH_3)_2^-$, etc., with organic (and other) neutrals having appreciable vapor pressures. A wealth of detail concerning kinetic mechanisms and energetics can then be obtained. This work is not being continued at ESSA, our only purpose in the work done so far being to demonstrate the potential of the technique to a field other than our own. Dr. Bohme will be continuing this work in the chemistry department at York University in Toronto.

Summary

Some results of quantitative studies of negative ion reactions with neutrals by the recently developed flowing afterglow technique have been discussed. The versatility of the method allows a wide variety of reactants to be investigated. The laboratory study of associative-detachment reactions has been opened up by this technique. The results obtained to date have contributed some information on negative ion energetics and mechanisms and have played a key role in advancing our understanding of D-region ionospheric chemistry. As the measurements are digested and extended it is to be anticipated that our theoretical understanding will be increased and other areas of application such as gas discharges, combustion, and radiation chemistry will become involved.

Mechanisms of Ligand Replacement in Octahedral Nickel(II) Complexes

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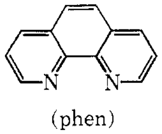
The replacement of one ligand coordinated to a metal center by another free ligand in solution is a fundamental process which permeates all aspects of coordination chemistry. The substitution of a coordinated solvent molecule, usually water, by another complexing molecule is the basis of the *formation* of metal complexes, while the reverse process is variously referred to as *hydrolysis*, *aquation*, or *dissociation*. These are illustrated in eq 1, with k_f representing the second-order formation rate constant and k_d, the first-order dissociative rate constant. The *direct* replacement of one ligand by another, without intervention of solvent molecules, appears not to be important with octahedral complexes, with which we are concerned in this Account. The replacement of coordinated by free solvent molecules (*solvent exchange*) is therefore a key process in our understanding of these replacement reactions.

$Ni(H_2O)_6^{2+}$ +



(phen)

$\rightleftarrows$ $Ni(H_2O)_4phen^{2+}$ + $2H_2O$ k_f, k_d, K (1)

Most of the early kinetic studies of substitution were concerned with the inert Co(III) complexes which Werner had so well characterized and which usually underwent reaction at conveniently measured rates. Taube's review in 1952[1] drew attention to the wider world of *labile* octahedral complexes of transition metals and to reactions which were complete within mixing time. Although the survey was based almost exclusively on qualitative observations taken from the literature, nevertheless, important conclusions relating to reactivity and electronic configuration of the complex ion could be made.[2] The collection of quantitative

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(1) H. Taube, *Chem. Rev.*, **50**, 69 (1952).

(2) The relevance of electronic configuration to the reaction rate was appreciated by others at about the same time, albeit with a quite restricted series of transition metals.[3,4]

(3) A. W. Adamson, J. P. Welker, and W. B. Wright, *J. Amer. Chem. Soc.*, **73**, 4786 (1951); A. W. Adamson, *ibid.*, **73**, 5710 (1951).

(4) J. Bjerrum and K. G. Poulsen, *Nature*, **169**, 463 (1952).

data for a large number of the rapidly reacting bivalent and tervalent transition metal complexes of the V–Zn group had to await the exploitation of existing flow methods as well as the development of new relaxation techniques, particularly by Eigen and his school at Göttingen.[5]

The decade of the 60's has produced much information.[5–12] The most important, and probably the only unequivocal, conclusion which emerges is: *the mechanisms of replacement reactions of octahedral complexes (both labile and inert) are dissociative in character, and in these bond breaking takes precedence over bond making.* However, there is strong support for further refinements.

The study of Ni(II) complexes has played an important role in our understanding of replacement mechanisms. Ni stands in about the same relation to the labile complexes as does Co(III) to the inert group. The complexes have been well characterized thermodynamically and spectrally. There is no interference from reduction or oxidation possibilities, and being a d^8 system, Ni is among the least reactive (and therefore the easiest to study experimentally) of the labile group. This characteristic applies particularly to the dissociation reactions involving very stable complexes, such as in eq 1.

The combination of a large formation constant K with a relatively small k_f can lead to an easily measurable k_d $(=k_f/K)$ value. Thus, conventional spectrophotometry[13,14] and isotopic exchange[15–17] methods were applied in the early studies of the dissociation of nickel complexes. Later, these were supplemented by flow spectrophotometry.[18–20] It thus emerged[18] that the varying values of K encountered with nickel complexes with different ligands resided largely in varying k_d values. The full significance of this was soon to become clear.[21] Ni complexing reactions involving about 100 different ligand species have now been studied with the almost complete armory of techniques,[5] of which flow and temperature jump are the most popular. Most of this Account will be concerned with the (formation) reactions of Ni in aqueous solution since it is through such studies that current attempts are being made to understand the mechanistic details of complexing and chelation as well as factors influencing reactivity. The last section will deal with the present situation in nonaqueous solvents and with other transition metal ions.

Replacement Reactions Involving only Unidentate Ligands

This is the simplest substitution process we shall encounter. At least one of the ligands involved will be a solvent molecule. We shall mainly consider the reactions of the most studied nickel species, the hydrated ion, assumed[22] $Ni(H_2O)_6^{2+}$. The second-order formation and first-order dissociation rate constants[23] are given in Table I for the replacement of one H_2O by a variety of unidentate ligands L^{n-} presenting N, O, and F donor atoms (eq 2). One is immediately struck by the similarity of rate constants for the formation of

$$Ni(H_2O)_6^{2+} + L^{n-} \rightleftharpoons Ni(H_2O)_5L^{(2-n)+} + H_2O \qquad k_f,\ k_d,\ K_1 \quad (2)$$

complexes by ligands of the same charge and, indeed, in the relatively small spread of values for the whole range of ligands shown. In the cases where activation parameters have been measured, these too are reasonably constant, $\Delta H_f^{\ddagger} = 9\text{–}11$ kcal mol^{-1} and $\Delta S_f^{\ddagger}$ values around 0 eu.

This type of data tends to discount an associative (SN2) mechanism and supports a dissociative one, with the ligand playing a relatively minor role during the act of H_2O loss from the coordination sphere of the metal. There have been two main contenders for dissociative mechanisms with octahedral complexes: an SN1 (lim)[24] or D[25] type in which a five-coordinate intermediate is generated with sufficient lifetime to discriminate between different nucleophiles (eq 3) and an SN1 IP[24] or I_d[25] type in which rate-determining H_2O–L^{n-} interchange occurs within a very rapidly formed outer-sphere complex leading to an inner-sphere complex (eq

$$\left.\begin{array}{ll} Ni(H_2O)_6^{2+} \rightleftharpoons Ni(H_2O)_5^{2+} + H_2O & k_1,\ k_{-1} \\ Ni(H_2O)_5^{2+} + L^{n-} \rightleftharpoons Ni(H_2O)_5L^{(2-n)+} & k_2,\ k_{-2} \end{array}\right. \quad (3)$$

$$\begin{array}{ll} Ni(H_2O)_6^{2+} + L^{n-} \rightleftharpoons (H_2O)_5Ni(H_2O)L^{(2-n)+} & K_0 \\ (H_2O)_5Ni(H_2O)L^{(2-n)+} \rightleftharpoons (H_2O)_5NiL^{(2-n)+} + H_2O & (4) \\ & k_0,\ k_{-0} \end{array}$$

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(5) M. Eigen and L. DeMaeyer in "Techniques of Organic Chemistry," S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., Vol. VIII, Part II, Interscience, New York, N. Y., 1963, p 895; E. F. Caldin, "Fast Reactions in Solution," Blackwell Scientific Publications, Oxford, 1964; L. I. Budarin and K. B. Yatsimirskii, *Russ. Chem. Rev.*, **37**, 209 (1968).

(6) M. Eigen and R. G. Wilkins, *Advan. Chem. Ser.*, **No. 49**, 55 (1965).

(7) N. Sutin, *Annu. Rev. Phys. Chem.*, **17**, 119 (1966).

(8) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, N. Y., 1967.

(9) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1966.

(10) A. G. Sykes, "Kinetics of Inorganic Reactions," Pergamon Press, New York, N. Y., 1966.

(11) C. H. Langford and T. R. Stengle, *Annu. Rev. Phys. Chem.*, **19**, 193 (1968).

(12) A. McAuley and J. Hill, *Quart. Rev., Chem. Soc.*, **23**, 18 (1969).

(13) F. Basolo, J. C. Hayes, and H. M. Neumann, *J. Amer. Chem. Soc.*, **75**, 5102 (1953); **76**, 3807 (1954).

(14) R. G. Wilkins, *J. Chem. Soc.*, 4521 (1957).

(15) D. Popplewell and R. G. Wilkins, *ibid.*, 4098 (1955).

(16) R. G. Wilkins and M. J. G. Williams, *ibid.*, 1763 (1957); 4514 (1957).

(17) C. M. Cook and F. A. Long, *J. Amer. Chem. Soc.*, **80**, 33 (1958).

(18) A. K. S. Ahmed and R. G. Wilkins, *Proc. Chem. Soc.*, 399 (1959); A. K. S. Ahmed and R. G. Wilkins, *J. Chem. Soc.*, 3700 (1959); 2895 (1960); 2901 (1960).

(19) G. A. Melson and R. G. Wilkins, *ibid.*, 4208 (1962).

(20) R. G. Wilkins, *ibid.*, 4475 (1962).

(21) M. Eigen, *Z. Elektrochem.*, **64**, 115 (1960); M. Eigen in "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., Macmillan, New York, N. Y., 1961, p 371; M. Eigen and K. Tamm, *Z. Elektrochem.*, **66**, 93, 107 (1962).

(22) Assumed because there is only indirect evidence for a hydration number of six by nmr (T. J. Swift and G. P. Weinberger, *J. Amer. Chem. Soc.*, **90**, 2023 (1968)), although spectral and other properties can be interpreted with this formulation.

(23) All rate constants in this Account are quoted in M^{-1} sec^{-1} at 25° unless otherwise stated.

(24) Reference 8, Chapter 3.

(25) Reference 9, Chapter 1.

Table I

Rate Constants for the Formation (k_f) and Dissociation (k_d) of Nickel(II) Complexes with Unidentate Ligands at 25°

L^{n-}	$10^{-3}k_f$ ($=K_0k_0$), M^{-1} sec^{-1}	$10^{-3}k_d$ ($=k_{-0}$), sec^{-1}	K_0,[a] M^{-1}	$10^{-4}k_0$, sec^{-1}	Ref
SO_4^{2-} [b]		100		1.5	*c*
$CH_3PO_4^{2-}$ [b]	290	7	40[d]	0.7	*d*
CH_3COO^-	100	5	3	3	*e*
SCN^-	6	0.2	1[o]	0.6	*f*
F^-	8	2	1[o]	0.8	*g*
HF	3		0.15	2	*g*
H_2O				3.0[h]	*h*
NH_3	5[i]	0.006[j]	0.15[i]	3	*i, j*
C_5H_5N (py)	~4[k]	0.040[j]	0.15	~3	*j, k*
$C_3N_2H_4$ (imid)	7	0.004	0.15	4	*l, m*
$NH_2(CH_2)_2N(CH_3)_3^+$	0.4[l]	0.045[j,l]	0.02[n]	2	*j, l*

[a] Calculated on the basis of eq 7 using 5 Å as the distance of closest approach. [b] These ligands may be bidentate. [c] Reference 21. [d] Experimentally determined value: H. Brintzinger and G. G. Hammes, *Inorg. Chem.*, **5**, 1286 (1966). [e] H. Hoffmann and E. Yeager, quoted in ref 39. [f] A. G. Davis and W. M. Smith, *Proc. Chem. Soc., London*, 380 (1961). [g] M. Eisenstadt, *J. Chem. Phys.*, **51**, 4421 (1969). [h] Exchange rate constant for a particular water molecule in $Ni(H_2O)_6^{2+}$: T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962). [i] D. B. Rorabacher, *Inorg. Chem.*, **5**, 1891 (1966). [j] Reference 19. [k] R. H. Holyer, C. D. Hubbard, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, **4**, 929 (1965). [l] J. C. Cassatt, Ph.D. Thesis, State University of New York at Buffalo, 1969, and unpublished results with R. G. Wilkins. [m] G. G. Hammes and J. I. Steinfeld, *J. Amer. Chem. Soc.*, **84**, 4639 (1962). [n] D. B. Rorabacher, T. S. Turan, J. A. Defever, and W. G. Nickels, *Inorg. Chem.*, **8**, 1498 (1969). [o] A lower value was estimated than for L = CH_3COO^- because studies were made at much higher μ.

4). For both mechanisms a similar rate law holds (eq 5,

$$d[NiL^{(2-n)+}]/dt = \frac{A[Ni^{2+}][L^{n-}]}{1 + B[L^{n-}]} \qquad (5)$$

$A = k_1k_2/(k_{-1}[H_2O])$ for mechanism 3 and K_0k_0 for mechanism 4
$B = k_2/(k_{-1}[H_2O])$ for mechanism 3 and K_0 for mechanism 4

ignoring the dissociation step for the present). Although the demonstrated presence of an outer-sphere complex in a reacting system does not necessitate its being an essential intermediate in the mechanism,[26] it is nevertheless an attractive candidate for such a role, and mechanism 4 has obtained general support since its formulation by Eigen based on the results of ultrasonics measurements on solutions of various metal sulfates.[21] Maxima in the absorption–frequency plot were associated with the equilibria depicted in (4). Significantly, the value of k_0 determined from the sound absorption experiments agreed closely with the water-exchange rate constant, *i.e.*, $Ni(H_2O)_6^{2+} + H_2O^* \rightleftarrows Ni(H_2O)_5H_2O^* + H_2O$, determined by nmr line-broadening experiments carried out at about the same time[27] (Table I).

Values of K_0 and k_0. Since in most experiments the concentration of reactants used is small, and the value of K_0 rarely much exceeds unity, the product $K_0[L^{n-}]$ is usually less than 1 and the experimentally observed rate law (6) follows.

$$d[NiL^{(2-n)+}]/dt = K_0k_0[Ni^{2+}][L^{n-}] - k_{-0}[NiL^{(2-n)+}] \qquad (6)$$

In only the Ni^{2+}–SO_4^{2-} system[21] and the Ni^{2+}–$CH_3PO_4^{2-}$ system[28] are the outer-sphere and inner-sphere complexes *both* present in sufficient amounts[29] that the sound-absorption[21] and temperature-jump data[28] can be used to determine experimental values for both K_0 and k_0. In all other cases in Table I, only the product K_0k_0 is obtained. Inordinately high concentrations of ligand would be necessary to produce deviations from second-order or the limiting first-order behavior, which arise when $K_0[L^{n-}] \sim 1$ or $\gg 1$, respectively. In order to deduce a value for k_0 (Table I), resort must therefore be made to the calculation of K_0 using eq 7[29,30]

$$K_0 = \frac{4\pi Na^3}{3000}e^{-U(a)/kT} \qquad (7)$$

where

$$U(a) = \frac{Z_1Z_2e^2}{aD} - \frac{Z_1Z_2e^2\kappa}{D(1 + \kappa a)}$$

and

$$\kappa^2 = \frac{8\pi Ne^2\mu}{1000DkT}$$

a = distance of closest approach of the two ions, k = Boltzmann's constant, and the other symbols have their usual meaning.

The remarkably small spread in deduced and experimental values of k_0, including the well-established water-exchange constant, lends strong support to the Eigen mechanism. In addition, the implication that k_0 values are not significantly influenced by outer-sphere complexing has experimental support from work with the inert systems. The consensus (*e.g.*, ref 33) is

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(26) J. Halpern, *J. Chem. Educ.*, **45**, 372 (1968).

(27) See Table I, footnote *h*.

(28) See Table I, footnote *d*.

(29) For meaning of terms, discussion, and application of this equation see, *e.g.*, ref 31 and 32.

(30) M. Eigen, *Z. Phys. Chem.* (Frankfurt), **1**, 176 (1954); R. M. Fuoss, *J. Amer. Chem. Soc.*, **80**, 5059 (1968).

(31) See Table I, footnote *i*.

(32) A. Kowalak, K. Kustin, R. F. Pasternack, and S. Petrucci, *J. Amer. Chem. Soc.*, **89**, 3126 (1967).

that K_0 values calculated from (7) for oppositely charged reactants are probably accurate to within a factor of 2–4. Undoubtedly, the present weakness and difficulty in applying the mechanism is in the estimation of values of K_0 for neutral, particularly bulky, multidentate ligands. Also, the limiting SN1 mechanism is undoubtedly important in reactions where a wide range of nucleophilicity is encountered as in certain reactions of cobalt(III) cyano and sulfite complexes.[34]

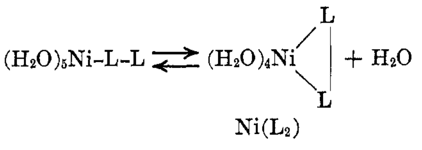
Since k_f values for reaction of a series of ligands of a similar type are approximately constant, differing values for K_1 for the complexes formed will be reflected in the value for k_d (eq 2).[35] It has been shown[36] that, for a series of related ligands, K_1 values are often inversely proportional to the acid dissociation constants of the (protonated) ligand, K_{HL}. Thus, it was expected and observed[37] that a relation of the type log $k_d = 1.58–0.21\mathrm{p}K_{HL}$ would govern the dissociative behavior of a series of mono nickel complexes with 3- and 4-substituted pyridines. A similar relation has been recently found for nickel–carboxylate complexes.[38,39]

Replacement Reactions Involving Bidentate Ligands

There is no reason to believe that replacement of water by the donor groups of a chelating agent is fundamentally different from that when only unidentate ligands are involved. However, we add a further dimension of difficulty in understanding the mechanism of substitution involving multidentate ligands, because of the multiplicity of steps. Naturally, the simpler, bidentate, ligands have been most studied. We can extend the Eigen mechanism to the formation of the monochelate with eq 8, representing the bidentate ligand by L–L, the inner-sphere complex with one end of the ligand free by $(H_2O)_5$Ni–L–L, and the final chelated product as Ni(L_2) (see eq 8c). Assuming (8a) is very rapid compared with (8b) and

$$(H_2O)_6Ni^{2+} + L\text{-}L \rightleftharpoons (H_2O)_5Ni(H_2O)L\text{-}L \qquad K_0 \quad (8a)$$

$$(H_2O)_5Ni(H_2O)L\text{-}L \rightleftharpoons (H_2O)_5Ni\text{-}L\text{-}L + H_2O \qquad k_2,\ k_{-2},\ K_2 \quad (8b)$$



$$(H_2O)_5Ni\text{-}L\text{-}L \rightleftharpoons \underbrace{(H_2O)_4Ni\begin{matrix}L\\ |\\ L\end{matrix}}_{Ni(L_2)} + H_2O \qquad k_3,\ k_{-3},\ K_3 \quad (8c)$$

(8c), as well as stationary-state conditions for the intermediates, eq 9 is obtained.[33b]

$$d[Ni(L_2)]/dt = k_f[Ni(H_2O)_6^{2+}][L\text{-}L] - k_d[Ni(L_2)] \quad (9)$$

with

$$k_f = K_0k_2k_3/(k_{-2} + k_3)$$

$$k_d = k_{-2}k_{-3}/(k_{-2} + k_3)$$

The Ratio k_3/k_{-2}. This function will dominate the kinetics of chelation. If $k_3 \gg k_{-2}$, then $k_f = K_0k_2$ and $k_d = k_2/K_3$. The overall rate of chelate formation will, in this case, be determined by the rate of formation of the Ni–L–L entity which we can assume is controlled by the same factors as apply with a unidentate ligand entry. If $k_2 \gg k_3$, $k_f = K_0K_2k_3$ and $k_d = k_{-3}$ and now the rate-determining step (naturally in both directions) will be the ring closure (or opening) process. This has been termed *sterically controlled substitution* in contrast to the *normal substitution* encountered with the first conditions.[40]

It was recognized in the early 60's that the rate constants for reactions of Ni^{2+} (and other M^{2+}) ions with a number of strongly binding bidentate ligands could be rationalized using reasonable values of K_0 and k_2, the latter being equated to the water-exchange constant.[6,21,33b,41–43] In these cases, $k_f \sim K_0k_2$, and there was no apparent inhibition to ring closure after the first bond was formed. This conclusion was reinforced, for example, by the fact that the rate constant for the formation of $Ni(H_2O)_4bipy^{2+}$ was very similar to that for $Ni(H_2O)_5py^{2+}$, in which, of course, only one Ni–N bond has to form.[42] Information bearing on these cases of positive values for k_3/k_{-2} also emerge from studies on the *dissociation* of the chelate. For bipyridyl[13] and aliphatic diamine[18] complexes, dissociation of the ligand at low acidities (limiting rate constant k_n) was markedly accelerated by acid, reaching a limiting value, k_a. This behavior was interpreted simply as arising from protonation of the free end of the Ni–L–L species and promotion of the complete rupture (k_{-2}) by preventing the reclosure (k_3). On this basis, $k_a = k_{-3}$ and $k_a/k_n \sim k_3/k_{-2}$.[13]

It is not difficult to understand why $k_3/k_{-2} \gg 1$ for the nitrogen chelates we have so far considered. The first bond formed will be relatively strong with $K_2 = k_2/k_{-2} \gg 1$. If we make the reasonable assumption that $k_3 \sim k_2$, then $k_3/k_{-2} \gg 1$ and *normal substitution* is observed. This appears to be the case for the reactions of $Ni(H_2O)_6^{2+}$ and *cis*-$Ni(NTA)(H_2O)_2^{-}$[44] with the ligands shown in Table II.

However, when water is replaced from a coordination sphere which already contains a large number of nitrogen donor atoms, the situation changes. Since K_2 is now probably only slightly greater than unity (consider, for example, the decreasing successive formation constants in the Ni–NH_3 system) there is every likelihood that the k_3/k_{-2} ratios will approximate unity and the full eq 9 apply. This appears to be the situation

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(33) (a) R. G. Pearson and P. Ellgen, *Inorg. Chem.*, **6**, 1379 (1967); (b) see Table I, footnote *m*.

(34) A. Haim, R. J. Grassi, and W. K. Wilmarth, *Advan. Chem. Ser.*, **No. 49**, 31 (1965); J. Halpern, R. A. Palmer, and L. M. Blakley, *J. Amer. Chem. Soc.*, **88**, 2877 (1966).

(35) R. G. Wilkins, *Quart. Rev., Chem. Soc.*, **16**, 316 (1962).

(36) F. J. C. Rossotti in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience, New York, N. Y., 1960, Chapter 1.

(37) P. Moore and R. G. Wilkins, *J. Chem. Soc.*, 3454 (1964).

(38) See Table I, footnote *e*. This was also quoted in ref 39.

(39) H. Hoffmann, *Ber. Bunsenges. Phys. Chem.*, **73**, 432 (1969).

(40) K. Kustin, R. F. Pasternack, and E. M. Weinstock, *J. Amer. Chem. Soc.*, **88**, 4610 (1966).

(41) R. G. Wilkins, *Inorg. Chem.*, **3**, 520 (1964).

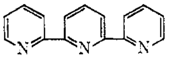
(42) See Table I, footnote *k*.

(43) G. H. Nancollas and N. Sutin, *Inorg. Chem.*, **3**, 360 (1964).

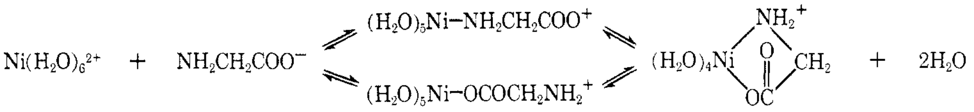
(44) L. M. Smith and R. G. Wilkins, unpublished results.

Table II

Rate Constants for the Formation ($10^{-3}k_f$) of Nickel(II) Complexes

Entering ligand	$Ni(H_2O)_6^{2+}$	$Ni(NTA)(H_2O)_2^{-}$ [a,b]	$Ni(tren)(H_2O)_2^{2+}$ [a,b]	$Ni(terpy)(H_2O)_3^{2+}$
H_2O	30[c]			50[d]
NH_3	5.0[e]	4.6[f]	260[f]	
phen	4.0[g]	3.9	13	6.0
bipy	1.5[g]	2.4	10	20
 (terpy)	1.4[h]	2.1	*i*	220[h]
$NH_2CH_2COO^-$ (Gly)	22[j]	14	90	
$^+NH_3(CH_2)_3CH(NH_2)COO^-$ (ornH$^+$)[k]	2.0[j]	2.0	12	0.7

[a] NTA = $N(CH_2COO)_3^{3-}$; tren = $N(CH_2CH_2NH_2)_3$ leaving two H_2O's cis. [b] Reference 44 (I = 0.3 M). [c] See Table I, footnote *h;* sec^{-1}. [d] D. Rablen and G. Gordon, *Inorg. Chem.*, **8,** 395 (1969); sec^{-1}. [e] See Table I, footnote *i.* [f] D. W. Margerum and H. M. Rosen, *J. Amer. Chem. Soc.*, **89,** 1088 (1967). J. P. Jones, E. J. Billo, and D. W. Margerum, *ibid.*, **92,** 1875 (1970). [g] See Table I, footnote *k.* [h] R. H. Holyer, C. D. Hubbard, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, **5,** 622 (1966). [i] Complex kinetic behavior. [j] J. C. Cassatt and R. G. Wilkins, *J. Amer. Chem. Soc.*, **90,** 6045 (1968). [k] ornH$^+$ represents a bidentate "neutral" amino acid.



(10)

with the reactions of *cis*-$Ni(tren)(H_2O)_2^{2+}$ (Table II) judging from the markedly lowered values for k_f for the bidentate ligands[44] compared with the unidentate NH_3.[45,46] This is more definite in the reaction of $Ni(en)_2(H_2O)_2^{2+}$ with en, where it has been possible to estimate the constituent rate constants.[47] These are shown in Table III, where an attempt has also been made to disect overall rate constants into their constituent values for four other systems.[18,39,42,48] The bases for these estimates are outlined in the footnotes to Table III, and it should be emphasized that, in particular, values of k_{-2} are "educated guesses," although a consistant pattern is obtained with their use.

It can be seen that the formation of the monoethylenediamine, monobipyridine, and even the planar bis(tetramethylethylenediamine) complexes of nickel is normal. It appears, however, that formation of the mono complex of mal^{2-} and other dicarboxylate ligands,[39] like the higher en species,[47] is attended by comparable values of k_3 and k_{-2}. These cases are difficult to recognize, and they constitute a real problem in unraveling the kinetics of just these simple systems. The implied low value for K_2 for the dicarboxylate ligands is understandable, and the effect is even more prominent in the abnormally low rate constants (8.0 and 5.0) for reaction of $Ni(H_2O)_6^{2+}$ with **1**[49] and **2**.[50] *Sterically controlled substitution,* with frequent first bond formation and rupture before completion of the first ring, can therefore explain these results.[49,50]

$(HOCH_2CH_2)_2N(CH_2)_2\overset{+}{N}H(CH_2CH_2OH)_2$

1

$CH_3COCH{=}C(OH)CH_3$

2

The amino acids represent an interesting class of unsymmetrical ligands where two distinct sequences of chelation are possible (eq 10). The formation rate constant (Table II) is of the expected order for a negatively charged ligand, with no apparent limitations in ring closing. This suggests that fruitful attack is from the nitrogen end of the amino acid, else we might have anticipated a distinctly reduced rate constant if chelation only accompanied initial attack from the labile carboxylate segment. Consistent with this idea are the results on the dissociation reaction, for which a reverse sequence must apply. The dissociation rate constant, k_d, is independent of pH from 7 to 3.5 and only becomes enhanced at pH <3,[51] a much lower pH than would be anticipated if a free NH_2 group was exposed first by Ni–N bond rupture,[18] but quite reasonable if the weakly basic carboxylate first detached.[52] At pH 1, Ni(Gly)$^+$ *rapidly* picks up one proton and then *measurably* decomposes to Ni^{2+} ion.[53] Once again this is understandable only if the Ni–N bond cleaves last.

Similar considerations apply to the coordination of glycinamide and the lower peptides, di-, tri-, and tetraglycine. All chelate to Ni^{2+} with virtually identical rate constants[54] (3–4 × 10^3) and activation parameters ($\Delta H_f^{\ddagger}$ = 13.2, $\Delta S_f^{\ddagger}$ = 0 eu for the oligoglycines[55]). This can be construed as initial attack by the common terminal NH_2 group and rapid ring closure by the amide residue.[54] It also suggests that the remote negative carboxylate group of the peptides does not influence the

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(45) See Margerum and Rosen, Table II, footnote *f.*

(46) See Jones, *et al.*, Table II, footnote *f.*

(47) J. P. Jones and D. W. Margerum, *J. Amer. Chem. Soc.*, 92, 470 (1970).

(48) R. G. Wawro and R. G. Wilkins, unpublished results.

(49) See Table I, footnote *n.*

(50) R. G. Pearson and O. P. Anderson, *Inorg. Chem.* **9,** 39 (1970).

(51) P. I. Chamberlain and R. G. Wilkins, unpublished results.

(52) See also ref 8, pp 223–225.

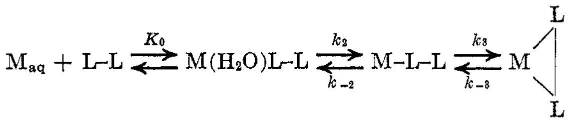
(53) P. Moore, Ph.D. Thesis, University of Sheffield, 1964.

(54) See Table II, footnote *j.*

(55) G. Davies, K. Kustin, and R. F. Pasternack, *Inorg. Chem.*, **8,** 1535 (1969).

Table III

Speculative Breakdown of Rate Constants for the Formation and Dissociation of Nickel(II) Complexes with Bidentate Ligands



$$M_{aq} + L{-}L \underset{}{\overset{K_0}{\rightleftharpoons}} M(H_2O)L{-}L \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} M{-}L{-}L \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} M\langle L, L \rangle$$

M_{aq}	L–L	K_0k_2, M^{-1} sec^{-1}	k_{-2}, sec^{-1}	k_3, sec^{-1}	k_{-3}, sec^{-1}
$Ni(H_2O)_6^{2+}$	en	4.0×10^5 [a]	45[b]	9×10^2 [c]	0.14[d]
$Ni(H_2O)_6^{2+}$	bipy	1.5×10^3 [e]	40[f]	3×10^3 [c]	0.0034[g]
$Ni(H_2O)_6^{2+}$	mal	8.5×10^5 [h]	3.5×10^3 [i]	4.5×10^3 [j]	1×10^2 [j]
$Ni(H_2O)_4$(tetrameen)	tetrameen	2.0×10^4 [k]	45[b]	9×10^2 [c,l]	0.003[l,m]
$Ni(en)_2(H_2O)_2^{2+}$	en[n]	5.5×10^6	1.2×10^5	2.2×10^5	87

[a] k_f, calculated from k_d[18] and K ($10^{7.6}$). [b] k_d for $Ni(H_2O)_5NH_2(CH_2)_2N(CH_3)_3^{3+}$, ref 19 and footnote *l*, Table I. The terminal positively charged nitrogen is expected to have little rate influence.[47] [c] $k_a/k_n = k_3/k_{-2}$; see text. [d] k_a.[18] [e] k_f.[42] [f] k_d for $Ni(H_2O)_5py^{2+}$. [g] k_a. [h] k_f for Ni^{2+} + adipate.[39] [i] Estimated from k_d–pK_a plot;[39] see text. [j] Estimated from eq 9. [k] k_f, calculated from k_d[14] and K_2 ($10^{8.0}$) (R. G. Wawro and R. G. Wilkins, unpublished results). [l] A. K. S. Ahmed, Ph.D. Thesis, University of Sheffield, 1960. [m] k_a.[l] [n] Values for this reaction were determined experimentally by studying the reaction at different pH values.[47]

rate (see, however, ref 55). Consistent with this idea is, once again, the inability of low [H^+] to accelerate ring opening of the glycinamide and diglycine complex.[51]

The progressive decrease in the value of k_f for reaction of Ni^{2+} with $NH_2CH_2COO^-$, $NH_2CH(C_2H_5)COO^-$, and $NH_2CH(CH_3)CH_2COO^-$, 4×10^4 (ref 55), 1×10^4 (ref 32), and 4×10^3 (ref 32), does, however, indicate partial steric control in the formation of the six-membered chelate ring.[32] This is an important effect, particularly with the very labile transition metal ion Cu^{2+}.[56,57]

Anomalous k_f Values. Notwithstanding the success in understanding k_f values in terms of the function K_0k_2 for a large number of systems, when replacement of the first water is rate controlling, there are cases where an estimated K_0 and/or k_0 value is anomalously, and *unpredictably*, high. A value for K_0 of 0.1–0.2 M^{-1} can account for the reaction rates of several neutral unidentate as well as bidentate ligands, such as phen or bipy,[58] but *not* of aliphatic diamines. The high rate constants for Ni^{2+} reacting with en (4×10^5)[60] and for $Ni(en)_2(H_2O)_2^{2+}$ reacting with en (5.5×10^6)[47] compared with the appropriate H_2O exchange rate constants (3×10^4 (ref 27) and 5.4×10^6 (ref 61), respectively) have been ascribed to both larger-than-normal K_0 and k_0 values when the aliphatic diamine interacts with the coordination sphere of the Ni. Hydrogen-bonding effects are invoked to explain this in a so-called *internal conjugate base mechanism.*[31] A similar explanation might hold for the high rate constants for reaction of Ni^{2+} with tetrameen (5×10^4, ref 48) and for $Ni(tetrameen)(H_2O)_4^{2+}$ with tetrameen (2×10^4, ref 14 and 48).

The rate constants for reaction of $Ni(terpy)(H_2O)_3^{2+}$ are puzzling (Table II). Compatibility of the water exchange rate constant[62] and the rate constant for reaction with terpy[63] requires a K_0 value of 4. Reactions with other ligands (Table II) would require lesser and different values. Some type of specific interaction between the free and coordinated terpy might explain the high k_f value,[62,63] but the situation at present is distinctly unsatisfactory.

Values of k_{-3}. Some values of the rate constant for opening of the chelate ring are shown in Table III. In certain cases, they represent the limiting rate constant in acid media (k_a). They can also be obtained for the diamines from the rate of exchange of hydrogen between the complex ion and water.[18,64] The values of k_{-3} are much smaller than those of k_{-0} for the appropriate unidentate ligand shown in Table I (compare en with NH_3, bipy with py, and $CH_2(COO)_2^{2-}$ with CH_3COO^-). This difference has been attributed to the necessity to twist an aliphatic chain and (in the case of the diamines) rotate the NH_2 ligand away from the metal atom.[18] The energy barriers which would be required to be overcome appear reasonable.[60] Carbon substitution of en reduces the values of k_{-3}[20] by providing higher rotational barriers to ring opening.[65] On this basis, larger chelate rings should be easier to open[65] and, in agreement, estimated values of k_{-3} for opening Ni(mal) are larger than for Ni(oxal).[39]

It might be thought that the lowered value of k_{-3} forms the basis of the enhanced stability of bidentate over unidentate ligands (*chelate effect*).[66] As has been pointed out, however,[52] the twisting energy barriers contribute equally to k_3, which would be substantially reduced but for the operation of the entropic neigh-

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(56) R. F. Pasternack and K. Kustin, *J. Amer. Chem. Soc.*, **90**, 2295 (1968).

(57) W. B. Makinen, A. F. Pearlmutter, and J. E. Stuehr, *ibid.*, **91**, 4083 (1969).

(58) This value of K_0 arises from eq 7 by equating the exponential term to unity and setting a = 4 Å. It is also obtained from simple consideration of random collisions.[59]

(59) J. E. Prue, *J. Chem. Soc.*, 7534 (1965).

(60) D. W. Margerum, D. B. Rorabacher, and J. F. G. Clarke, Jr., *Inorg. Chem.*, **2**, 667 (1963); trien = $NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$; tetraen = $NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$; these bind through 4 or 5 N's.

(61) A. G. Desai, H. W. Dodgen, and J. P. Hunt, *J. Amer. Chem. Soc.*, **91**, 5001 (1969).

(62) See Table II, footnote *d*.

(63) See Table II, footnote *h*.

(64) See Table III, footnote *l*.

(65) D. W. Margerum, *Advan. Chem. Ser.*, **No. 49**, 75 (1965).

(66) G. Schwarzenbach, *Helv. Chim. Acta*, **35**, 2344 (1952).

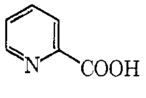
boring group effect. It is the latter then that is the major cause of the chelate effect.

Behavior of Protonated Ligands. Protonation of the free end of the Ni–L–L^{2+} fragment could conceivably slow down the ring closure. As well as the proton having to be lost (not always very rapid[67]), more important, the concentration of the effective ring closer, Ni–L–L^{2+}, could be substantially reduced. This apparently is not important with the reactions of enH$^+$ with Ni^{2+} (we could predict this from dissociative behavior[18]) or with Ni(en)$_2$(H$_2$O)$_2$$^{2+}$.[47] The rate constants are those expected using a calculated value of K_0 of 0.02. Furthermore, enH$^+$ reacts with Ni^{2+} with a rate constant (6 × 10^2)[54,68] similar to that of the unidentate $^+$N(CH$_3$)$_3$CH$_2$CH$_2$NH$_2$ (4 × 10^2).[68,69]

The situation where the proton can effectively block the donor sites is quite a different matter. The monoprotonated forms of bipy and phen react abnormally slowly with nickel complexes. This cannot simply reflect a low K_0 value but probably represents the difficulty in the nickel species getting at the blocked nitrogen donor atom and lowering the value of k_2 in (8b). The consistently higher rate constant for reactions of bipyH$^+$ compared to phenH$^+$ with Ni^{2+} (∼20 and ∼2)[69] and with Ni(NTA)(H$_2$O)$_2^-$ (∼10^2 and ∼0)[44] probably results from the ability of the bipy to twist compared with the rigidity of the phenanthroline.[69]

The most striking example of the unreactivity of the monoprotonated ligands occurs on protonation of amino carboxylates or amino acid amides. Thus, the protonated forms of simple amino acids, amides, and peptides, iminodiacetates, nitrilotriacetates, and piperidinecarboxylates react with Ni^{2+} (and other metal ions) *at least* 10^4 times slower than do the deprotonated species.[54,67] The inactivity of the $\geqslant$N$^+$CH$_2$COR unit may represent an extreme operation of *sterically controlled substitution*, since the first attachment must be through the carboxylate or amide residue, which will be a very labile arrangement, and this, together with proton loss,[67] could markedly reduce the overall rate constant. The unreactivity of the zwitterion may, however, reside in the strong intramolecular interactions which must be broken down before even initial reaction can occur.

Irrespective of the *modus operandi* of the effect, it has useful ramifications in the study of complex ion reactions. (a) The most labile metal ions, such as Cu^{2+}, may be studied by working at low pH where the concentration of the reacting species and the rate are drastically reduced (*e.g.*, see ref 57). (b) The site of protonation or mode of bonding of certain polybasic ligands may be deduced from the rate behavior of the various protonated forms.[44,54] As examples, the definite rate constant (∼30) for reaction of the monoprotonated form of pyridine-2-carboxylate suggests that a small amount (about 2%) of the reactive nonzwitterion form **3** is present in solution, for which there is independent spectral and pK_a evidence.[54] On the other hand, the normal values (for a neutral ligand) for the reaction of **4** with Ni^{2+} (1.3 × 10^3) indicate that any hydrogen bonding in the ligand is weak.[70]



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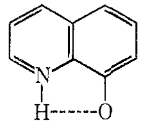
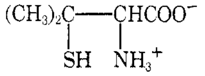


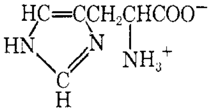
4

The rate constants for reaction of **5** and **6** with Ni(phen)$_2$(H$_2$O)$_2$$^{2+}$, which has only two replaceable waters, are 1.5 × 10^3 and 1.0 × 10^2. These relatively high values indicate that initial attack must be through the S, N or N, N donor atoms, respectively.[44] Since no subsequent changes are observed, it is surmised that these represent the final products also.



$$\underset{\displaystyle \mathrm{SH}}{(\mathrm{CH_3})_2\mathrm{C}}\text{—}\underset{\displaystyle \mathrm{NH_3^+}}{\mathrm{CHCOO^-}}$$

5



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Effect of Substituents on Replacement Rates. This is an area which is little understood at present. We are concerned with the effect of L on the rate of reaction 11. It has been found that in the reaction of

$$\mathrm{NiL(H_2O)}_n + \mathrm{L'} \rightleftarrows \mathrm{NiL(H_2O)}_{n-1}\mathrm{L'} + \mathrm{H_2O} \qquad (11)$$

Ni complex ions with 4-(2-pyridylazo)resorcinol (= L′) the order of reactivity increases for L = F$^-$ < H$_2$O < OCOCH$_3^-$ < OH$^-$ < N$_3^-$ with a tenfold effect over the whole range. The effect of ligands parallels their ability to donate electrons to the central metal and thus weaken the coordinated H$_2$O.[71]

Negatively charged carboxylate groups only slightly labilize coordinated water,[45] and the small accelerating effect of amino acids[33b] can be mainly attributed to the Ni–NH$_2$ residue. As the number of coordinated nitrogens increases in the Ni–NH$_3$,[72] –en,[61] or –polyamine[45] complexes, the rate constants for replacement of the remaining coordinated water increase monotonically,[72] judged by either H$_2$O exchange (L′ = H$_2$O) or NH$_3$ (L′ = NH$_3$) replacement. The results are in contrast to the small observed effect with bipy, terpy, or phen substituents. Thus, the rate constants for reaction of Ni^{2+} with NH$_3$[31] or phen[42] (4 × 10^3), Ni(phen)(H$_2$O)$_4$$^{2+}$ with NH$_3$[45] (2 × 10^3) or phen[6] (3 × 10^3), Ni(phen)$_2$(H$_2$O)$_2$[24] with phen[44] (1 × 10^3), and Ni(bipy)$_2$(H$_2$O$_2$)$^{2+}$ with bipy[63] (5 × 10^3) all lie within a fivefold range. This is consistent with similar water-exchange rate constants ranging from 3 to 7 × 10^4 sec^{-1} for Ni^{2+}, Ni(bipy)(H$_2$O)$_4$$^{2+}$, Ni(bipy)$_2$(H$_2$O)$_2$$^{2+}$, and Ni(terpy)(H$_2$O)$_3$$^{2+}$ ions.[62,73] The labilizing influence as a result

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[67] D. L. Rabenstein and R. J. Kula, *J. Amer. Chem. Soc.*, **91**, 2492 (1969).

[68] G. A. Melson, Ph.D. Thesis, University of Sheffield, 1962.

[69] See Table I, footnote *l*.

[70] W. A. Johnson and R. G. Wilkins, *Inorg. Chem.*, **9**, 1917 (1970).

[71] S. Funahashi and M. Tanaka, *ibid.*, **8**, 2159 (1969).

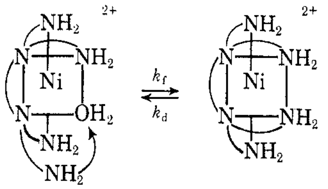
[72] A. G. Desai, H. W. Dodgen, and J. P. Hunt, *J. Amer. Chem. Soc.*, **92**, 798 (1970).

of the electron-donor properties of aliphatic nitrogens is apparently neutralized by back-π-bonding effects when aromatic rings are involved.[45,72,73]

A *small* effect of substitution at the 5 position of phen is observed in the reaction of $Ni(phen\text{-}5\text{-}X)(H_2O)_4^{2+}$ with NTA^{3-} or $dienH^+$. This is ascribed to changes in k_2 (eq 8b), the value of which increases with increasing electron-donating properties of the 5 substituents. A Hammett LFER holds (ρ negative),[74] as it does for the removal of the phen-5X itself from $Ni(phen\text{-}5\text{-}X)(H_2O)_4^{2+}$. Now, interestingly, for the latter reaction, the effects of X are in the opposite direction (ρ positive).[75] It appears, not unreasonably, that groups which strengthen the phen–Ni bonding weaken the remaining coordinated waters.

Coordination of Multidentate Ligands

The similar rate constants for the reaction of Ni^{2+} with SO_4^{2-} and with $EDTAH^{3-}$ ions were used originally to illustrate the dissociative character of the formation process;[21] this also implied that the first step of chelation of the multidentate ligand was rate determining and was followed by a rapid sequence of ring closures (see also concluding section). Margerum and coworkers in a perceptive study concluded, from the nature of the rate law and from a consideration of the values of the rate constants for the reaction of Ni^{2+} with $trienH^+$ and $tetraenH_2^{2+}$, that the formation of the first Ni–N bond was rate limiting.[60] The final ring-closing step with these polyamines is quite rapid, as can be shown from a reasonably accurate estimation of the rate constant, k_f, for (12).



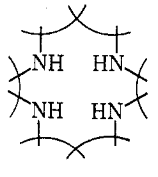
(12)

—— represents $-CH_2CH_2-$

The value of k_d (70 sec^{-1} at 5°)[76] combined with K for reaction 12 (~25)[77] leads to a k_f value of ~2×10^3 sec^{-1} (5°). Similar treatment of available kinetic[76] and thermodynamic data[77] gives for the free NH_2 arm moving in and completing the chelate of $Ni(ptn)(H_2O)_3^{2+}$ and $Ni(trien)(H_2O)_2^{2+}$ rate constants of 6×10^2 and 2×10^4 sec^{-1}, respectively (ptn = $NH_2CH_2CH(NH_2)CH_2NH_2$).

The $\Delta H^{\ddagger}$ values for the *first* bond rupture for these polyamine complexes fall neatly into groups. It is highest for en, containing the most strain-free ring (~20 kcal mol^{-1}), *ca.* 18 for complexes with terdentate ligands, and only 15 kcal mol^{-1} for those with quadri- and quinquedentate amines and with NH_3 itself.[76] Interestingly, the strain associated with the formation of a chelate ring is *ca.* 3–4 kcal mol^{-1}, from calorimetry measurements.[78]

The rupture of a pyridine nitrogen–metal bond is also slightly faster when it forms part of a double ring system (terpy) than when it is in a single ring (bipy).[79] There is a *large* effect of H^+ on the dissociation of $Ni(terpy)_2^{2+}$, and this is a requirement of the rapid chelation of terpy once the first bond has been made (Table II).[79] In fact, the establishment of the first bond appears to signal rapid successive ring closures with all the multidentate ligands, usually containing strong nitrogen donors, which have so far been examined. However, reaction might be expected to be abnormally slow with any of the metal ions when the ligand is part of a rigid structure as in the macrocycle **7**[80] or particularly with some of the apoenzymes (*e.g.*, apocarbonic anhydrase[81]), an area which has been little explored. Structural features of the ligand may lead to low rate constants, as in the example of **8** (*cis,cis*-tach). The equatorial NH_2 groups in the free ligand have to be rotated into axial ring positions so as to occupy the trigonal face of an octahedral complex (**9**). Both dissociation of $Ni(\textit{cis,cis}\text{-tach})(H_2O)_3^{2+}$ in acid[82] and the formation of the complex (k_f = 9 at 45° for $tachH^+$ [48]) are orders of magnitude slower than normal for Ni.



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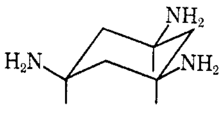

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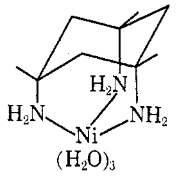

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Other Solvents and Other Metal Ions

Nickel ion has, once again, proved the most popular of the labile ions for studies in solvents other than water. Solvent exchange (eq 13) in some half-dozen

$$NiS_6^{2+} + S^* \rightleftharpoons NiS_5S^{*2+} + S \qquad (13)$$

solvents has been studied by nmr techniques. The exchange rate constants are remarkably similar for a variety of solvents,[11] but there are wide variations in the more difficult to measure activation parameters (sometimes for the same solvent, *e.g.*, DMSO and DMF, by different investigators![83]). It has not yet proved

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[73] M. Grant, H. W. Dodgen, and J. P. Hunt, *J. Amer. Chem. Soc.*, **92**, 2321 (1970).

[74] R. K. Steinhaus and D. W. Margerum, *ibid.*, **88**, 441 (1966).

[75] P. Ellis, R. Hogg, and R. G. Wilkins, *J. Chem. Soc.*, 3308 (1959).

[76] G. Melson and R. G. Wilkins, *ibid.*, 2662 (1963).

[77] It can be shown that log $K \simeq$ log $K^{Ni}{}_{Ni(penten)^{2+}}$ − log $K^{Ni}{}_{Ni(penten\,H)^{3+}}$ − 2.0 where 2.0 represents the approximate difference in the pK_1 for protonation of free penten and $Ni(penten)(H_2O)^{2+}$. For the meaning of symbols and thermodynamic data see G. Schwarzenbach and P. Moser, *Helv. Chim. Acta*, **36**, 581 (1953); G. Schwarzenbach, *ibid.*, **33**, 974 (1950); J. E. Prue and G. Schwarzenbach, *ibid.*, **33**, 995 (1950).

[78] M. Ciampolini, P. Paoletti, and L. Sacconi in "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., Macmillan, New York, N. Y., 1961, p 303.

[79] R. Farina, R. Hogg, and R. G. Wilkins, *Inorg. Chem.*, **7**, 170 (1968).

[80] T. Kaden in "Progress in Coordination Chemistry," M. Cais, Ed., Elsevier, Amsterdam, 1968, p 114.

[81] R. W. Henkens and J. M. Sturtevant, *J. Amer. Chem. Soc.*, **90**, 2669 (1968); S. A. Rudolph and J. M. Sturtevant, *Biophys. Soc. Abstr.*, 189a (Feb 1970).

[82] R. F. Childers and R. A. D. Wentworth, *Inorg. Chem.*, **8**, 2218 (1969).

[83] R. G. Little, Ph.D. Thesis, State University of New York at Buffalo, June 1969.

Table IV

Log k for Reactions of Aquated Bivalent Metal Ions of the First Transition Series at 25°

Entering ligand	V^{2+}	Cr^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}
H_2O[a]	2.0[b]	8.5[c]	7.5[d]	6.5[d]	6.0[d]	4.3[d]	8.5[c,e]	7.5[e]	8.4[e]
NH_3[f]					5.1[g]	3.7[g]		6.6[g]	
HF[f]			6.3[h]	6.0[h]	5.7[h]	3.5[h]	7.5[i]		
phen[f]	0.5[j,k]	~8.0[l]	~5.4[m]	5.9[n]	5.3[l]	3.4[e]	7.9[l]	6.8[l]	>7.0[m]

[a] Water exchange rate constant (sec^{-1}) from nmr or sound absorption experiments. [b] M. V. Olson, Y. Kanazawa, and H. Taube, *J. Chem. Phys.*, **51,** 289 (1969). [c] Reference 86. [d] See Table I, footnote *h*. [e] G. Maass, *Z. Phys. Chem.* (Frankfurt), **60,** 138 (1968). [f] k_f, M^{-1} sec^{-1}. [g] See Table I, footnote *i*. [h] M. Eisenstadt, *J. Chem. Phys.*, **51,** 4421 (1969). [i] M. Eisenstadt and H. L. Friedman, *ibid.*, **48,** 4445 (1968). [j] R. G. Pearson and O. A. Gansow, *Inorg. Chem.*, **7,** 1373 (1968). [k] Many electron transfer reactions of V^{2+} appear controlled by substitution with log $k_{redox} \sim 1$: N. Sutin, *Accounts Chem. Res.*, **1,** 225 (1968). [l] See Table I, footnote *l*. [m] See Table I, footnote *k*. [n] R. S. Bell and N. Sutin, *Inorg. Chem.*, **1,** 359 (1962).

possible to correlate these rates with different solvent properties[84] or the preferred $\Delta H^{\ddagger}$ values with spectral Dq values of the solvent,[85] which is demanded by most current theories of reactivity.[24,86,87]

The independence of the solvent exchange rate on the concentration of solvent (in mixed solvents) is consistent with a dissociative mechanism. This has been observed with $Ni(NH_3)_6^{2+}$ exchange with NH_3 in NH_3–H_2O mixtures[88] and with $Ni(DMSO)_6^{2+}$ and also ($Co(DMSO)_6^{2+}$) exchange with DMSO in DMSO–CH_3NO_2[83,89] and DMSO–CH_2Cl_2 mixtures.[89] The solvents CH_3NO_2 and CH_2Cl_2 are inert and do not interfere with the solvation of DMSO by nickel ion.[83,89] In calculations of the kinetic parameters for water exchange of a number of bivalent transition metal ions, a dissociative model for ligand exchange has been used.[86]

The study of ligand substitution in nonaqueous solution has barely commenced. The rate constants for reactions of nickel ion with charged and neutral ligands in CH_3OH, compared with H_2O, can be logically explained in terms of the interchange mechanism.[33a] The study of the reaction of Ni^{2+} with bipy in CH_3OH–H_2O mixtures[90] and a variety of nonaqueous solvents,[91] however, suggested that other factors, such as solvent structure, are involved. Specifically, the value of k_f/K_0k_0 (k_f = observed second-order formation rate constant) should be a constant for a variety of solvents. This is not observed.[91] This expectation is, however, based on a constant value for K_0 for the outer-sphere interaction of bipy with NiS_6^{2+} in different solvents, as well as the display of *normal* substitution by the bidentate ligand. These assumptions may not be correct, but it is evident that further studies of this kind will be valuable.

It will be difficult to amass the quantity of information for the other bivalent transition metal ions which exists for Ni. However, the data already available for H_2O exchange and for unidentate and bidentate ligand entry are convincing evidence for a dissociative type of mechanism of the kind already described (Table IV). The values of k_f are appreciably constant for a particular metal ion and are sensibly related to the corresponding k_0, except for the case of Mn(II). The rate constants[6] for reaction of even the multidentate $EDTAH^{3-}$ with Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+}, in conjunction with k_0 values (Table IV), can all be accommodated with reasonable values of K_0 of ~10–20. With these systems, however, a very labile metal ion–acetate bond formation may precede the rate-determining step of coordination to the nitrogen.[92] For the inert octahedral complexes also, a dissociative interchange mechanism best describes many of their substitution reactions.[93] There is a reasonably good understanding of the magnitude of the rate constants and activation parameters for octahedral complexes in terms of electron configuration and crystal-field considerations, but space limitations prevent our developing this.[24,86,87]

Phase I, a *broad* understanding of octahedral substitution, can be considered completed. The gaps in our detailed understanding, alluded to in this Account, will indicate the directions of some of the future efforts. The next developments, a detailed comprehension embracing solvation effects, activation parameters, and so on, is likely to be much more difficult in view of the subtler effects which are being uncovered and which have been partly alluded to in this Account.

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