Kinetics of Ternary Complex Formation between Nickel Species and 5-Nitrosalicylic Acid

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Stopped-flow and temperature-jump relaxation methods have been used to measure rate constants and activation parameters for the formation and dissociation of a 1 : 1 complex between nickel(II) and 5-nitrosalicylate(2−) (nsa) and of ternary complexes between nsa and nickel(II)–polytriphosphate, –iminodiacetate, –nitrilotriacetate, –ethylenediamine-*NN'*-diacetate, –diethylenetriamine, –triethylenetetramine, and –2,2',2''-triaminotriethylamine complexes. Rate constants and activation parameters have also been measured for the reaction between the Ni^{II} complex of ethylenediamine-*NN'*-diacetate and pyridine-2-azo-*p*-dimethylaniline. The results can be rationalized in terms of the normal dissociative model provided the local charge density on the metal species is considered rather than its overall charge. The results provide further evidence that the number of binding nitrogen atoms on the first ligand has a larger influence on ternary complex formation than its charge.

THE kinetics of formation and dissociation of 1 : 1 complexes of nickel(II) in water have been widely studied [1] since the introduction of rapid-reaction techniques. Rate constants for the formation of such complexes, k_f, are usually in the range 10^3—10^5 l mol^{-1} s^{-1} and it is generally accepted that the mechanism of complex formation with a unidentate ligand involves rapid diffusing together of the two species to form an outer-sphere complex, followed by rate-limiting replacement of a water molecule in the inner co-ordination sphere of the metal ion by the ligand. Where the incoming ligand contains a second or further binding group, the rate-determining step is usually formation of the first metal–ligand bond. If K_{os} is the formation constant of the outer-sphere intermediate, it can be shown that, provided the concentration of the intermediate is small, k_f is given by $K_{os}k_{ex}$, where k_{ex} is the (first-order) rate constant for water exchange. In most cases the value of K_{os} obtained from k_f/k_{ex} is comparable to that calculated on the basis of the Fuoss equation,[2] but low values have been rationalized in terms of rate-limiting ring closure [3] and high values in terms of an internal conjugate-base mechanism.[4]

Comparatively little is known about the influence exerted by a ligand which is already bound to the nickel(II) ion on the subsequent reaction of the latter with another ligand, although it has been found [5] that there is a general increase in k_{ex} as the number of bound aliphatic nitrogen atoms increases. This labilisation of the remaining water molecules by N atoms is reflected in increased values of k_f for the neutral incoming ligands NH_3 [6] and pyridine-2-azo-*p*-dimethylaniline (pada),[7] and in both cases the presence of negatively charged oxygen atoms in the inner co-ordination sphere of nickel(II) has little influence on k_f. The purpose of the present study is to investigate the effect of charge on the incoming ligand. Rate constants and activation parameters, as measured by the stopped-flow and temperature-jump methods, are reported for formation in aqueous solution of complexes between 5-nitrosalicylate(2−) (nsa, which acts as a bidentate ligand) and hydrated nickel(II), and the complexes of nickel(II) with polytriphosphate (tp), iminodiacetate (ida), nitrilotriacetate (nta), ethylenediamine-*NN'*-diacetate (edda), diethylenetriamine (dien), triethylenetetramine (trien), and 2,2',2''-triaminotriethylamine (tren). The kinetics are also reported for the reaction of pada with the complex [Ni(edda)].

EXPERIMENTAL

Solutions were prepared from nickel(II) nitrate (Fisons, AnalaR) and standardized against the disodium salt of EDTA. 5-Nitrosalicylic acid (Fluka) and $Na_5P_3O_{10},6H_2O$ (Albright and Wilson) were twice recrystallized from water and aqueous ethanol, respectively, and 2,2',2''-triaminotriethylamine (tren) was isolated from technical grade triethylenetetramine (trien).[8] The following chemicals were used without further purification: nitrilotriacetic acid, diethylenetriamine (dien), trien (Fluka, puriss. grade); iminodiacetic acid, 2,4,6-collidine (Fisons); ethylenediamine-*NN'*-diacetic acid (K. and K.); pyridine-2-azo-*p*-dimethylaniline (pada) (Sigma).

The solutions were made up with triply distilled water, the middle distillation being from alkaline potassium permanganate. An ionic strength of 0·30M was maintained with $NaNO_3$ and the solutions were buffered with 2,4,6-collidine (*ca.* 10^{-3}M). The pH ranges used are quoted in Table 1; no evidence was found for metal hydrolysis in these regions, although there was curvature in the kinetic plot for the complex $[Ni(tp)]^{3-}$ (tp = polytriphosphate) above pH 8·5. Kinetic and equilibrium measurements were undertaken by standard methods [7-10] and in all cases pseudo-first-order conditions were maintained (metal concentrations in the range 10^{-3}—10^{-1}M being used). The kinetic data reported here refer to relaxation effects observed in the 100 μs—2 s region and were generally obtained

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[1] See, for example, M. Eigen and R. G. Wilkins, 'Mechanisms of Inorganic Reactions,' ed. R. F. Gould, *Adv. Chem. Series*, No. 49, Amer. Chem. Soc., Washington, D.C., 1965, p. 55; D. J. Hewkin and R. H. Prince, *Co-ordination Chem. Rev.*, 1970, **5**, 45; R. G. Wilkins, *Accounts Chem. Res.*, 1970, **3**, 408.

[2] R. M. Fuoss, *J. Amer. Chem. Soc.*, 1958, **80**, 5059; see also ref. 1.

[3] See, for example, A. Kowalak, K. Kustin, R. F. Pasternack, and S. Petrucci, *J. Amer. Chem. Soc.*, 1967, **89**, 3126.

[4] See, for example, D. B. Rorabacher, *Inorg. Chem.*, 1966, **5**, 1891.

[5] J. P. Hunt, *Co-ordination Chem. Rev.*, 1971, **7**, 1.

[6] D. W. Margerum and H. M. Rosen, *J. Amer. Chem. Soc.*, 1967, **89**, 1088; J. P. Jones, E. J. Billo, and D. W. Margerum, *ibid.*, 1970, **92**, 1875.

[7] M. A. Cobb and D. N. Hague, *J.C.S. Faraday I*, 1972, **68**, 932.

[8] L. J. Wilson and N. J. Rose, *J. Amer. Chem. Soc.*, 1968, **90**, 6041.

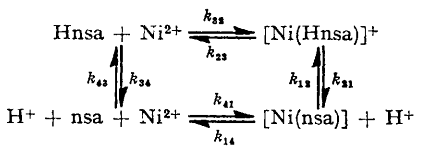
[9] G. R. Cayley and D. N. Hague, *J.C.S. Faraday I*, 1972, **68**, 2259.

[10] G. R. Cayley and D. N. Hague, *Trans. Faraday Soc.*, 1971, **67**, 786.

at 380 5-nitrosalicylate(2−) (nsa) or 550 nm (pada), although identical relaxation times were obtained at several other wavelengths. Temperatures were accurate to ±0·2 °C.

RESULTS

The mechanism postulated for the formation of the complex [Ni(nsa)] from nickel(II) and 5-nitrosalicylate(1−) (Hnsa) is shown in Scheme (1). It is a two-path mechanism in which the path involving the fully deprotonated form nsa



Scheme 1

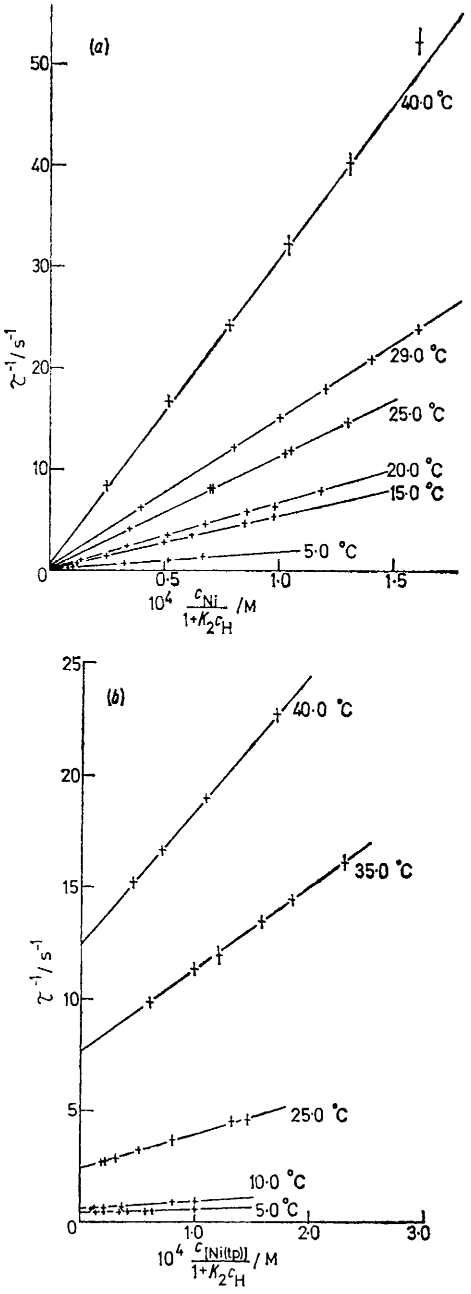


Figure 1

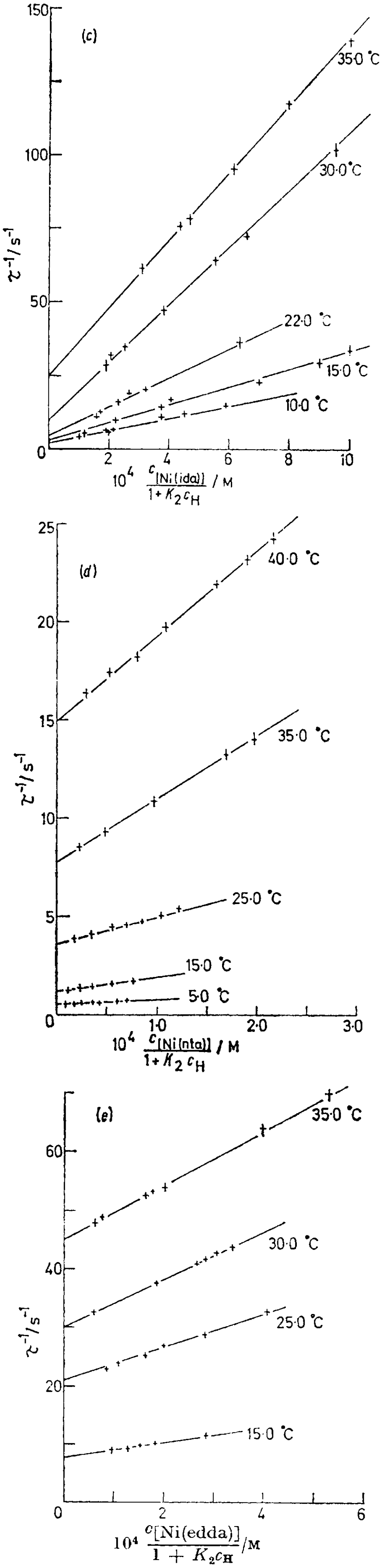


Figure 1

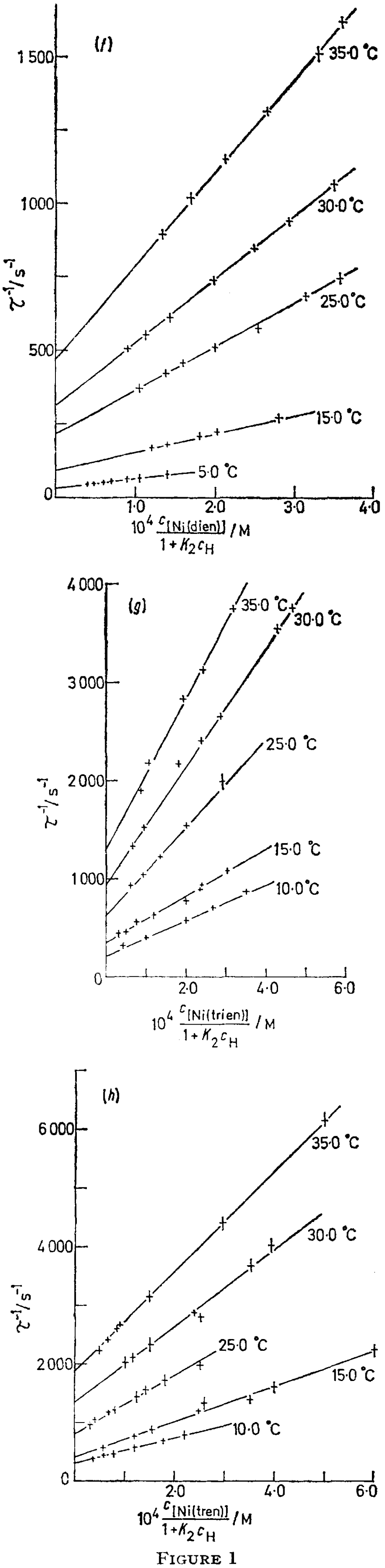


FIGURE 1

is important at higher pH and the other, involving the form in which the phenolic oxygen atom is protonated, is important at lower pH. The relaxation expression for the longer of the two observed relaxation effects is as in equation (1),[9] where $K_1 = k_{41}/k_{14}$, $K_2 = k_{43}/k_{34}$, c_H and c_{Ni} are the

$$\tau^{-1} = c_{Ni}\left(\frac{k_{41}}{1 + K_2c_H} + k_{32}\right) + c_Hk_{32}\frac{K_2}{K_1} + k_{14} \quad (1)$$

hydrogen- and nickel-ion concentrations, respectively, and activity coefficients have been neglected. The terms in k_{14} and k_{32} could be neglected and k_{41} was evaluated from a plot of τ^{-1} against $c_{Ni}(1 + K_2c_H)^{-1}$ using pK_a values for Hnsa reported previously[9] (Figure 1).

Reactions of nsa with the substituted nickel species [NiL] follow a similar scheme but in these cases it was possible to evaluate k_{14} in addition to k_{41} (the k_{32} terms alone being negligible). The results are given in Figure 1 and Table 1. The [Ni(edda)]-pada system (edda = ethylenediamine-*NN'*-diacetate) was analysed by the method described previously;[7] the results are given in Figure 2 and Table 2. Stability constants of most of the complexes were determined spectrophotometrically[7,9] at 25·0 °C. The agreement between spectrophotometrically and kinetically determined values (Tables 1 and 2) is satisfactory.

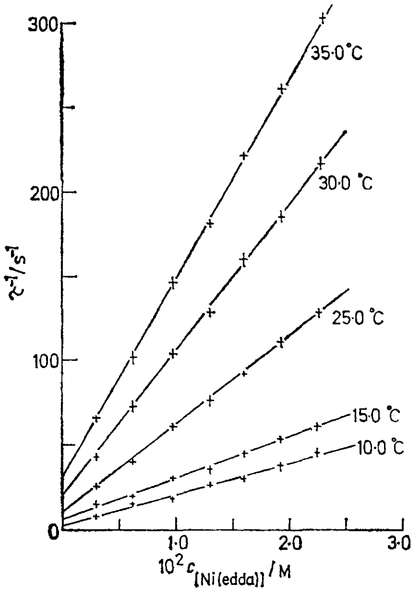


FIGURE 2 Variation of τ^{-1} with concentration for reaction of the complex [Ni(edda)] with pada at different temperatures. The vertical lines on each point indicate experimental scatter

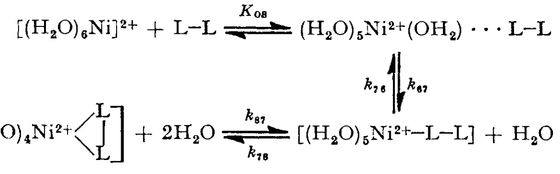
DISCUSSION

Scheme (2) illustrates the mechanism of formation of the complex between $[Ni(H_2O)_6]^{2+}$ and the bidentate ligand L–L outlined above. If the steady-state approximation is applied to formation of the intermediate $[(H_2O)_5Ni^{2+}\text{–}L\text{–}L]$, the observed rate constant for formation of the chelate complex is given by $k_f = K_{os}K_{67}k_{78}/(k_{76} + k_{78})$ which, if $k_{78} \gg k_{76}$, reduces to $K_{os}k_{67}$ and the

Caption to Figure 1

FIGURE 1 Variation of τ^{-1} with $c_M(1 + K_2c_H)^{-1}$ for reactions of nickel species with nsa at different temperatures [the vertical lines on each point indicate experimental scatter (representing, on average, five or six experiments)]: (a) Ni^{2+}; (b) $[Ni(tp)]^{3-}$; (c) [Ni(ida)]; (d) $[Ni(nta)]^-$; (e) [Ni(edda)]; (f) $[Ni(dien)]^{2+}$; (g) $[Ni(trien)]^{2+}$; (h) $[Ni(tren)]^{2+}$

kinetics of formation of the chelate complex are identical to those for a unidentate ligand. However, if the first metal–ligand bond is very weak (*i.e.* $k_{76} \gg k_{78}$) the expression reduces to $k_f = K_{os}k_{67}k_{78}/k_{76}$ and the rate-determining step now becomes ring closure.



SCHEME 2

It has been suggested that, with Ni^{II}, the two steps can become comparable when the ring-closure step is sterically hindered (especially when the resulting chelate complex contains a six-membered ring[3]) or when the first binding group of the ligand forms a particularly weak bond to the metal ion (*e.g.*, when it binds through oxygen[11]). Although nsa forms a six-membered ring with $Ni^{2+}(aq)$ in which both metal–ligand bonds involve oxygen, the value of k_f (Table 1; $\log k_f = 5{\cdot}01$) is comparable to those found for complex formation between nickel(II) and many other dianions,[1] and we conclude that the rate-determining step is replacement of the first water molecule in the inner co-ordination sphere of the metal ion (*i.e.* $k_{78} \gg k_{76}$). This conclusion is strengthened by the observation that $\Delta H_f^\ddagger$ (13·1 kcal mol^{-1}) is comparable to activation enthalpies for water exchange at nickel(II) [for which several values have been quoted, the latest being 12·1 ± 0·5 (ref. 12) and 13·88 kcal mol^{-1} (ref. 13)] and the reaction of $Ni^{2+}(aq)$ with several other ligands.[1,7] Thus, for example, with the neutral ligands pada, 1,10-phenanthroline, and 2,2′-bipyridine the values are 13·6,[7] 13·1,[14] and 13·2[14] kcal mol^{-1}, respectively, and the difference in k_f between nsa and the neutral ligands (a factor of 50—100) merely reflects the greater desolvation associated with the charge neutralisation which occurs on forming the transition state in the former case (seen as a more positive $\Delta S_f^\ddagger$ value).

Partial replacement of the inner hydration sphere of the metal ion by a multidentate ligand L might be expected to affect k_f in several ways. (*i*) A reduction in k_f is expected on statistical grounds since the number

TABLE 1

Rate and equilibrium constants and activation parameters for reaction of nickel(II) species with nsa (estimated errors in parentheses)

	$Ni^{2+}(aq)$	$[Ni(tp)]^{3-}$ ($n = 3$)	$[Ni(ida)]$ ($n = 3$)	$[Ni(nta)]^-$ ($n = 4$)
pH	7·5—8·0	7·4—8·4	7·5—8·4	7·5
k_{41}/l mol^{-1} s^{-1}	1·02(0·15) × 10^5	1·48(0·15) × 10^4	6·3(0·4) × 10^4	1·48(0·22) × 10^4
k_{41}^s/l mol^{-1} s^{-1}	1·0 × 10^5	3·0 × 10^4	1·3 × 10^5	4·4 × 10^4
$\Delta H_{41}^\ddagger$/kcal mol^{-1}	13·1(0·8)	16·0(1·0)	11·4(2·4)	14·3(1·4)
$\Delta S_{41}^{\ddagger(s)}$/cal K^{-1} mol^{-1}	+8(3)	+16(3)	+3(7)	+11(5)
k_{14}/s^{-1}	0·2 [a]	2·9(0·8)	5·2(1·3)	3·5(0·4)
$\Delta H_{14}^\ddagger$/kcal mol^{-1}		17·1(1·0)	16·6(3·1)	16·3(1·1)
$\Delta S_{14}^\ddagger$/cal K^{-1} mol^{-1}		+1(3)	+1(9)	−1(4)
$\log_{10} K_1$ (*a*) kinetic		3·71(0·18)	4·07(0·17)	3·53(0·21)
(*b*) spectrophotometric	5·62(0·15)	3·38(0·15)		3·53(0·15)
$\log_{10} K_1^s$ (mean)	5·62	3·85	4·37	4·01
	$[Ni(edda)]$ ($n = 4$)	$[Ni(dien)]^{2+}$ ($n = 3$)	$[Ni(trien)]^{2+}$ ($n = 4$)	$[Ni(tren)]^{2+}$ ($n = 4$)
pH	7·3—8·2	7·5—8·4	7·5—8·3	7·5—8·5
k_{41}/l mol^{-1} s^{-1}	2·6(0·3) × 10^4	1·53(0·05) × 10^6	4·6(0·2) × 10^6	5·2(0·3) × 10^6
k_{41}^s/l mol^{-1} s^{-1}	7·8 × 10^4	3·1 × 10^6	1·4 × 10^7	1·6 × 10^7
$\Delta H_{41}^\ddagger$/kcal mol^{-1}	11·3(2·5)	12·5(1·5)	9·5(1·8)	8·5(1·3)
$\Delta S_{41}^{\ddagger(s)}$/cal K^{-1} mol^{-1}	+2(8)	+13(5)	+6(6)	+3(4)
k_{14}/s^{-1}	20(2)	220(25)	650(50)	930(140)
$\Delta H_{14}^\ddagger$/kcal mol^{-1}	14·3(1·0)	14·3(1·4)	12·2(2·4)	11·6(1·4)
$\Delta S_{14}^\ddagger$/cal K^{-1} mol^{-1}	−4(3)	0(5)	−5(8)	−6(5)
$\log_{10} K_1$ (*a*) kinetic	3·11(0·09)	3·84(0·07)	3·85(0·05)	3·75(0·09)
(*b*) spectrophotometric	3·16(0·08)		3·74(0·14)	3·72(0·12)
$\log_{10} K_1^s$ (mean)	3·61	4·14	4·28	4·22

Rate constants refer to 25 °C and ionic strength 0·3M ($NaNO_3$); n is the number of co-ordination positions of Ni^{2+} assumed to be occupied by the ligand L.

[a] Estimated; a superscript s indicates that a statistical correction has been applied (see text).

TABLE 2

Rate and equilibrium constants and activation parameters for reaction of the nickel(II)–ethylenediamine-*NN′*-diacetate complex with pada (estimated errors in parentheses)

k_f/l mol^{-1} s^{-1}	5·9(0·3) × 10^3
$\Delta H_f^\ddagger$/kcal mol^{-1}	13·1(1·1)
$\Delta S_f^{\ddagger(s)}$/cal K^{-1} mol^{-1}	+4(4)
k_d/s^{-1}	11(4)
$\Delta H_d^\ddagger$/kcal mol^{-1}	15·8(3·0)
$\Delta S_d^\ddagger$/cal K^{-1} mol^{-1}	−1(9)
$\log_{10}K$ (*a*) kinetic	2·56(0·38)
(*b*) spectrophotometric	2·98 (0·15)

Rate constants refer to 25 °C and ionic strength = 0·3M ($NaNO_3$). A superscript s indicates that a statistical correction has been made to allow for the fact that in the complex [Ni(edda)] there are only two remaining water molecules (see the text and ref. 7).

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[11] *E.g.*, H. Hoffmann, *Ber. Bunsengesellschaft Phys. Chem.*, 1969, **73**, 432.

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

[13] J. W. Neely and R. E. Connick, *J. Amer. Chem. Soc.*, 1972, **94**, 8646.

[14] R. H. Holyer, C. D. Hubbard, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, 1965, **4**, 929.

of replaceable water molecules is reduced; this can be allowed for by multiplying the measured k_f by an appropriate statistical factor [in the present case by $6/(6 - n)$, where n is the number of co-ordination positions occupied by L, since the co-ordination number of Ni^{2+} remains at six] to give k_f^s. (*ii*) Strengthening of the metal–ligand bonds could be accompanied by a weakening of the remaining metal–water bonds; this would result in an increase in k_{67}, and so k_f^s, and a decrease in $\Delta H_f^\ddagger$. (*iii*) The value of k_{78} could be reduced, thus allowing ring closure to contribute to the rate-determining step (this effect would be expected to be more important the larger and more highly charged are L and L–L). (*iv*) In the case of a negatively charged incoming ligand L–L, K_{os} would be reduced if L was also charged since the net positive charge on the metal ion would be reduced. Effects (*iii*) and (*iv*) would both lead to a reduction in k_f^s. Consideration of the rate constants for complex formation between nickel species and nsa, NH_3, and pada and for water exchange allows us to decide on the relative importance of factors (*ii*), (*iii*), and (*iv*).

In Figure 3 most of these rate constants [suitably adjusted to take account of factor (*i*)] are shown for hexa-aquonickel(II) and the seven substituted nickel species. The latter have been ordered along the abscissa according to the number of bound nitrogen atoms, as indicated, with the result that the overall charge on the nickel species fluctuates along the series. The general increase in k_f^s found with NH_3, pada, and H_2O as the number of bound aliphatic nitrogen atoms increases is, as expected, found also with nsa [factor (*ii*)]. The other principal feature of Figure 3 is that, for a given complex [NiL], k_f^s for the charged nsa is always larger than for the neutral NH_3 and pada ligands. The ratio of k_f^s for nsa and the neutral ligands varies from 15 to 70 for the cationic [NiL] species {Ni^{2+}(aq), $[Ni(dien)]^{2+}$, $[Ni(trien)]^{2+}$, and $[Ni(tren)]^{2+}$} whereas it is generally less than 10 for the neutral and anionic [NiL] species {[Ni(ida)], $[Ni(nta)]^-$, and $[Ni(tp)]^{3-}$}, being smallest (*ca.* 3) for $[Ni(nta)]^-$. (The larger difference between k_f^s for nsa and pada with the complexes $[Ni(trien)]^{2+}$ and $[Ni(tren)]^{2+}$ is probably associated with the contribution of ring closure to the rate-determining step for the latter incoming ligand [7].) This is an important result and it confirms the indications of similar studies with the d^0 and high-spin d^5 metal ions Mg^{2+} (refs. 9 and 15) and Mn^{2+} (ref. 15) where, however, the water-exchange data for the partially substituted ions are generally not available. Thus, the complex-formation rate data can be rationalized in terms of the normal dissociative model used for 1 : 1 complexes [Scheme (2)] only if the *local* charge density on the metal ion is considered rather than the *overall* charge on the substituted metal ion. In particular, the net charge on the metal species should not be used to calculate K_{os} from the Fuoss equation.[2]

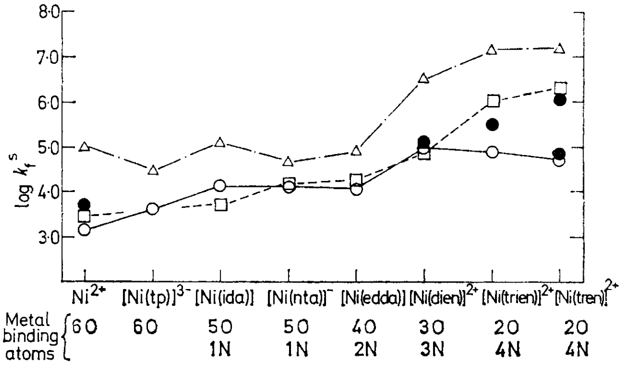

FIGURE 3 Statistically adjusted rate constant (log k_f^s) for reaction of nickel(II) species with charged and neutral ligands. Sources of data: nsa (△), this work; pada (○), this work and ref. 7; NH_3 (□), refs. 6 and 7; H_2O (●), ref. 5. In the case of water exchange, the first-order rate constants quoted in ref. 5 have been converted into second-order rate constants by treating the solvent as a reagent of concentration 55·5M to permit direct comparison with the other rate constants

The dissociation rate constants k_d for the [NiL(nsa)] complexes on the whole reflect the formation rate constants k_f^s, so there is less variation in K^s than in k_f^s or k_d. {There is notably less difference in K^s as L is varied than between the values for the complexes [NiL(nsa)] and [Ni(nsa)].} Similar results have been obtained before,[16] but this is by no means a universal picture.

We are indebted to A. R. White, who did some of the preliminary work on these systems.

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[15] D. N. Hague, S. R. Martin, and M. S. Zetter, *J.C.S. Faraday I*, 1972, **68**, 37.

[16] M. A. Cobb and D. N. Hague, *Trans. Faraday Soc.*, 1971, **67**, 3069.