# Kinetics of Ternary Complex Formation between Nickel Species and 2,2′-Bipyridine: Parametrization of Bound Ligand Effects

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Stopped-flow and temperature-jump relaxation methods have been used to measure rate constants $k_f$ for the formation of ternary complexes between 2,2′-bipyridine (bipy) and nickel(II)–nitrilotriacetate, –ethylenediamine-*N,N*-diacetate, –ethylenediamine-*N,N′*-diacetate, –diethylenetriamine, – triethylenetetramine, and –2,2′,2″-triaminotriethylamine complexes. Rate and equilibrium constants are also reported for the reaction of the nickel(II)–ethylenediamine-*N,N*-diacetate complex with pyridine-2-azo-*p*-dimethylaniline (pada) and the dianion from 5-nitrosalicylic acid (nsa). Comparison of the rate constants $k_f$ for the three series involving, respectively, bipy, pada and nsa suggests a simple parametrization scheme in which the terms are linked directly to structural features of the reactants. Major factors involved are the charges on the two ligands and the number of bound nitrogen atoms. The mechanistic interpretation of the terms is also considered.

The kinetics of the formation of 1 : 1 labile metal complexes in water has been widely studied and the determining factors are now sufficiently well understood[1,2] that it is usually possible to predict the values of the formation and dissociation rate constants ($k_f$ and $k_d$, respectively) from a knowledge of stability constants. Much less is known about the kinetics of formation of complexes involving metal ions in which the inner hydration sphere has already been partially replaced by another ligand, although there have been many investigations of their stability. An understanding of the effect of bound ligands on the kinetics of ternary complex formation is important since many catalytic reactions requiring metal ions, including a wide range of metal–enzyme reactions, involve reactions of this type.

Among the bivalent metal ions, nickel(II) has received much more attention than the others, principally because ligand-field effects make it one of the least reactive, and therefore most easily studied experimentally. Moreover, its stability with respect to oxidation and reduction and its $d^8$ electronic configuration have meant that its complexes tend to be relatively well characterized. The fact that it almost invariably retains octahedral co-ordination in water makes its complexes particularly suitable for establishing the effects on reactivity of such factors as ligand charge, steric hindrance and the transmission of electronic effects through the metal, without the complication of facile changes in co-ordination geometry which are found, for example, with zinc.

This paper reports the rate constants, as measured by stopped-flow and temperature-jump methods, for the formation in aqueous solution of ternary complexes involving the neutral bidentate ligand 2,2′-bipyridine (bipy) and the complexes of nickel(II) with nitrilotriacetate (nta), ethylenediamine-*N,N*-diacetate (*N,N*-edda), ethylenediamine-*N,N′*-diacetate (*N,N′*-edda), diethylenetriamine (dien), triethylenetetramine (trien) and 2,2′,2″-triaminotriethylamine (tren). Our choice of bipy as the incoming ligand was made largely because the spectral and thermodynamic characteristics of its complexes with several metals suggested that it would be useful for comparative purposes. While the free ligand adopts a variety of conformations in solution, [3] it is constrained in its complexes to take on the cisoid conformation in which the two rings are approximately coplanar.[4] Complex formation with bipy would thus be expected to exhibit rather stringent steric requirements —although there is evidence from rate constant, activation enthalpy,[2,5] and activation volume[6] measurements that water substitution is rate determining for reaction with $Ni(aq)^{2+}$. It should therefore provide an interesting comparison with our studies involving complex formation under the same conditions between the above nickel(II) species and two other bidentate ligands, the neutral molecule pyridine-2-azo-*p*-dimethylaniline (pada)[7] and the dianion from 5-nitrosalicylic acid (nsa).[8] Limiting values are estimated for the dissociation rate constants of the ternary complexes of bipy. Rate and equilibrium constants are also reported for the reaction of pada and nsa with [Ni(*N,N*-edda)].

Comparison of the three series of formation rate constants $k_f$ (which cover more than four orders of magnitude) suggests a parametrization scheme involving four terms, each of which is linked directly to a structural feature of the reactants. We discuss the mechanistic interpretation of the terms and consider briefly the use of this approach for the prediction of the formation rate constants of other ternary complexes.

## Experimental

Solutions were prepared from nickel(II) nitrate (BDH AnalaR) and standardized against the disodium salt of ethylenediamine-*N,N,N′,N′*-tetraacetic acid ($H_4$edta). Ethylenediamine-*N,N′*-diacetic acid (K. and K.) was purified by boiling a solution containing a slight excess of NaOH over activated charcoal for 30 min, filtering, cooling and adding $HClO_4$ until pH 3 to produce white crystals which were washed in cold water and propan-2-ol, and dried. Ethylenediamine-*N,N*-diacetic acid was prepared from 1,2-diaminoethane (Fisons) by the method of Schwarzenbach *et al.*[9] *via* *N*-ethoxycarbonyl.[10] 2,2′,2″-Triaminotriethylamine was isolated from technical grade triethylenetetramine (BDH, which typically contained up to 20% tren) by fractional crystallization of the hydrochlorides from ethanolic solution,[11] the regenerated amine being distilled under reduced pressure (127–128 °C, 0.15 Torr, ≈20 Pa). Diethylenetriamine (Fluka) and 2,4,6-trimethylpyridine (Fisons) were purified by fractional distillation, and 5-nitrosalicylic acid (Fluka) by recrystallization from water, while triethylenetetramine and nitrilotriacetic acid (Fluka, puriss. grade), 2,2′-bipyridine (BDH), and pyridine-2-azo-*p*-dimethylaniline (Sigma) were used without further purification.

The solutions for kinetic and equilibrium measurements were made up with triply distilled water, the middle distillation being from alkaline potassium permanganate. An ionic strength of

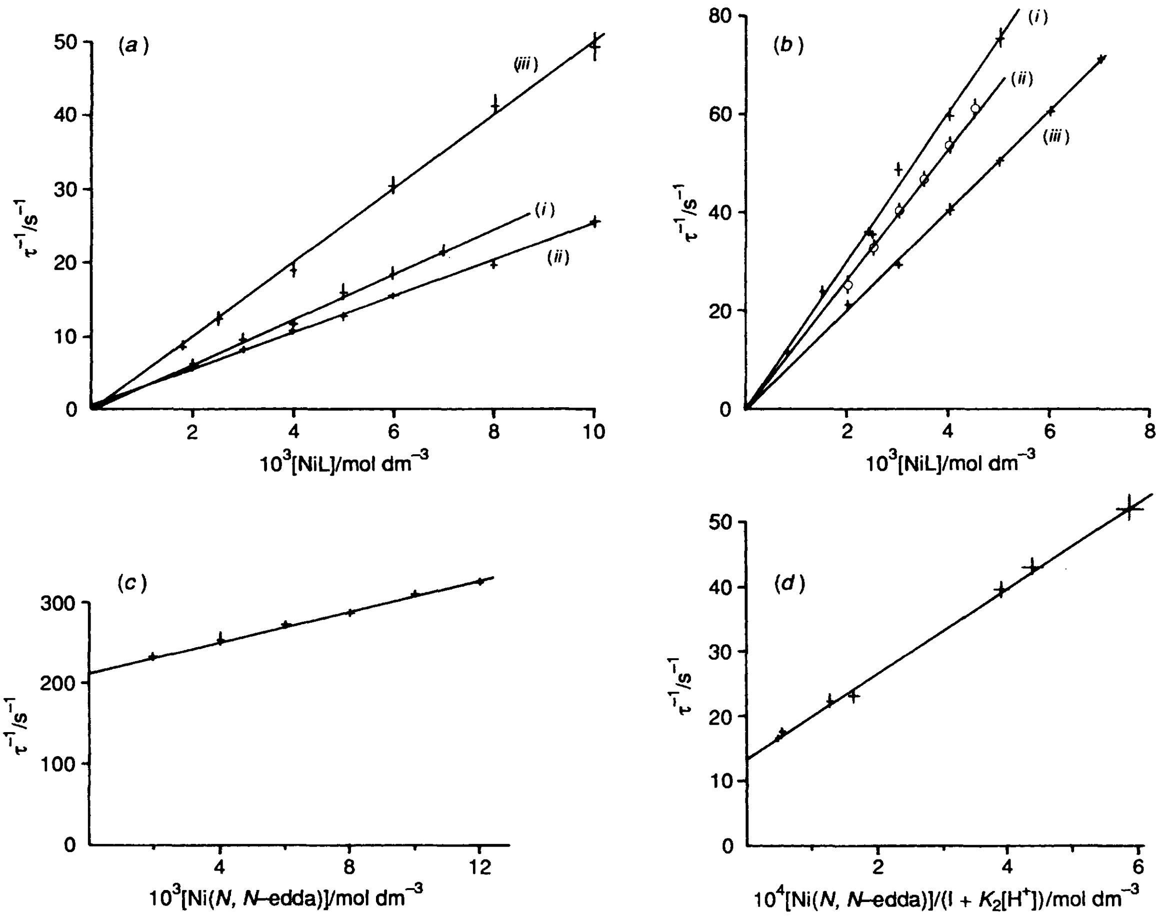


**Fig. 1** Variation of $\tau^{-1}$ with concentration for the reaction of nickel(II) species with bipy [(*a*), (*b*)], pada (*c*) or nsa (*d*). The vertical lines [also horizontal lines in (*d*)] on each point indicate experimental scatter (representing, on average, 5 or 6 experiments): (*a*) [NiL], with L = nta (*i*), *N*,*N*-edda (*ii*) or *N*,*N*′-edda (*iii*); (*b*) [NiL], with L = dien (*i*), trien (*ii*) or tren (*iii*); (*c*), (*d*) [Ni(*N*,*N*-edda)]

**Table 1** Rate constants for the reaction of nickel(II) species with bipy (estimated errors in parentheses)*

| | [Ni(nta)]$^-$ ($n$ = 4) | [Ni(*N*,*N*′-edda)] ($n$ = 4) | [Ni(*N*,*N*-edda)] ($n$ = 4) |
|---|---|---|---|
| $k_f$/dm$^3$ mol$^{-1}$ s$^{-1}$ | 3.1 (0.2) × $10^3$ | 5.1 (0.3) × $10^3$ | 2.6 (0.3) × $10^3$ |
| log $k_f^s$ | 3.97 | 4.18 | 3.89 |
| $k_d$/s$^{-1}$ | $\leqslant 1$ | $\leqslant 1$ | $\leqslant 1$ |
| $10^3$[NiL]/mol dm$^{-3}$ | 2.0–7.0 | 1.6–10.0 | 0.15–2.0 |
| $10^4$[bipy]/mol dm$^{-3}$ | 1.0–2.0 | 1.0–2.0 | 0.15 |
| | [Ni(dien)]$^{2+}$ ($n$ = 3) | [Ni(trien)]$^{2+}$ ($n$ = 4) | [Ni(tren)]$^{2+}$ ($n$ = 4) |
| $k_f$/dm$^3$ mol$^{-1}$ s$^{-1}$ | 1.6 (0.2) × $10^4$ | 1.35 (0.09) × $10^4$ | 1.05 (0.05) × $10^4$ |
| log $k_f^s$ | 4.51 | 4.61 | 4.50 |
| $k_d$/s$^{-1}$ | $\leqslant 2$ | $\leqslant 1$ | $\leqslant 2$ |
| $10^3$[NiL]/mol dm$^{-3}$ | 1.0–10.0 | 2.0–7.0 | 2.0–5.0 |
| $10^4$[bipy]/mol dm$^{-3}$ | 0.5–1.0 | 1.0–2.0 | 1.0–2.0 |

* Rate constants refer to pH 7.0–7.5, 25 °C and ionic strength 0.3 mol dm$^{-3}$ (NaCl, $NaClO_4$); $n$ is the number of co-ordination positions of $Ni^{2+}$ assumed to be occupied by the ligand L; a superscript s indicates that a statistical adjustment has been made (see text).

0.30 mol dm$^{-3}$ (NaCl or $NaClO_4$ for bipy, $NaNO_3$ for pada and nsa) and a temperature of 25.0 (± 0.01) °C were maintained, and the solutions were buffered with 2,4,6-trimethylpyridine (*ca.* 5 × $10^{-3}$ mol dm$^{-3}$) + $HClO_4$. The amine stock solutions were prepared from the free amine by weighing, the concentrations being checked by titration against HCl using an appropriate indicator.[12]

Kinetic (stopped-flow or temperature-jump) and equilibrium (UV/VIS spectrophotometric) measurements were undertaken by standard methods[7,13] and in all cases pseudo-first-order conditions were maintained (metal concentrations in the range $10^{-3}$–$10^{-2}$ mol dm$^{-3}$ being used, which were at least 10 times higher than the concentration of bipy, pada or nsa). The kinetic data reported here refer to relaxation effects observed in the 3–200 ms region and were generally obtained at *ca.* 300 (bipy), 380 (nsa) or 550 nm (pada), although identical relaxation times were obtained at several other wavelengths for each system. Published stability constants[14] were used to compute the concentrations of the various species present at different total concentrations of Ni$^{II}$ and L (nta, *N*,*N*-edda, *N*,*N*′-edda, dien, trien, tren) and different pH values. The total concentration of L was chosen so as to maximize the fraction of nickel present as [NiL] and in all cases it was possible to eliminate relaxation effects associated with free $Ni^{2+}$ and [$NiL_2$]. The L : Ni ratios used were 1.05 : 1 (nta, *N*,*N*-edda, *N*,*N*′-edda, trien, and tren), 1.2 : 1 (*N*,*N*-edda and dien) and 1.5 : 1 (dien).

**Table 2** Rate and equilibrium constants for the reaction of [Ni(*N*,*N*-edda)] with pada and nsa (estimated errors in parentheses) *

| | pada | nsa |
|---|---|---|
| $k_f$/dm$^3$ mol$^{-1}$ s$^{-1}$ | 9.7 (0.6) × 10$^3$ | 6.6 (0.4) × 10$^4$ |
| log $k_f^s$ | 4.46 | 5.30 |
| $k_d$/s$^{-1}$ | 2.1 (0.1) × 10$^2$ | 13 (1) |
| 10$^3$[Ni(*N*,*N*-edda)]/mol dm$^{-3}$ | 5.0–10.0 | 2.0–24.0 |
| 10$^4$[pada] or 10$^4$[nsa]/ mol dm$^{-3}$ | 0.50 | 1.0 |
| pH | 7.3–7.4 | 7.98–8.26 |
| $\log_{10} K_{kin}$ | 1.66 (0.04) | 3.69 (0.07) |
| $\log_{10} K_{spec}$ | 1.68 (0.02) | 3.82 (0.08) |

* Rate and equilibrium constants refer to 25 °C and ionic strength 0.3 mol dm$^{-3}$ ($NaNO_3$). A superscript s indicates that a statistical adjustment has been made to allow for the fact that in the complex [Ni(*N*,*N*-edda)] there are only two remaining water molecules (see text).

## Results

In the temperature-jump relaxation technique, the position of a chemical equilibrium is altered by means of a sudden temperature rise. The new equilibrium condition is approached exponentially and the relaxation time τ for reaction (1) (from

$$[\mathrm{NiL}] + \mathrm{bipy} \underset{k_d}{\overset{k_f}{\rightleftharpoons}} [\mathrm{NiL(bipy)}] \qquad (1)$$

which charges have been omitted) is given by equation (2) where

$$\tau^{-1} = k_f(\bar{c}_{ML} + \bar{c}_{bipy}) + k_d \qquad (2)$$

$\bar{c}_{ML}$ is the (new) equilibrium concentration of free [NiL] and $\bar{c}_{bipy}$ is the (new) equilibrium concentration of free bipy. Under the pseudo-first-order conditions used here, this reduces to equation (3) where [ML] is the computed concentration of

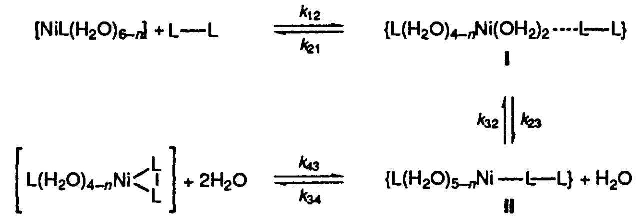
$$\tau^{-1} = k_f[\mathrm{ML}] + k_d \qquad (3)$$

[NiL] and a plot of $\tau^{-1}$ against [ML] results in a straight line with slope $k_f$ and intercept $k_d$. For some of the systems the relaxation times were inconveniently long for the temperature-jump technique but were suitable for the stopped-flow method. A similar analysis may be employed as long as pseudo-first-order conditions are maintained.

The results are given in Fig. 1 and Tables 1 and 2, the latter of which shows the data obtained for the [Ni(*N*,*N*-edda)]-pada and -nsa systems. In the two latter cases, it was possible to evaluate both $k_f$ and $k_d$, and hence the ratio $k_f/k_d$ which is equal to the stability constant of the complex ($K_{kin}$). For these two systems it was also possible to determine the ternary stability constant spectrophotometrically ($K_{spec}$) and the agreement between $K_{spec}$ and $K_{kin}$ (Table 1) is excellent. Unfortunately, the intercept of the $\tau^{-1}$/[ML] plot is too small to permit reliable estimation of $k_d$ for the bipy systems; neither was it possible to evaluate reliable stability constants for the bipy ternary complexes spectrophotometrically owing to the steady formation of the more stable bis- and tris-bipy complexes. However, the agreement between our values of $k_f$ and published values {log $k_f$ for [Ni(nta)] = 3.38,[15] [Ni(*N*,*N*′-edda)] = 3.74,[16] [Ni(dien)] = 4.20,[17] [Ni(trien)] = 3.88,[18] [Ni(tren)] = 4.00[19]} obtained under a variety of conditions is good.

The nsa system was analysed by the method used previously.[8] This involved plotting $\tau^{-1}$ against {[ML]/(1 + [H$^+$]/$K_2$)}, where log $K_2$ is the higher p$K_a$ of $H_2$nsa (for which an interpolated value[20] of 9.86 was used), to generate $k_f$ and $k_d$ as the slope and intercept, respectively.

## Discussion


**Scheme 1**

The mechanism for the formation of the complex between [NiL($H_2O$)$_{6-n}$] and the bidentate ligand L–L is shown in Scheme 1, where L is a ligand of denticity *n*, species **I** is an outer-sphere complex and **II** is a singly co-ordinated inner-sphere complex. The first step is rapid (diffusion controlled) and can be treated as a pre-equilibrium; $K_{os}$ ($=k_{12}/k_{21}$), the formation constant for the outer-sphere intermediate, can be calculated by the Fuoss equation (4) where $b = z_{ML}z_{L-L}e_0^2/a\varepsilon kT$ and *a* is the centre-

$$K_{os} = (4\pi N_0 a^3/3000)\exp(-b) \qquad (4)$$

to-centre distance between the metal M and ligand L–L, $z_{ML}$ and $z_{L-L}$, respectively, the formal charges on ML and L–L, $N_0$ is Avogadro's number, $e_0$ the electronic charge, ε the relative permittivity of the solvent, *k* the Boltzmann constant and *T* the absolute temperature. The same mechanism applies for the reaction of L–L with Ni(aq)$^{2+}$, in which case the Fuoss equation contains $z_M$, the charge on M, in place of $z_{ML}$. If the steady-state approximation is applied to the formation of intermediate **II**, the observed rate constant for the formation of the chelate complex is given by $k_f = K_{os}k_{23}k_{34}/(k_{32} + k_{34})$. If the ring-closure step is rapid compared with step $\mathbf{I} \rightleftharpoons \mathbf{II}$ this reduces to $K_{os}k_{23}$ which is equivalent to $K_{os}k_{ex}$, where $k_{ex}$ is the rate constant for water exchange. If it is not, $k_f$ is less than $K_{os}k_{23}$ and in the limit (*i.e.* $k_{34} \ll k_{32}$) ring closure becomes the rate-limiting process, with $k_f = K_{os}k_{23}k_{34}/k_{32}$.

Partial replacement of the inner hydration sphere of the metal ion by L could affect $k_f$ in several ways. (*i*) A reduction in $k_f$ is expected on statistical grounds because the number of replaceable water molecules is reduced. Since the co-ordination number of Ni$^{2+}$ remains six, this effect is conveniently allowed for by multiplying the measured $k_f$ by a statistical factor 6/(6 − *n*), where *n* is the number of co-ordination positions occupied by L, to give $k_f^s$. (*ii*) A change in $K_{os}$ is expected if the bound and incoming ligands are both negatively charged since the net positive charge on the metal ion would be reduced or replaced by a negative charge. (*iii*) The value of $k_{34}$ could be reduced, thus allowing ring closure to contribute to (or, in the limit, become) the rate-determining step. This effect could be steric or electronic in origin and its importance will depend on the detailed structures of L and L–L. (*iv*) 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 $k_{23}$ and therefore $k_f^s$, which would be reflected in an increased $k_{ex}$. On the other hand, effects (*ii*) and (*iii*) would both lead to a reduction in $k_f^s$ but not alter $k_{ex}$.

Hunt[21] and Margerum[22] have shown by measurement of water-exchange rates[21] and the rate constants for the formation of ternary complexes with $NH_3$[22] that the lability of remaining water molecules in [NiL] increases regularly with an increasing number of (aliphatic) nitrogens co-ordinated to the metal.[2] We[7,8] and others[2] have confirmed this trend with other systems and it appears, rather surprisingly, that the labilization caused by bound aminocarboxylates is attributable to the neutral amino group(s) rather than the anionic carboxylate group(s).

Funahashi and Tanaka[23] have attempted to parametrize these labilization effects by correlating the changes in water-exchange rate $k_{ex}$ ($\equiv k_{23}$) with the nucleophilicity scale of Edwards.[24] For a limited range of bound ligands, initially uni- and bi-dentate but later[25] also multidentate, they found an approximately linear relationship between the (logarithm of

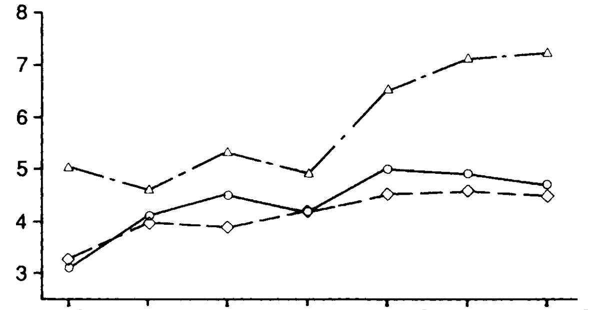


**Fig. 2** Statistically adjusted rate constant (log $k_f^s$) for reaction of nickel(II) species with bipy (◇), pada (○) or nsa (△)

**Table 3** Numerical values[a] of parameters for equation (5) (see text)

| | | |
|---|---|---|
| log $k_f^0$ | Starting value | 3.3 (pada, bipy) 5.0 (nsa) |
| $a_1$ | each bound N atom | $+0.5_2$ ($0.0_2$) |
| $a_2$ | pyramidal L[b] | $+0.1_8$ ($0.0_6$) |
| $r_1$ | steric interaction (L/L–L)[c] | $-0.4_8$ ($0.0_9$) |
| $r_2$ | electrostatic interaction (L/L–L)[d] | $-1.05_5$ ($0.0_8$) |

[a] Values of log $k_f^0$ are from the literature; values of other parameters were obtained by least-squares regression analysis with standard deviations shown in brackets. [b] Applied for nta, *N*,*N*-edda and tren. [c] Applied for L = *N*,*N*-edda, dien, trien, tren and L–L = bipy. [d] Applied in the cases of L = nta, *N*,*N*-edda, *N*,*N*′-edda and L–L = nsa.

the) ratio of $k_{ex}$ for substituted and unsubstituted Ni$^{2+}$ and the electron-donating ability of the ligand $E_{(A)}$. The parameter $E_{(A)}$ was derived from Edwards' $E_n$ values in the case of multidentate ligands by considering the number of bidentate segments as well as the nature of the binding atoms. Comparison of the results with bipy (Table 1) with those for pada and nsa (Table 2, refs. 7 and 8) shows a remarkably similar pattern for the variation of log $k_f^s$ with the nature of the bound ligand L. This is brought out in Fig. 2, which is a revised version of Fig. 3 in ref. 8 (from which the data for L = polytriphosphate and iminodiacetate have had to be omitted since it was not possible to find conditions under which the bipy reaction could be studied for these ligands), and suggests that it might be possible to parametrize the labilization effects on the overall complex formation rate constant in an analogous way.

*Development of an Empirical Relationship for* $k_f^s$.—The approach we have taken is to express $\log_{10} k_f^s$ by equation (5),

$$\log_{10} k_f^s = \log_{10} k_f^0 + pa_1 + a_2 + r_1 + r_2 \qquad (5)$$

where $k_f^0$ is the 'starting' rate constant and refers to the reaction of the unsubstituted metal ion with the appropriate L–L. The other parameters, of which up to three may be used in a particular case, are 'accelerating' ($a_1$, $a_2$) or 'retarding' ($r_1$, $r_2$) terms which depend on the identities of the two ligands; $p$ is the number of bound nitrogen atoms. The numerical values of $a_1$, $a_2$, $r_1$ and $r_2$ were determined by a least-squares multiple regression analysis of the experimental data. The values used[2,6,8] for the 'starting' rate constants $\log_{10} k_f^0$ were 3.3 for pada and bipy and 5.0 for nsa. Because they are obviously outlying points, the data for the reaction of pada and bipy with [Ni(trien)] and [Ni(tren)] were excluded from the analysis; this will be discussed below.

The regression analysis was performed using the Minitab system and the parameters giving the best fit are listed in Table 3. The fit was excellent, producing a standard deviation of $0.1_2$ about the regression line and an $R^2$ value of 0.993. We now consider briefly the rationale behind the inclusion of each parameter and comment on the values obtained.

(*a*) *The labilizing effects of the bound ligand* (pa$_1$, a$_2$). The labilization of remaining water molecules by bound nitrogen atoms [effect (*iv*) above] is well established for Ni$^{II}$ and Margerum *et al.*[2] obtained a slope of about +0.5 from a plot of the (logarithm of the) rate constants for water exchange and reaction with NH$_3$ against the number of bound N atoms. Our value of $+0.5_2$ for $a_1$ agrees well with this.

The other acceleration parameter $a_2$ ($+0.1_8$) represents the small additional labilizing effect associated with the presence of a pyramidally bound ligand L. Supporting spectroscopic evidence for distortion comes from our observation[26] that the absorption coefficients of the peaks centred at about 500 nm are higher for the complexes of the three tripodal ligands than for Ni(aq)$^{2+}$ and the complexes of the straight-chain ligands. Similar distortion in [Co(nta)(H$_2$O)$_2$]$^-$ produces[27] even greater rate enhancements.

(*b*) *The retarding effect of interactions between bound and incoming ligands* (r$_1$, r$_2$). Two aspects of Fig. 2 suggest that the interaction between bound and incoming ligands envisaged in effects (*ii*) and (*iii*) above can be important. In the first place, the value of $k_f^s$ for bipy is less than that for pada in some cases (L = *N*,*N*-edda, dien, trien, tren) but the same for the others. We attribute this reduction (parameter $r_1$) to steric interaction of the type proposed by Steinhaus and Kopajlo[18] to rationalize the low $k_f^s$ values for the reaction of bipy or 1,10-phenanthroline with [Ni(trien)]. Interestingly, molecular models indicate that such steric crowding would occur during the ring-closure step with each of the four complexes listed above (assuming that dien adopts the facial configuration) but not in the case of L = *N*,*N*′-edda where a reaction pathway exists which avoids it.

The second feature of Fig. 2 which suggests that ligand–ligand interaction can lead to a reduction in $k_f^s$ is that the coulomb enhancement for nsa found with Ni(aq)$^{2+}$ is substantially reduced in some instances (L = nta, *N*,*N*-edda, *N*,*N*′-edda) but not in others (L = dien, trien, tren). Parameter $r_2$ is therefore associated with coulombic repulsion between nsa and carboxylate groups on the bound ligand occupying positions *cis* to the replaceable waters. The values[8] of $k_f^s$ for the reaction of nsa with [NiL] (L = iminodiacetate or polytriphosphate) are consistent with the operation of the effect in these systems also.

(*c*) *Mechanistic interpretation.* For 'normal' reaction, in which neither $r_1$ nor $r_2$ is invoked, the condition $k_{34} \gg k_{32}$ is obeyed and the rate determining step is first-water substitution with $k_f^s = K_{os}k_{23}$. The value of $k_{23}$, equivalent to the water-exchange rate, is determined by the nature of the bound ligand L through the parameters $pa_1$ and $a_2$ [effect (*iv*) above]. As we have seen, there are two reasons why the observed rate constant $k_f^s$ could be less than 'normal' for the other reactions: due to a reduction in the value of $K_{os}$ [effect (*ii*)], and because ring closure is now contributing to, or has become, the rate-determining step [effect (*iii*)].

In reactions involving the electrostatic retardation parameter $r_2$ the most likely explanation for the low value of $k_f^s$ is that there has been a reduction in $K_{os}$ compared with the value for the dications.

The steric parameter $r_1$ is numerically less than $r_2$ and, although it is possible to assume that it also is associated with a reduction in $K_{os}$, it is difficult to identify the structural feature which could produce the effect in the reaction of bipy with, say, [Ni(*N*,*N*-edda)] but not with [Ni(*N*,*N*′-edda)]. It seems more likely that $r_1$ is associated with a ring-closure effect: the relevant modifying term for $k_f^s$ is $k_{34}/(k_{32} + k_{34})$, so $k_{34}$ would only need to be about $\frac{1}{2}k_{32}$ to give the required reduction in $k_f^s$.

(*d*) *Reactions of* [Ni(trien)] *and* [Ni(tren)]. The reactions of the two tetraamines are interesting in that the values of $k_f^s$ for nsa are both 'normal' but those for pada and bipy are depressed. The values of log $k_f^s$ calculated by equation (5) using the parameters listed in Table 3 exceed the experimentally determined values by $0.4_8$ and $0.3_0$, respectively, for [Ni(trien)] and by $0.8_6$ and $0.5_8$ for [Ni(tren)]. These discrepancies are statistically significant. In our work with pada[7] we concluded from the relatively low activation energies that ring closure was contributing to the rate-determining process and this has been confirmed by Grant and Wilson[28] who determined the activation volumes. It appears that ring closure is even more important in the bipy reactions. Presumably the reason for the different behaviour of nsa is that steric interference does not occur owing to the single aromatic ring being relatively far from the co-ordinating atoms.

In summary, we are proposing a simple parameterization scheme for 'predicting' the statistically adjusted rate constant $k_f^s$ for the formation of a ternary complex of nickel(II) from the value $k_f^o$ for the formation of the analogous binary complex from Ni(aq)$^{2+}$. Rate enhancements are found where the bound ligand L is attached through nitrogen atoms ($pa_1$) and, to a much lesser extent, where L is pyramidal in structure ($a_2$). Rate reductions may be seen if there are steric ($r_1$) or electrostatic ($r_2$) interactions between bound and incoming ligands.

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