Kinetics of Ternary Complex Formation between Cobalt(II) Species and 2,2′-Bipyridine: Parametrization of Bound-ligand Effects†

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Temperature-jump and stopped-flow relaxation methods have been used to measure rate constants (and in some cases activation enthalpies and entropies) for the formation and dissociation of the 1 : 1 complex between cobalt(II) and 2,2′-bipyridine (bipy), and of ternary complexes between bipy and cobalt(II)-polytriphosphate, -nitrilotriacetate, -ethylenediamine-*N,N*-diacetate, -ethylenediamine-*N,N′*-diacetate, -triethylenetetramine and -2,2′,2″-triaminotriethylamine complexes. The rate constants k_f for the three series involving, respectively, bipy, *N,N*-dimethyl(*p*-pyridin-2-ylazo)aniline and the dianion from 5-nitrosalicylic acid have been compared. The data are found to fit the simple parametrization scheme recently developed for analogous reactions of nickel(II) in which the terms are linked directly to structural features of the reactants. The relative behaviour of the two metals is discussed.

Many kinetic investigations have been reported on the formation of 1 : 1 labile metal complexes in aqueous solution and it is now usually possible to predict[1,2] reliably the values of the formation and dissociation rate constants (k_f and k_d, respectively) if the stability constant[3] is known. Relatively little is known about the kinetics of formation of complexes involving metal ions in which some of the water molecules of the inner hydration sphere have already been replaced. It is important to gain an understanding of the factors governing the kinetics of ternary complex formation since many catalytic reactions, including a wide range of metal–enzyme reactions, are of this type.

Among the bivalent metal ions nickel(II) has been the most widely studied, principally because ligand-field effects make it one of the least reactive. Half-times for complex formation (ternary as well as 1 : 1) are typically in the millisecond range which makes the reactions suitable for study by the stopped-flow method. Other factors which contribute to the mechanistic pre-eminence[1,2] of nickel(II) are its stability with respect to oxidation and reduction, the range of spectroscopic techniques available for characterizing its complexes, and the tenacity with which it retains octahedral co-ordination in water. In consequence, we are now able to predict[2,4] in many cases the effect of a particular bound ligand L on the reactivity of nickel(II) towards a second ligand L–L.

The situation with cobalt(II) is less clear. While its complexes are also well characterized (due to its d^7 configuration), their reactivities are considerably more difficult to establish than those of their nickel(II) analogues. Not only are they frequently too labile for the stopped-flow method but they tend to autoxidise when two or more of the co-ordinating atoms are nitrogen. Nonetheless, there have been indications[2,5] that the factors influencing the reactivity of [ML] are similar for the two metals.

With this in mind we have undertaken[4,6–10] a comparative investigation of the formation kinetics of a series of cobalt(II) and nickel(II) ternary complexes, as in equation (1) ($M = Co^{II}$ or Ni^{II}).

$$[ML(H_2O)_{6-n}]^{2+} + L\text{–}L \longrightarrow [ML(L\text{–}L)(H_2O)_{4-n}] + 2H_2O \quad (1)$$

Here, L is a ligand of denticity n (or H_2O) and, as far as possible, we have used the complete range of ligands L for all combinations M = Co or Ni and different L–L. For both the neutral ligand L–L = *N,N*-dimethyl(*p*-pyridin-2-ylazo)aniline (pada)[9] and the dianionic ligand L–L = 5-nitrosalicylate(2–) (nsa)[10] we found a high degree of congruence between the behaviour of the cobalt(II) and nickel(II) complexes with a range of neutral and anionic ligands L.

The present paper reports the rate constants, as measured by the temperature-jump and stopped-flow methods, for reaction (1) with $M = Co^{II}$, L–L = the neutral ligand 2,2′-bipyridine (bipy) and L = polytriphosphate(5–) (tp), nitrilotriacetate(3–) (nta), ethylenediamine-*N,N′*-diacetate(2–) (*N,N′*-edda), ethylenediamine-*N,N*-diacetate(2–) (*N,N*-edda), triethylenetetramine (trien) and 2,2′,2″-triaminotriethylamine (tren); also for the reaction of bipy with Co^{2+} (aq) and, where possible, the activation enthalpies and entropies. We chose bipy as the incoming ligand largely because the spectral and thermodynamic characteristics of its complexes with several metals suggested that it would be useful for comparative purposes. In addition, ternary complex formation with bipy would be expected[4] to exhibit rather stringent steric requirements, yet the activation enthalpies[2,11] and activation volumes[12] for its reaction with several aqua-ions [including Co^{2+}(aq) and Ni^{2+}(aq)] indicate that in 1 : 1 complex formation at least, substitution of the first water molecule is rate determining.

Following our practice with the nickel(II) data,[4] we compare the formation rate constants k_f (which cover almost four orders of magnitude) for the three cobalt(II) series. The values are represented by the same parametrization scheme involving four terms as was used for nickel(II), each term of which is linked to a structural feature of the reactants. We discuss briefly the mechanistic implications of this and compare the values obtained for the two metals in the light of their co-ordination chemistry.

Experimental

Solutions were prepared from cobalt(II) nitrate (BDH AnalaR) and standardized against the disodium salt of ethylenediamine-*N,N,N′,N′*-tetraacetic acid (H_4edta) using xylenol orange

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† *Supplementary data available* (No. SUP 57056, 5 pp.): plots of τ^{-1} *vs.* complex concentration. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

as indicator.[13] Ethylenediamine-*N*,*N*′-diacetic acid, ethylenediamine-*N*,*N*-diacetic acid and 2,2′,2″-triaminotriethylamine were obtained as described previously.[9,10] 2,4,6-Trimethylpyridine (Fisons) was purified by fractional distillation and $Na_5P_3O_{10}\cdot 6H_2O$ (Albright and Wilson) by double recrystallization from water, while nitrilotriacetic acid, triethylenetetramine (Fluka, puriss. grade) and 2,2′-bipyridine (BDH) 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 0.30 mol dm^{-3} (NaCl or $NaClO_4$) was maintained and, apart from those involving nta, the solutions were buffered with 2,4,6-trimethylpyridine (4×10^{-2} or 5×10^{-3} mol dm^{-3}, depending on whether the technique used was temperature-jump or stopped-flow, respectively) + $HClO_4$. The concentration of the bipy solutions was checked spectrophotometrically.[14] Temperatures were accurate to better than ±0.1 °C. The amine stock solutions were prepared from the free amine by weighing, the concentrations being checked by titration against HCl using an appropriate indicator.[13] Solutions of the complexes of cobalt(II) with ligands containing two or more nitrogen atoms were, to a greater or lesser extent, sensitive to autoxidation and all manipulations involving them were therefore carried out under nitrogen. The ligand was added last as a concentrated solution (0.1–0.5 mol dm^{-3}) by means of a micrometer syringe (accurate to ±0.0001 cm^3); solutions in the temperature-jump cell showed no signs of oxidation within 30 min and evidence of only slight oxidation after several hours.

Kinetic (temperature-jump or stopped-flow) and equilibrium (UV/VIS spectrophotometric) measurements were undertaken by standard methods[7,15] and in all cases except for the nta system 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). The kinetic data reported here were obtained by the stopped-flow method for the aqua, tp and *N*,*N*′-edda systems and the temperature-jump method for the remainder. They were generally obtained at *ca.* 300 nm, although identical relaxation times were obtained at several other wavelengths in the range 290–330 nm for each system. Each data point is the average of five or six separate determinations with the same solution. Published stability constants[3] were used to calculate the concentrations of the various species present at different total concentrations of Co^{II} and L (tp, nta, *N*,*N*′-edda, *N*,*N*-edda, trien or tren) and different pH values. The total concentration of L was chosen so as to maximize the fraction of cobalt present as [CoL] and in all cases it was possible to eliminate relaxation effects associated with free Co^{2+} and $[CoL_2]$. The L:Co ratios used were 1.1:1 (nta and trien), 1.2:1 (tren), 1.3:1(tp), 1.5:1 (*N*,*N*-edda) and 1.8:1 or 2.0:1 (*N*,*N*′-edda).

Results

In the temperature-jump relaxation method, the position of equilibrium is changed slightly by means of a sudden temperature rise. The new equilibrium position is approached exponentially and the relaxation time τ for reaction (2) (from

$$[CoL] + bipy \underset{k_d}{\overset{k_f}{\rightleftharpoons}} [CoL(bipy)] \qquad (2)$$

which charges have been omitted) is given by equation (3) where

$$\tau^{-1} = k_f(\bar{c}_{CoL} + \bar{c}_{bipy}) + k_d \qquad (3)$$

$\bar{c}_{CoL}$ is the (new) equilibrium concentration of free [CoL] and $\bar{c}_{bipy}$ is the (new) equilibrium concentration of free bipy. Under pseudo-first-order conditions this reduces to equation (4) and

$$\tau^{-1} = k_f\bar{c}_{CoL} + k_d \qquad (4)$$

a plot of τ^{-1} against $\bar{c}_{CoL}$ results in a straight line with slope k_f and intercept k_d. The ternary stability constant K_{kin} is given by k_f/k_d. A similar analysis may be used for systems studied by the stopped-flow method provided pseudo-first-order conditions are maintained; also for the reaction of bipy with Co^{2+}(aq), in which case $\bar{c}_{CoL}$ in equation (4) is replaced by $\bar{c}_{Co}$.

The results for the systems Co^{2+}(aq) and [CoL], L = tp, *N*,*N*′-edda, *N*,*N*-edda, trien or tren are shown in Fig. 1, SUP 57056 and Table 1. As expected, no change in relaxation time was observed on varying the total bipy concentration. The relaxation time was also independent of pH in the ranges indicated, and of buffer concentration. In all cases except L = trien and tren the size of the relaxation effects and/or the unfavourable stability constants precluded a temperature-variation study. It also proved impossible to determine the ternary stability constant spectrophotometrically in all cases. Attempts were made to study the reaction of bipy with [CoL], L = iminodiacetate(2−) (ida) or diethylenetriamine (dien), but it proved impossible to find suitable conditions.

The system with L = nta was studied by the temperature-jump method under second-order conditions ($\bar{c}_{CoL} = \bar{c}_{bipy}$) since the ternary stability constant is too high to permit the use of pseudo-first-order conditions and the relaxation time too short for the use of stopped-flow. An attempt to analyse the system by an iterative computer procedure [in which τ^{-1} was plotted against ($\bar{c}_{CoL} + \bar{c}_{bipy}$) calculated using an estimate of K_{kin}] failed owing to the comparatively low value of k_d and consequent failure of the data to converge. Instead, the stability constant was determined spectrophotometrically at various temperatures and the required values for the kinetic analysis obtained by interpolation from a plot of log *K vs.* T^{-1}. The values of $\log_{10} K$ determined spectrophotometrically were:

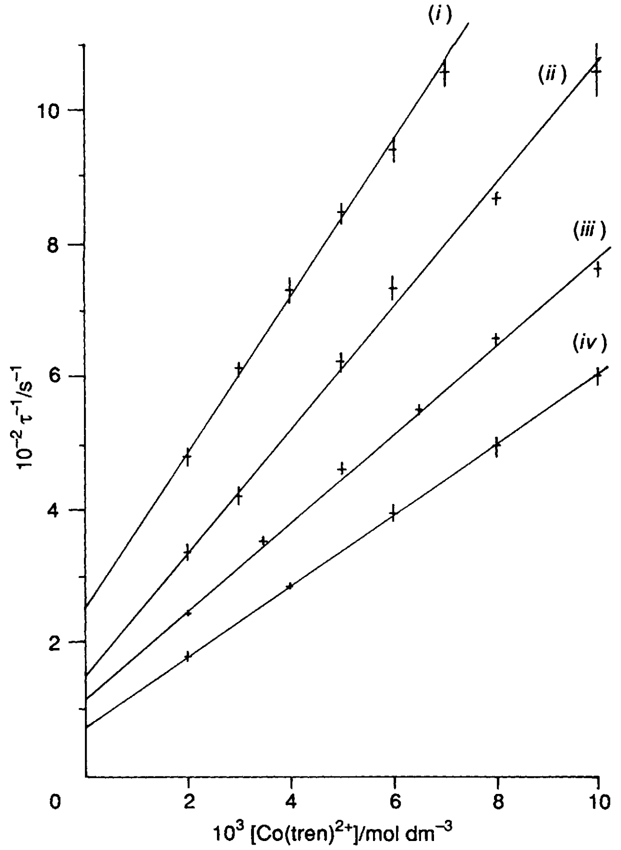


Fig. 1 Variation of τ^{-1} with concentration for the reaction of $[Co(tren)]^{2+}$ with bipy at (*i*) 31, (*ii*) 25, (*iii*) 19 or (*iv*) 13 °C. The vertical lines on each point indicate experimental scatter (representing, on average, 5 or 6 experiments)

Table 1 Rate and equilibrium constants and activation parameters for the reactions of cobalt(II) species with bipy (estimated errors in parentheses)[a]

	$Co^{2+}(aq)$	$[Co(tp)]^{3-}$ ($n = 3$)	$[Co(nta)]^-$ ($n = 4$)	$[Co(N,N'\text{-edda})]$ ($n = 4$)	$[Co(N,N\text{-edda})]$ ($n = 4$)	$[Co(trien)]^{2+}$ ($n = 4$)	$[Co(tren)]^{2+}$
$k_f/dm^3\ mol^{-1}\ s^{-1}$	$7.5(0.5) \times 10^4$	$7.6(0.8) \times 10^4$	$9.0(1.1) \times 10^5$	$3.8(0.5) \times 10^4$	$3.8(0.4) \times 10^5$	$2.3(0.2) \times 10^5$	$9.2(0.7) \times 10^4$
$k_f^s/dm^3\ mol^{-1}\ s^{-1}$	7.5×10^4	1.5×10^5	2.7×10^6	1.1×10^5	1.1×10^6	6.9×10^5	
$\Delta H_f^‡/kJ\ mol^{-1}$			30(2)			27(5)	31(3)
$\Delta S_f^{‡(s)}/J\ K^{-1}\ mol^{-1}$			−20(7)			−41(17)	−34(10)
k_d/s^{-1}			3(5)	5(4)	50(60)	80(15)	$1.6(0.3) \times 10^2$
$\Delta H_d^‡/kJ\ mol^{-1}$			52(13)			40(9)	44(6)
$\Delta S_d^‡/J\ K^{-1}\ mol^{-1}$			−60(40)			−67(25)	−56(18)
$K_{kin}/dm^3\ mol^{-1}$	4.5×10^5[b]		$3(4) \times 10^5$[c]	$8(8) \times 10^3$	$8(10) \times 10^3$	$3(1) \times 10^3$	$6(2) \times 10^2$
$10^3[c_{CoL}]/mol\ dm^{-3}$	0.6–1.5	0.5–1.5	0.05–0.3	0.75–2.0	1.0–5.0	1.0–6.0	2.0–10.0
$10^5[c_{bipy}]/mol\ dm^{-3}$	4–8	4–8	5–30	5–10	8–20	5–10	10
pH	6.5–7.5	7.0–7.5	7.1–7.9	7.8–8.0	7.6–7.8	7.7–8.3	7.7–8.4

[a] The rate and equilibrium constants refer to 25 °C and ionic strength 0.3 mol dm^{-3} (NaCl, $NaClO_4$); n is the number of co-ordination positions of Co^{2+} assumed to be occupied by the ligand L; a superscript s indicates that a statistical adjustment has been made (see text). [b] Value taken from ref. 16. [c] Interpolated value determined spectrophotometrically (see text).

5.31(0.04) at 12.3, 5.22(0.02) at 19.3, 5.03(0.03) at 30.3 and 4.94(0.03) at 37.1 °C. The constant k_d was then calculated from the interpolated equilibrium constant and the slope ($= k_f$) of the τ^{-1} *vs.* ($\bar{c}_{CoL} + \bar{c}_{bipy}$) plot, Fig. 2.

Discussion

Ternary complex formation between a partially-substituted metal ion $[ML(H_2O)_{6-n}]$ and a bidentate ligand L–L [equation (1)] is generally discussed[2] in terms of Scheme 1, from which charges have been omitted for clarity. For M = Co^{II}, as for Ni^{II}, the first step can be treated as a rapid pre-equilibrium. The formation constant for the outer-sphere intermediate **I**, K_{os} ($= k_{12}/k_{21}$), is calculated by the Fuoss equation,[17] which involves the charges on the reactants, z_{ML} and z_{L-L}, respectively, and the reaction distance a. If the steady-state approximation is applied to the formation of intermediate **II**, the singly co-ordinated inner-sphere complex, the observed rate constant for the formation of the chelate complex is given by equation (5). Two limiting conditions can be recognized, depending on the relative values of k_{32} and k_{34}. Usually,[2] ring closure is rapid compared with step **II** ⟶ **I** and k_f reduces to $K_{os}k_{23}$. This is equivalent to $K_{os}k_{ex}$, where k_{ex} is the rate constant for water exchange at $[ML(H_2O)_{6-n}]$. If it is not, k_f is less than $K_{os}k_{23}$ and in the extreme case of rate-limiting ring closure it becomes $K_{os}k_{23}k_{34}/k_{32}$.

$$k_f = K_{os}k_{23}k_{34}/(k_{32} + k_{34}) \qquad (5)$$

A similar scheme applies[2] for the formation of the 1:1 complex of $Co^{2+}(aq)$ or $Ni^{2+}(aq)$ with L–L and there is good evidence that in both cases bipy reacts by rate-limiting first-water substitution (*i.e.* $k_{34} \gg k_{32}$). Our value of 7.5×10^4 $dm^3\ mol^{-1}\ s^{-1}$ for $Co^{2+}(aq)$ (Table 1), which agrees well with those of Wilkins and co-workers[11] and Mohr and van Eldik[12] (7.2×10^4 and 6.5×10^4 $dm^3\ mol^{-1}\ s^{-1}$, respectively), is typical[2] for reaction of this metal with a neutral ligand. Similar agreement has been found[4] for $Ni^{2+}(aq)$. Moreover, the activation volumes for reaction of both metals with bipy[12] are similar to those for water exchange,[18] and all are consistent with an I_d mechanism[19] ($\Delta V^‡ = +7.5$ and $+6.1$ $cm^3\ mol^{-1}$, respectively, for cobalt, and $+7.2$ and $+7.2$ $cm^3\ mol^{-1}$ for nickel). By comparison, the values[20] of $\Delta V^‡$ for the reaction of pada with $Co^{2+}(aq)$ and $Ni^{2+}(aq)$ (nitrate) are $+7.2$ and $+7.7$ $cm^3\ mol^{-1}$, respectively, and it can therefore be assumed that both bipy and pada are 'normal' ligands in their reaction with the aquametal ions.

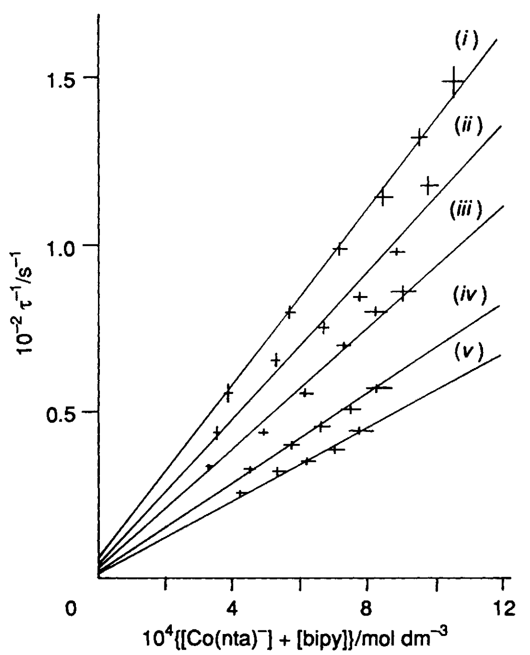
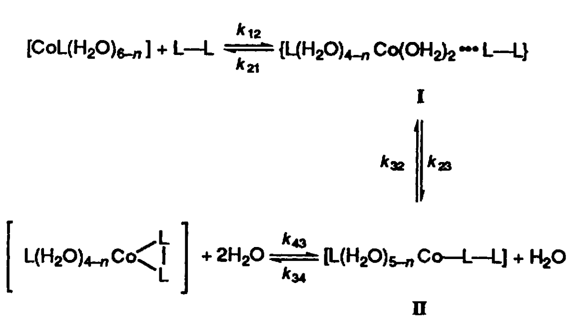


Fig. 2 Variation of τ^{-1} with concentration for the reaction of $[Co(nta)]^-$ with bipy under second-order conditions {$[Co(nta)^-]$ = [bipy]} at (*i*) 35, (*ii*) 30, (*iii*) 25, (*iv*) 19.3 or (*v*) 15.2 °C



Scheme 1

There are four main ways in which the partial replacement of the inner hydration sphere of $Co^{2+}(aq)$ or $Ni^{2+}(aq)$ by L could affect k_f. (*i*) A statistical reduction is expected because the number of replaceable water molecules is reduced. If the co-ordination number of the metal remains six, this effect can be 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 from the Fuoss equation[17] if the bound and incoming ligands are both negatively charged since a net positive charge on the metal ion would be reduced or replaced by a net negative charge on [ML]. (*iii*) For steric or electronic reasons depending on the structures of L and L–L the value of k_{34} could be reduced, thus allowing ring-closure to contribute to (or even become) the rate-determining process. (*iv*) Strengthening or weakening of the metal–ligand bonds could be accompanied by a weakening or strengthening, respectively, of the remaining metal–water bonds. This would lead to a change in k_{23} and therefore k_f^s, which would be reflected in a modified k_{ex}. Earlier work[9,10] has focussed on effects (*ii*) and (*iv*); our main concern here is with effect (*iii*) and the extent to which k_f^s for bipy is less than 'expected' owing to interaction with particular bound ligands L.

In Fig. 3 are plotted the values of k_f^s for the reactions of bipy (Table 1) and pada[6,9] with Co^{2+}(aq) and [CoL], along with those for the dianion nsa.[10] In the six cases where we have data for both neutral ligands, k_f^s for bipy is the same as for pada in three cases (the aqua-ion and L = tp or *N*,*N*′-edda) and about a fifth of the pada value in the other three (nta, *N*,*N*-edda and trien). It may be significant that the latter group comprises the three in which the water molecules (and therefore, presumably, the ligand L in intermediate **I**, Scheme 1) are particularly labile ($k_f^s = 10^6$–10^7 dm^3 mol^{-1} s^{-1} compared with *ca.* 10^5 dm^3 mol^{-1} s^{-1} for the former group) but certainly the interpretation suggested in terms of Scheme 1 is that ring closure is important in the reaction of bipy with [CoL], where L = nta, *N*,*N*-edda or trien, but not in the other cases. If this is correct, consideration of equation (5) suggests that k_{34} is only about a quarter of k_{32} for these three systems but four times it (or more) for the others. However, re-examination of Fig. 3 in the light of the comparable plot for [NiL] systems (Fig. 2 of ref. 4) suggests another approach.

Following the discovery[21] of an approximately linear relationship between log k_{ex} and the electron-withdrawing ability of the ligand in a group of nickel complexes [NiL], we found[4] that the labilization effects of L on complex formation with bipy, pada or nsa (L–L) could be parametrized in an analogous way. Specifically, $\log_{10} k_f^s$ is given by equation (6),

$$\log_{10} k_f^s = \log_{10} k_f^0 + pa_1 + a_2 + r_1 + r_2 \qquad (6)$$

where k_f^0 is the rate constant for the reaction of the unsubstituted metal ion with the appropriate L–L and up to three of the modifying terms may be used in a particular case, a_1 and a_2 being 'accelerating' parameters and r_1 and r_2 'retarding' parameters which depend on the identities of one or both of the 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 ($R^2 = 0.99_3$ and standard deviation = 0.1_2) and are given in Table 2. The many similarities between the two log k_f^s *vs.* [ML] plots (Fig. 3 and Fig. 2, ref. 4) led us to perform a similar regression analysis on the cobalt data.

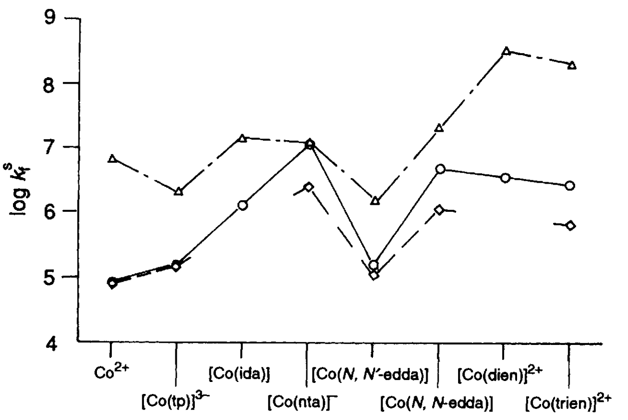


Fig. 3 Statistically adjusted rate constant (log k_f^s) for the reaction of cobalt(II) species with bipy (◇), pada (○) or nsa (△)

Table 2 Numerical values[a] of parameters for equation (6) (see text)

		Ni[b]	Co
log k_f^0	Starting value (pada, bipy)	3.3	4.9
	(nsa)	5.0	6.8
a_1	each bound N atom	$+0.5_2(0.0_2)$	$+0.4_0(0.0_6)$
a_2	pyramidal L[c]	$+0.1_8(0.0_6)$	+1.0(0.2)
r_1	steric interaction (L/L–L)[d]	$-0.4_8(0.0_9)$	−0.6(0.4)
r_2	electrostatic interaction (L/L–L)[e]	$-1.0_5(0.0_8)$	−0.9(0.3)

[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] Values taken from ref. 4. [c] Applied for nta, *N*,*N*-edda and tren. [d] Applied for L = *N*,*N*-edda, dien, trien, tren and L–L = bipy. [e] Applied for L = tp, ida, nta, *N*,*N*-edda, *N*,*N*′-edda and L–L = nsa.

Again, the Minitab system was used and the best fit parameters are listed in Table 2. Data for the reaction of bipy with $[Co(tren)]^{2+}$ were omitted from the analysis for the reason given below and we have unfortunately been unable to obtain data for the reaction of bipy with [Co(ida)] or $[Co(dien)]^{2+}$. While the fit of the regression line ($s = 0.5_1$ and $R^2 = 0.84_7$) is not as good as for nickel, its statistical significance is still high. In the nickel analysis, four outlying points were removed because of evidence of rate-limiting ring closure. Removal of the five worst-fitting points for cobalt would substantially improve the fit ($s = 0.3_1$ and $R^2 = 0.94_9$) but we can see no other justification for doing this and therefore do not propose to do so. Removal of the three bipy points for which the previous analysis suggests that ring closure could be important ([CoL], L = nta, *N*,*N*-edda or trien) actually worsens the fit ($s = 0.5_4$ and $R^2 = 0.81_5$). However, comparison of the two sets of derived data (Table 2) suggests that the difference in quality of fit for the two metals may, in fact, be attributable to a difference in their co-ordination chemistry.

The differences in the 'starting' parameters log k_f^0 for the neutral ligands (1.6) and nsa (1.8) represent[9,10] differences in the 'inherent' labilities of the two aqua-ions and are mirrored by differences in the k_{ex} values. The differences between the values for nsa and the neutral ligands (1.7 for Ni and 1.9 for Co) are attributable[10] to the additional electrostatic contribution to K_{os} provided by a charged incoming ligand. The first 'accelerating' parameter (a_1) represents the effect of each nitrogen atom in the inner co-ordination sphere of the metal. (In Fig. 3 and Fig. 2, ref. 4, the complexes have been placed in order of increasing number of bound nitrogen atoms.) The labilizing effect of aliphatic nitrogens on nickel-bound water is well established, and our value[4] of 0.5_2 confirmed the estimate of Margerum *et al.*,[2] obtained from a plot of data from several sources. Our value of 0.4_0 for cobalt(II) suggests that the same factors are important here. The two 'retarding' parameters r_1, r_2 represent, respectively, a steric interaction between bipy and the bound amino groups, and an electrostatic interaction between nsa and the bound anionic groups [both of which are aspects of effect (*ii*), above]. The fact that both are almost identical for the two metals is not surprising in view of the similarity in effective ionic radii[22] (r_{Co} = 74.5, r_{Ni} = 69 pm) and therefore, presumably, in the reaction distances a and other relevant aspects of the reaction geometries.

The only significant difference between the Co^{II} and Ni^{II} parameters (apart from their starting values) is in their second 'accelerating' parameter a_2. This represents an additional labilizing effect associated with the presence of a pyramidally bound ligand L (nta, *N*,*N*-edda or tren). While in Ni^{II} it is relatively small ($+0.1_8$), in Co^{II} it is rather large (+1.0) and is the main reason for the remarkably high values of k_f^s for the reaction of $[Co(nta)]^-$ with the neutral ligands (Fig. 3, *cf.* Fig. 2, ref. 4). If, as we have argued,[4] it is associated with distortion of the ligand field in [ML] induced by geometrical constraints within the ligand, then the difference in importance for the two metals is not surprising; neither is the greater scatter of the cobalt data about the regression line since there are likely to be many more subtleties in the kinetic behaviour of [CoL] complexes than [NiL].

Although there are now thought[23] to be small differences between typical transition states for the two metals, substitution of a water molecule in an octahedral complex is still widely accepted as requiring crystal-field activation energy for nickel(II) but not for cobalt(II).[24] This is the main reason for the greater lability of $Co^{2+}(aq)$ than $Ni^{2+}(aq)$, and therefore its higher 'starting value' k_f^0 (Table 2). It follows that cobalt(II) will be less resistant than nickel(II) to ligand-induced distortions away from a strictly octahedral geometry. Also where, as molecular mechanics evidence suggests[25] to be the case in $[M(nta)]^-$, the distortion is towards the transition state for water exchange, there will be a larger rate enhancement for ternary complex formation at cobalt(II) than at nickel(II). An extreme example of ligand-induced distortion is provided by $[Co(tren)]^{2+}$ which is actually trigonal bipyramidal[26] rather than octahedral. We will explore further the influence of changing co-ordination numbers on the reactivity of a substituted metal ion but sometimes it can clearly be difficult to predict: whereas bipy can readily bring about an expansion to octahedral geometry in $[Co(tren)]^{2+}$, neither pada[9] nor nsa[10] can do so.

In summary, we have found that a simple parametrization scheme proposed 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^0 for the formation of the analogous binary complex from $Ni^{2+}(aq)$ can be used also with cobalt(II). The numerical values of the parameters are about the same for the two metals except for the starting value k_f^0 and one of the accelerating terms a_2, both of which reflect the greater co-ordinational flexibility of cobalt(II) than nickel(II).

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