Kinetics of Ternary Complex Formation between Cobalt(II) Species and *N,N*-Dimethyl(*p*-pyridin-2-ylazo)aniline†

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The temperature-jump relaxation method has been used to measure the rate constants and the activation enthalpies and entropies for the formation and dissociation of the ternary complexes between *N,N*-dimethyl(*p*-pyridin-2-ylazo)aniline (pada) and cobalt(II)–*N*–methyliminodiacetate, –ethylenediamine-*N,N*-diacetate, –ethylenediamine-*N,N'*-diacetate, –diethylenetriamine, and –triethylenetetramine complexes. Independently determined equilibrium constants are also reported for the complexes involving ethylenediamine-*N,N*-diacetate, -*N,N'*-diacetate and triethylenetetramine. The rate parameters reported here, and previously for four related cobalt(II) systems, are compared with those for the corresponding nickel(II) reactions. It is confirmed that some of the factors influencing reactivity are the same for the two metals (notably the number of bound nitrogen atoms) but there are also significant differences.

The kinetics of formation of labile 1 : 1 metal complexes in aqueous solution has been widely studied since the introduction of fast reaction techniques and in most cases the formation and dissociation rate constants (k_f and k_d, respectively) are readily predicted if the effective stability constant K^c ($=k_f/k_d$) is known.[1–3] Much less is known about the kinetics of comparable reactions in which the inner hydration sphere of the metal has already been partially replaced by another ligand.[3] It is important to gain an understanding of the factors influencing reactions of this type because ternary complex formation is involved or implicated in many reactions of metal enzymes and other catalytic systems.

Of the bivalent metal ions, nickel(II) has received much more attention than the others, largely because the formation of most of its complexes (both 1 : 1 and ternary) falls conveniently in the stopped-flow range. In addition, its stability with respect to oxidation and reduction, and the relative ease with which the solvent-exchange rates of its complexes can be determined by NMR spectroscopy, have meant that we are now able to predict[3,4] quite well the effect of a particular bound ligand L on the reactivity of Ni^{II} towards a second ligand A. The effects of bound ligands on the subsequent reactivity of cobalt(II) are considerably less well understood.

This paper reports the rate constants and activation parameters ($\Delta H^‡$ and $\Delta S^‡$), as measured by the temperature-jump method, for the formation in aqueous solution of the ternary complexes between the neutral bidentate ligand *N,N*-dimethyl(*p*-pyridin-2-ylazo)aniline (pada) and the complexes of cobalt(II) with *N*-methyliminodiacetate (mida), ethylenediamine-*N,N'*-diacetate (*N,N'*-edda), -*N,N*-diacetate (*N,N*-edda), diethylenetriamine (dien) and triethylenetetramine (trien). Taken with those in a previous paper[5] on the reaction of pada with Co^{2+}(aq) and $[Co^{II}L]$, where L is iminodiacetate (ida), nitrilotriacetate (nta) or polytriphosphate (tp), our results represent the largest systematic study on the reactivity of cobalt(II) complexes [CoL] in water. The results are compared with those[4] for the corresponding nickel(II) reactions and confirm previous indications[6] that some of the factors influencing reactivity are the same for the two metals.

In addition to the systems already mentioned, we attempted to study the reactivity towards pada of the cobalt(II) complexes of 2,2',2''-triaminotriethylamine (tren) and 3,7-diazanonane-1,9-diamine (dadn). We hoped with the tren system to investigate the effect of a change in co-ordination number since $[Co(tren)]^{2+}$ is reported[7] to be five-co-ordinate, presumably with a water molecule in the fifth position. The disposition of the ligand in $[Co(dadn)]^{2+}$ is not known but the corresponding nickel complex is thought to have the two water molecules in *trans* positions and has been found[8] not to form a ternary complex with pada. In the event, relaxation effects were observed under certain conditions with both cobalt tetramines but they are shown to be associated with the formation of the 1 : 1 Co–pada complex rather than a ternary complex ML(A).

Experimental

Solutions were prepared from cobalt(II) nitrate (BDH AnalaR) and standardized against the disodium salt of ethylenediaminetetraacetate (edta) using xylenol orange as indicator. 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*-ethoxycarbonylethylenediamine.[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). The purity was monitored by GC and ^{13}C NMR spectroscopy.[12] Diethylenetriamine (Fluka), 3,7-diazanonane-1,9-diamine (Eastman) and 2,4,6-trimethylpyridine (Fisons) were purified by fractional distillation (82–83 °C, 2–3 Torr; 100–102 °C, 0.05 Torr; and 168–170 °C, 760 Torr, respectively), while triethylenetetramine (Fluka, puriss. grade), *N*-methyliminodiacetic acid (Aldrich), tris(hydroxymethyl)-methylamine (Tris) (Fisons AnalaR) 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 0.30 mol dm^{-3} ($NaNO_3$) was maintained and the solutions were buffered with 2,4,6-trimethylpyridine (*ca.* 4×10^{-2} mol dm^{-3}) or

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† *Supplementary data available* (No. SUP 56973, 6 pp.): plots of τ^{-1} *vs.* complex concentration. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.
Non-SI unit employed: Torr ≈ 133 Pa.

Tris (*ca.* 5×10^{-3} mol dm^{-3}) + HNO_3. 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] The solutions of pada were made up immediately before use. Solutions of the complexes of cobalt(II) with ligands L containing two or more N atoms were, to a greater or lesser extent, sensitive to autoxidation. All manipulations involving them were therefore carried out under nitrogen, L being 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).

Kinetic (temperature-jump) and equilibrium (UV/VIS spectrophotometric) measurements were made by standard methods[8,14] 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 pada). Except where otherwise noted, the kinetics was followed at 550 nm. Temperatures were accurate to better than ± 0.1 °C. Published[15] protonation and stability constants were used to calculate the concentrations of the various species present at different total concentrations of Co^{II} and L (mida, *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 cobalt present as [CoL] and in all cases except L = dadn and tren it was possible to eliminate relaxation effects associated with free Co^{2+} and [CoL_2]. The L/Co ratios used were 1.1 (mida and trien), 1.2 (tren and dadn), 1.5 (dien and *N*,*N*-edda), 1.8 (*N*,*N*′-edda), 2.0 (*N*,*N*′-edda) and 3.0 : 1 (trien).

Results

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

$$[CoL] + pada \underset{k_d}{\overset{k_f}{\rightleftharpoons}} [CoL(pada)] \qquad (1)$$

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

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

where $\bar{c}_{ML}$ and $\bar{c}_{pada}$ are the (new) equilibrium concentrations of free [CoL] and pada, respectively. Under the pseudo-first-order conditions used here, this reduces to equation (3) where [ML] is

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

the computed concentration of [CoL] and a plot of τ^{-1} against [ML] produces a straight line with slope k_f and intercept k_d. The formation of the 1 : 1 Co–pada complex from Co^{2+}(aq) and pada is characterized by similar relaxation expressions with $\bar{c}_{ML}$, [ML] replaced by $\bar{c}_M$, [M].

The results for the systems L = mida, *N*,*N*′- and *N*,*N*-edda, dien and trien are shown in Fig. 1, SUP 56973 and Table 1. As expected, no change in relaxation time was observed on varying the total pada concentration. The relaxation time was also

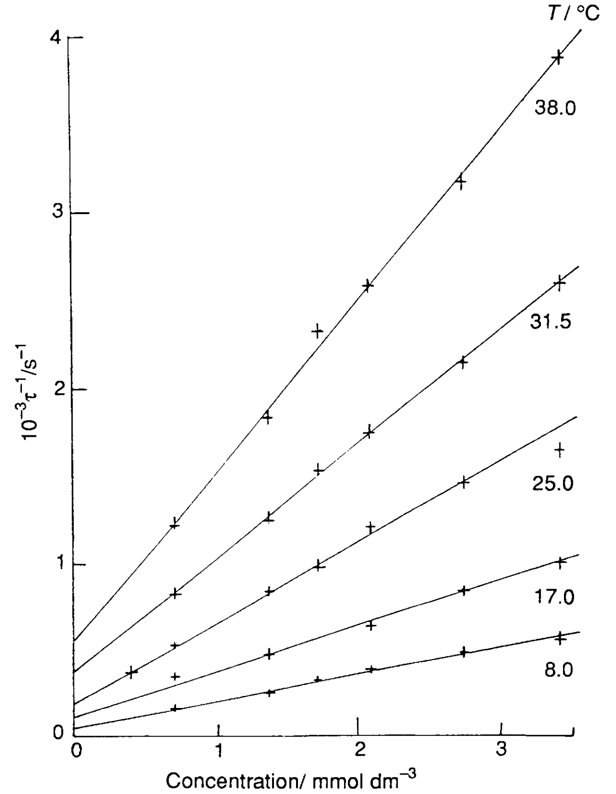


Fig. 1 Variation of τ^{-1} with concentration for the reaction of the cobalt(II) species [Co(mida)] with pada at different temperatures. The vertical lines on each point indicate experimental scatter (representing, on average, five or six experiments)

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

	[Co(mida)] (*n* = 3)	[Co(*N*,*N*′-edda)] (*n* = 4)	[Co(*N*,*N*-edda)] (*n* = 4)	$[Co(dien)]^{2+}$ (*n* = 3)	$[Co(tren)]^{2+}$ (*n* = 4)
k_f/dm^3 mol^{-1} s^{-1}	$4.6(0.4) \times 10^5$	$5.3(0.3) \times 10^4$	$1.7(0.1) \times 10^6$	$1.8(0.2) \times 10^6$	$9.0(1.2) \times 10^5$
k_f^s/dm^3 mol^{-1} s^{-1}	9.2×10^5	1.6×10^5	5.1×10^6	3.6×10^6	2.7×10^6
$\Delta H_f^{\ddagger}$/kJ mol^{-1}	42(3)	49(5)	30(2)	28(3)	28(16)
$\Delta S_f^{\ddagger(s)}$/J K^{-1} mol^{-1}	+10(8)	+17(17)	−15(6)	−23(8)	−27(40)
k_d/s^{-1}	$2.1(0.2) \times 10^2$	$3.6(0.2) \times 10^2$	$2.1(0.2) \times 10^2$	$2.6(0.3) \times 10^3$	$1.6(0.1) \times 10^4$
$\Delta H_d^{\ddagger}$/kJ mol^{-1}	56(4)	51(8)	37(3)	63(5)	46(3)
$\Delta S_d^{\ddagger}$/J K^{-1} mol^{-1}	−13(13)	−23(25)	−37(10)	+33(13)	−8(10)
K_{kin}/dm^3 mol^{-1} s^{-1}	$2.2(0.4) \times 10^3$	$1.5(0.2) \times 10^2$	$8.1(1.2) \times 10$	$6.9(1.7) \times 10^2$	$5.6(1.2) \times 10$
K_{spec}/dm^3 mol^{-1} s^{-1}	—	$2.0(0.2) \times 10^2$	$1.2(0.1) \times 10^2$	—	$4.8(1.0) \times 10$
10^3[CoL]/mol dm^{-3}	0.4–3.5	1.0–13.0	1.0–16.0	0.3–4.2	1.0–17.0
10^5[pada]/mol dm^{-3}	2–3	5–12	5–12	2–3	5–16
pH	7.0–7.1[b]	7.6–8.2[c]	7.7–8.3[c]	7.0–7.1[b]	7.0–9.5[c]

[a] The rate constants refer to 25 °C and ionic strength 0.3 mol dm^{-3} ($NaNO_3$); *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] Tris buffer. [c] 2,4,6-Trimethylpyridine buffer.

Table 2 Relaxation behaviour of $[Co(trien)]^{2+}$ + pada

trien : Co^{2+}	1.0_5	1.0_5	1.0_5	1.2	1.8	1.0_5	0.7	1.0_5	1.0_5
pH	5.4	5.8	6.4	6.6	6.7	7.1	7.2	7.7	9.5
$10^{-4}\tau_I^{-1}/s^{-1}$	*	*	1.5	1.7	2.1	1.7	1.5	2.1	2.1
τ_{II}^{-1}/s^{-1}	400	290	100	80	*	75	160	*	*

Data refer to 25 °C and an ionic strength of 0.3 mol dm^{-3} ($NaNO_3$). The total concentrations of cobalt(II) and pada in each case were 5.00×10^{-3} and 2.5×10^{-5} mol dm^{-3}, respectively. * A relaxation effect was either absent or too small to measure reliably.

independent of pH in the ranges indicated, and of the buffer concentration. For the systems L = *N,N'*- and *N,N*-edda and trien (but see below) 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 good.

$[Co(trien)]^{2+}$.—The electronic spectrum of $[Co(trien)]^{2+}$ in the range pH 6.8–8.0 is consistent with an octahedral geometry [ε_{484}^{max} 7.6,[16] 8.0,[17] ε_{460}^{sh} 6.6 dm^3 mol^{-1} cm^{-1} (ref. 17)]. It is not known whether the two H_2O molecules are *cis* or *trans* but molecular models suggest[18] that a *cis* configuration is favoured. Steinhaus and Kolopajlo[19] have concluded that $[Ni(trien)]^{2+}$ in solution is *cis* and there are thermodynamic reasons for thinking[20] that the conformations of $[Co(trien)]^{2+}$ and $[Ni(trien)]^{2+}$ are similar.

Two relaxation effects were found with $[Co(trien)]^{2+}$ + pada in the range pH 6–7, of which only the faster (τ *ca.* 50 μs) was seen at higher and only the slower (τ *ca.* 10 ms) at lower pH. By varying the wavelength of observation it was possible to detect isosbestic points at 500 and 480 nm for the slow and fast processes, respectively. This indicates that three absorbing species are involved in the two reactions under study and rules out an interpretation involving the reaction of pada with, respectively, *cis* and *trans* forms of $[Co(trien)]^{2+}$ since the same ternary complex, *cis*-$[Co(trien)(pada)]^{2+}$, would be produced in each case.

A simple interpretation is that the second (slower) relaxation effect is caused by the reaction of pada with free Co^{2+}(aq) formed by the displacement of reaction (4) to the right as the pH

$$[Co(trien)]^{2+} + nH^+ \rightleftharpoons Co^{2+}(aq) + H_n trien^{n+} \quad (4)$$

is lowered. Evidence in favour of this includes the following results of varying the pH and ligand : metal ratio at a fixed metal concentration (Table 2): (*i*) at pH 6.6/6.7, increasing the trien : cobalt ratio from 1.2 to 1.8 : 1 causes the slower effect to disappear and the value of τ^{-1} for the faster (τ_I^{-1}) to increase to the limiting value of 2.1×10^4 s^{-1} observed at high pH; (*ii*) at pH 7.1/7.2, decreasing the trien : cobalt ratio from 1.05 to 0.7 : 1 reduces τ_I^{-1} and increases τ_{II}^{-1}; (*iii*) on reducing the pH at constant trien : cobalt ratio (1.05 : 1), τ_I^{-1} falls and τ_{II}^{-1} rises.

In addition, we have been able to reproduce the main features of Table 2 using the concentrations of $[Co(trien)]^{2+}$ and Co^{2+}(aq) calculated from the published[15] pK_a values and stability constants and the measured rate constants for reaction (1), L = trien and Co^{2+}(aq). Finally, the isosbestic point for a mixture of pada and Co^{2+}(aq) of approximately the same concentration as that calculated for one of the $[Co(trien)]^{2+}$ + pada mixtures showing two relaxation effects was 500 nm. A consequence of the relative complexity of the cobalt–trien–pada system is that the estimated errors in $\Delta H_f^\ddagger$, $\Delta S_f^\ddagger$ and *K* (Table 1) are unusually high.

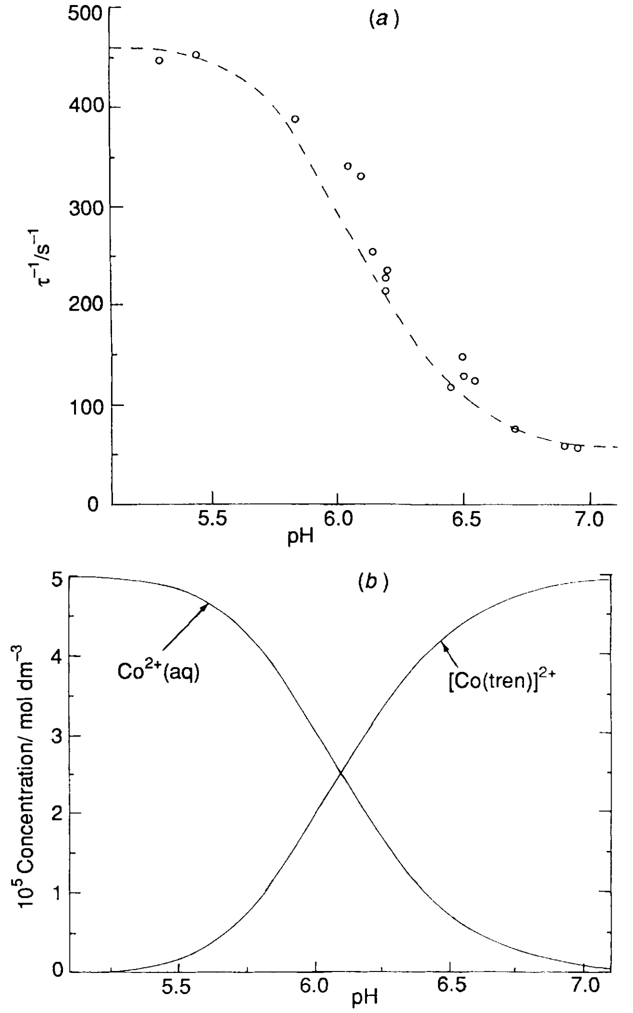


Fig. 2 (*a*) Variation of τ^{-1} with pH for the system Co^{2+} + tren + pada. The total concentrations of cobalt(II), tren and pada were, respectively, 5.0×10^{-3}, 5.25×10^{-3} and 3.0×10^{-5} mol dm^{-3}; temperature = 25 °C. The dashed line shows the variation predicted on the assumption that the effect observed is the formation/dissociation of $[Co(pada)]^{2+}$ (see text). (*b*) Distribution diagram for the Co^{2+} + tren system at varying pH from published[15] protonation and stability constants. Total concentrations of cobalt(II) and tren are, respectively, 5.0×10^{-3} and 5.25×10^{-3} mol dm^{-3}

$[Co(tren)]^{2+}$ *and* $[Co(dadn)]^{2+}$.—A single relaxation effect was observed with the cobalt–tren–pada system in the range pH 5–7 and the dependence of τ^{-1} on pH is shown by the points in Fig. 2(*a*). It is unlikely that the titration curve is associated with deprotonation or protonation of $[Co(tren)(H_2O)]^{2+}$ since the pK_a of this complex is 10.22[21] and no evidence has been found[22] for the presence of $[Co(Htren)(H_2O)]^{3+}$ or similar species. By analogy with the cobalt–trien–pada system a reasonable assumption is that the relaxation effect is associated with the reaction of pada with free Co^{2+}(aq) and not $[Co(tren)]^{2+}$.

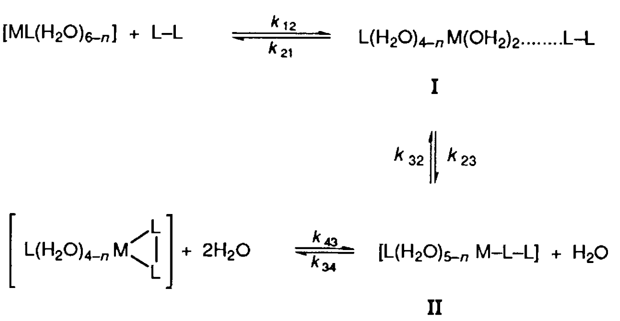
The distribution diagram calculated for the cobalt–tren system on the basis of published[15] stability constant and pK_a values is shown in Fig. 2(*b*). The pH range over which the changeover from $[Co(tren)]^{2+}$ to Co^{2+}(aq) is greatest is the same as that over which the value of τ^{-1} changes most rapidly.

The dashed line in Fig. 2(*a*) is obtained from the values of k_f and k_d for the Co^{2+}(aq) + pada reaction and the calculated concentrations of Co^{2+}(aq) and is in good agreement with the observed values. We therefore conclude that the complex formed in the range pH 5–7 is $[Co(pada)]^{2+}$ and that $[Co(tren)]^{2+}$ does not form a ternary complex with pada {or, at least, that the stability of such a complex is very low since no additional relaxation effect was observed even at a $[Co(tren)]^{2+}$ concentration of 2×10^{-2} mol dm^{-3} and a pada concentration of 6×10^{-5} mol dm^{-3}}.

A relaxation effect was also observed in the range pH 5–7 with the Co–dadn–pada system. The effects of varying the pH and ligand : metal ratio were similar to those described for tren and we therefore conclude that, as with the nickel analogue,[8] no pada ternary complex is formed with $[Co(dadn)]^{2+}$.

Discussion

The formation of a complex between an octahedral metal species containing two or more replaceable water molecules $[ML(H_2O)_{6-n}]$ and a bidentate ligand L–L is commonly discussed in terms of Scheme 1 where species **I** is an outer-sphere complex and **II** is a singly co-ordinated inner-sphere complex; L represents a 'firmly bound' ligand of denticity *n*, and a similar scheme applies for reaction of L–L with the aqua-ion M(aq). The first step is rapid (diffusion controlled) and can often be treated as a pre-equilibrium. The formation constant for the outer-sphere intermediate, K_{os} $(=k_{12}/k_{21})$, can be calculated by the Fuoss equation[23] and, if a steady state is assumed for intermediate **II**, the observed rate constant for the formation of the chelate complex is usually given by $k_f = K_{os}k_{23}$. This is equivalent to $K_{os}k_{ex}$, where k_{ex} is the rate constant for water exchange at the metal species $[ML(H_2O)_{6-n}]$. When comparing results for ions with different numbers of replaceable waters it is necessary to make a simple statistical adjustment. If the co-ordination number of the metal remains six, the measured k_f for [ML] is multiplied by a factor $6/(6 - n)$, where *n* is the number of co-ordination positions occupied by L, to give k_f^s.



Scheme 1

For many years it was argued[1,2] that the mechanism of complex formation and solvent exchange at Co^{2+}(aq) and Ni^{2+}(aq) involved dissociatively activated interchange[24] and important confirmatory evidence for this has come[25] recently from the measurement of activation volumes. Although the $\Delta V^{\ddagger}$ values for Co^{2+} are usually slightly less than those for Ni^{2+}, an I_d mechanism can generally be assumed for both. Of particular relevance to the present paper is that the values[26] of $\Delta V^{\ddagger}$ 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, which are typical for these aqua-ions and confirm pada as a 'normal' ligand.

Comparatively little is known about the effect of partial replacement of the inner hydration sphere of Co^{2+}(aq) on the lability of the remaining waters. With nickel(II) it has been shown that k_f and k_{ex} increase regularly with increasing number of (aliphatic) nitrogens co-ordinated to the metal.[3] Rather surprisingly, the labilization caused by bound aminocarboxylates is attributable to the neutral amino group(s) and not the ionic carboxylate group(s). Based on results for pada and two other incoming bidentate ligands L–L we have found[4] evidence for a small additional labilization if L is pyramidal. In view of the indication[6] that similar factors are important in determining the reactivity of substituted cobalt(II) species, we have compared our present and earlier[5] cobalt + pada results with those for the nickel + pada systems.[4,8,27]

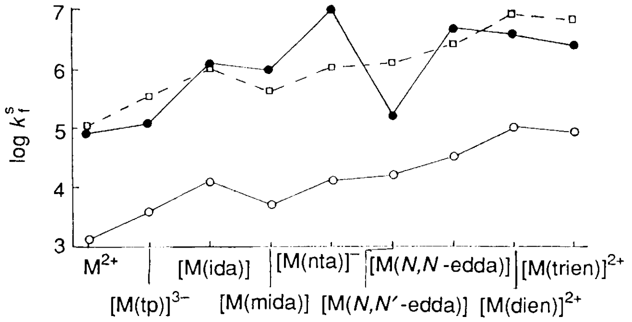


Fig. 3 Statistically adjusted rate constant (log k_f^s) for the reaction of cobalt(II) (●) and nickel(II) (○) species with pada; also (1.9 + log k_f^s) for the reaction of the nickel(II) species with pada (□) (see text)

Fig. 3 shows that there is a similar pattern to the variation of log k_f^s with the nature of the bound ligand. To emphasize how close the similarity is we have plotted also (and connected with a dashed line) the values of log k_f^s for nickel to which have been added 1.9. The value 1.9 is the average between Δlog *k* $[Co^{2+}(aq) - Ni^{2+}(aq)]$ for water exchange[28] (k_{ex}) and complex formation with pada[5,8] (k_f) and is being used in this way as a measure of the difference in the 'inherent' labilities of the two metals. In all but two cases the observed value of log k_f^s for Co is within 0.4 of the nickel-derived value, much of which difference could, in our view, be accounted for by experimental error. The two exceptions are $[Co(nta)]^-$, which is substantially more labile and $[Co(N,N'$-edda)] which is substantially less labile than would be predicted by this comparison.

In line with the rate constants k_f^s, the activation enthalpies $\Delta H_f^{\ddagger}$ are approximately 14 kJ mol^{-1} higher for the nickel complexes than for the corresponding cobalt species (Table 3) with the exception of L = nta and *N,N'*-edda where the differences are 27 and 6 kJ mol^{-1}, respectively. {Comparison is not possible in two cases since the value for $[Ni(N,N$-edda)] is not available and the estimated error on that for $[Co(trien)]^{2+}$ is abnormally high.}

For all five nickel systems where it has been possible to measure the activation parameters for the dissociation reaction (Table 3) the value of $\Delta H_d^{\ddagger}$ is close to 66 kJ mol^{-1} and the variation in k_d is associated entirely with the differences in $\Delta S_d^{\ddagger}$ (the values of which range from −25 to +13 J K^{-1} mol^{-1}). It is also noteworthy that for each L the difference* in {log k_d[CoL(pada)] − log k_d[NiL(pada)]} is close to 1.9 (see above), although for the cobalt complexes there are large variations in both $\Delta H_d^{\ddagger}$ and $\Delta S_d^{\ddagger}$ (Table 3).

In summary, we have found considerable similarity between the behaviour of substituted cobalt(II) species towards pada and the rather better-understood systems involving nickel(II). As with nickel, it seems that the lability of the remaining water molecules is influenced by the number of bound nitrogens but there must be at least one additional factor involved since, although the values of k_f^s cover two orders of magnitude in each case, the bound ligand which produces the greatest labilization is different for Co (nta) and Ni (dien).

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* The relevant values of log k_d[ML(pada)] are: for Co, L = tp, 1.56;[5] nta, 3.71;[5] *N,N'*-edda, 2.56 (Table 1); dien, 3.41 (Table 1); trien, 4.20 (Table 1); for Ni, L = tp, −0.23;[9] nta, 1.30;[8] *N,N'*-edda, 1.04;[27] dien, 1.56;[8] trien, 2.00.[8]

Table 3 Activation parameters for the formation and dissociation of pada complexes with cobalt(II) and nickel(II) species [ML]*

	$\Delta H_{\mathrm{f}}^{\ddagger}$/kJ mol^{-1}		$\Delta S_{\mathrm{f}}^{\ddagger}$/J K^{-1} mol^{-1}		$\Delta H_{\mathrm{d}}^{\ddagger}$/kJ mol^{-1}		$\Delta S_{\mathrm{d}}^{\ddagger}$/J K^{-1} mol^{-1}	
	Co	Ni	Co	Ni	Co	Ni	Co	Ni
(aq)	43	57	−8	4	63	—	−4	—
tp	44	59	4	21	67	66	13	−25
ida	40	53	8	17	57	—	−13	—
mida	42	55	10	17	56	—	−13	—
nta	25	52	−25	8	45	69	−21	13
N,*N*′-edda	49	55	17	17	51	66	−23	−4
N,*N*-edda	30	—	−15	—	37	—	−37	—
dien	28	43	−23	−4	63	65	33	4
trien	(28)	37	(−27)	−29	46	66	−8	13

* Data are from refs 4, 5, 8 and 27 and Table 1.

One important difference between these two metals lies in the relative importance of the electronic demands of the central metal ion and the steric requirements of the ligand in determining the geometry of the complex. With Ni$^{\mathrm{II}}$ the former is the more important due to the large crystal-field stabilization energy (c.f.s.e.), and the co-ordination number in high-spin complexes of Ni$^{\mathrm{II}}$ is nearly always six. With Co$^{\mathrm{II}}$ the c.f.s.e. associated with a co-ordination number of six is lower and the geometric requirements, as determined by bond lengths and angles in the ligand and the ionic radius of the metal, become relatively more important. In the light of this, the difference in the effects of the three tripodal ligands *N*,*N*-edda, tren and nta on the reactvity of the two metals is interesting. With nickel(II) the octahedral geometry is retained throughout and the effect of the accompanying ligand-field distortion on the substitutional reactivity of the metal is slight. For cobalt(II) the situation is more complicated and apparently subtle differences in ligand geometry can have large effects on reactivity. With *N*,*N*-edda and nta, where a co-ordination number of six is retained, the $k_{\mathrm{f}}^{\mathrm{s}}$ value for pada is 50–100 times larger than for Co^{2+}(aq). With the third ligand tren, the co-ordination number falls to five (trigonal bipyramidal) and we find that no ternary complex is formed with pada. We will explore further the influence of changing co-ordination numbers on the reactivity of a substituted metal ion. In the meantime, it is clearly not the case that the reactivity of substituted cobalt(II) always follows closely that of substituted nickel(II), though it often does.

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