# Kinetics of Ternary Complex Formation between Cobalt(II) Species and 5-Nitrosalicylic Acid: The Effect of Charge†

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The temperature-jump relaxation method has been used to measure rate constants and activation parameters for the formation and dissociation of a 1 : 1 complex between cobalt(II) and 5-nitrosalicylate-(2−) (nsa$^{2-}$), and of ternary complexes between nsa$^{2-}$ and cobalt(II)–nitrilotriacetate, –ethylenediamine-*N,N*-diacetate, –ethylenediamine-*N,N'*-diacetate, and –triethylenetetramine; also, rate constants for the formation and dissociation of ternary complexes between nsa and cobalt(II)–polytriphosphate, –iminodiacetate and –diethylenetriamine. Independently determined equilibrium constants are reported for [Co(nsa)] and for the ternary complexes involving polytriphosphate, nitrilotriacetate, ethylenediamine-*N,N*-diacetate and -*N,N'*-diacetate. The rate parameters are compared with those for the corresponding nickel(II) reactions and for the corresponding reactions of both metals with the neutral ligand *N,N*-dimethyl(*p*-pyridin-2-ylazo)aniline. The results for nsa are only partly explicable in terms of the Fuoss equation.

There have been many kinetic investigations into the formation of substitution-labile 1 : 1 metal complexes in aqueous solution 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] There have been far fewer studies of analogous reactions where part of the inner hydration sphere of the metal ion has already been replaced by another ligand.[3] An understanding of the reactivity patterns of ternary complexes is important since many catalytic reactions requiring metal ions involve their formation and dissociation.

Of the bivalent metal ions, nickel(II) has received the greatest attention, mainly because the formation of most of its complexes (both 1 : 1 and ternary) occurs conveniently in the stopped-flow range. Its stability with respect to oxidation and reduction and its d$^8$ configuration also mean that its complexes are relatively well characterized, and in many cases 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 L–L.

The position with cobalt(II) is less clear, though there are indications[3] that its behaviour is in some ways like that of nickel(II). For a series of nine cobalt(II) species reacting with the neutral bidentate ligand *N,N*-dimethyl(*p*-pyridin-2-ylazo)-aniline (pada) we have recently reported[5] a reactivity pattern similar to that established previously[4,6,7] for Ni$^{II}$. The main focus of the present investigation is the effect of electrostatic charge on ternary complex formation, in particular the extent to which the reactivity of Co$^{II}$ is changed when both ligands L and L–L are negatively charged. To make comparison with earlier results easier, we have used eight of the cobalt(II) species employed previously[5] and the same incoming ligand L–L as that used in our investigation[7] of charge effects with Ni$^{II}$.

This paper reports the rate constants, as measured by the temperature-jump method, for the formation and dissociation in aqueous solution of the 1 : 1 complex between Co$^{2+}$ (aq) and the bidentate ligand 5-nitrosalicylate(2−) (nsa$^{2-}$);‡ also for the ternary complexes between nsa$^{2-}$ and the complexes of cobalt(II) with polytriphosphate(5−) (tp$^{5-}$), iminodiacetate(2−) (ida$^{2-}$), nitrilotriacetate(3−) (nta$^{3-}$), ethylenediamine-*N,N'*-diacetate (2−) (*N,N'*-edda$^{2-}$), ethylenediamine-*N,N*-diacetate(2−) (*N,N*-edda$^{2-}$), diethylenetriamine (dien) and triethylenetetramine (trien). Activation parameters ($\Delta H^{\neq}$ and $\Delta S^{\neq}$) are also reported. In the hope of investigating the effect of a change in co-ordination number, we attempted to study the reactivity towards nsa$^{2-}$ of the cobalt(II) complex of 2,2',2''-triaminotriethylamine (tren), which is reported[8] to be five-co-ordinate. Unfortunately, a relaxation was only observed at high pH and it was too small to analyse.

Equilibrium constants have been obtained independently in the cases of the aqua, tp$^{5-}$, nta$^{3-}$, *N,N'*- and *N,N*-edda$^{2-}$ systems.

## 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$_4$edta) using xylenol orange as indicator.[9] 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 Pr$^i$OH, and dried. Ethylenediamine-*N,N*-diacetic acid was prepared from 1,2-diaminoethane (Fisons) by the method of Schwarzenbach *et al.*[10] *via* *N*-ethoxycarbonylethylenediamine.[11] 2,2',2''-Triaminotriethylamine was isolated from technical grade triethylenetetramine as described previously.[5] Diethylenetriamine (Fluka) and 2,4,6-trimethylpyridine (Fisons) were purified by fractional distillation, and 5-nitrosalicylic acid (Fluka) and Na$_5$P$_3$O$_{10}$·6H$_2$O (Albright and Wilson) by double recrystallization from water, while iminodiacetic acid (Fisons), triethylenetetramine and nitrilotriacetic acid (Fluka, puriss. grade) 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 (4 × 10$^{-2}$ mol dm$^{-3}$) + HClO$_4$. The amine stock solutions were prepared

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† *Supplementary data available* (No. SUP 57041, 8 pp.): plots of $\tau^{-1}$ *vs.* complex concentration. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

‡ Following the recommendation of a referee, we indicate the charges on the anionic forms of ligands and the specific complexes [ML].

from the free amine by weighing, the concentrations being checked by titration against HCl using an appropriate indicator.[9] Solutions of the complexes of cobalt(II) with ligands 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 undertaken by standard methods[6,12] 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 nsa). The kinetic data reported here (which refer to the relaxation effect observed in the 20 μs–5 ms range) were obtained at 380 nm, although identical relaxation times were obtained at several other wavelengths in the range 350–400 nm for each system. Each data point is the average of five or six separate determinations with the same solution. Published stability constants[13] were used to calculate the concentrations of the various species present at different total concentrations of Co$^{II}$ and L (tp, ida, nta, *N,N'*- and *N,N*-edda, dien, trien) 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 (tp, nta, trien), 1.5 (ida, *N,N*-edda, dien), and 1.8 and 2.0:1 (*N,N'*-edda). A separate, faster relaxation effect was seen under certain conditions. This is attributable to proton transfer involving nsa.

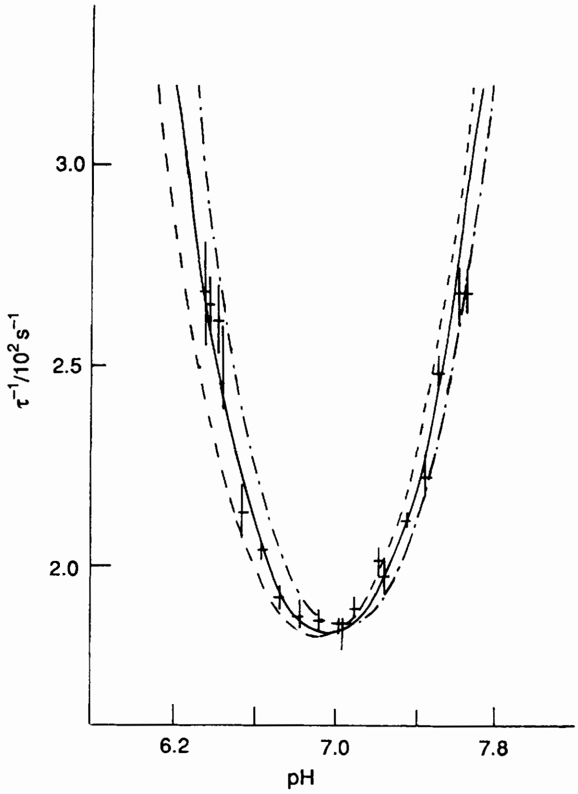


**Fig. 1** Variation of $\tau^{-1}$ with pH for the reaction of Co$^{2+}$(aq) (4.0 × $10^{-3}$ mol dm$^{-3}$) with nsa (1.0 × $10^{-4}$) at 25.0 °C. The vertical lines on each point indicate experimental scatter. The lines are theoretical curves calculated using the following respective values of $k_{41}/10^6$ dm$^3$ mol$^{-1}$ s$^{-1}$, $k_{14}/10^2$ s$^{-1}$, $k_{32}/10^3$ dm$^3$ mol$^{-1}$ s$^{-1}$, and $K_1/10^4$ mol dm$^{-3}$ (see text): ——, 6.5, 1.05, 2.7, 6.2; — — —, 7.0, 1.10, 2.4, 6.9; —·—, 6.0, 1.05, 4.0, 5.5

## Results

In the temperature-jump relaxation technique the position of equilibrium is changed by means of a sudden temperature rise. The new equilibrium condition is approached exponentially and the relaxation time τ is a function of the rate constants of the reaction(s) involved.

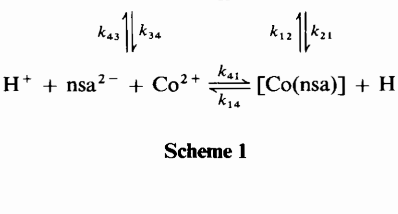
The simplest way of rationalising the observed pH profile for the Co$^{2+}$(aq)–5-nitrosalicylic acid system (Fig. 1) is to assume a two-pathway scheme in which the fully deprotonated form nsa$^{2-}$ is important at higher pH and Hnsa$^-$ (in which the phenolic oxygen is protonated) is important at lower pH (Scheme 1).

Since the hydrogen-ion concentration $c_H$ was buffered and pseudo-first-order conditions were maintained for the metal concentration $c_{Co}$, the relaxation expression for the slower of the two observed relaxation effects is[14] as in equation (1), where

$$\tau^{-1} = c_{Co}[k_{41}/(1 + K_2c_H) + k_{32}] + (c_Hk_{32}K_2/K_1) + k_{14} \quad (1)$$

$K_1 = k_{41}/k_{14}$ and $K_2 = k_{43}/k_{34}$. In deriving equation (1) it has also been assumed that the concentration of the protonated intermediate [Co(Hnsa)]$^+$ is always small and that $k_{21} \gg k_{23}$.

Three methods were used to evaluate rate constants for the Co$^{2+}$(aq) system. (*i*) The full pH profile (Fig. 1) for $c_{Co}$ = 4.0 × $10^{-3}$ mol dm$^{-3}$ at 25.0 °C was analysed by a curve-fitting procedure using the rate and equilibrium constants $k_{32}$, $k_{41}$, $k_{14}$ and $K_1$ as variables. An interpolated value[14] of 9.86 was used for log $K_2$. The values used for the 'best' curve (solid line, Fig. 1) are given in Table 1, the two broken lines in Fig. 1 indicating the limits of experimental error. The pH range available for study was restricted by a rapid deterioration in the quality of the traces at the extremities of the profile.



**Scheme 1**

(*ii*) To the right of the pH minimum the term $c_Hk_{32}K_2/K_1$ is unimportant and equation (1) becomes (2). A plot of $\tau^{-1}$ *vs.*

$$\tau^{-1} = c_{Co}[k_{41}/(1 + K_2c_H) + k_{32}] + k_{14} \quad (2)$$

$c_{Co}/(1 + K_2c_H)$ at two different metal concentrations gives two parallel lines of slope $k_{41}$ and intercept ($k_{32}c_{Co} + k_{14}$). This plot is shown in SUP 57041 for the metal concentrations 4.0 × $10^{-3}$ and 8.0 × $10^{-3}$ mol dm$^{-3}$ at four different temperatures, over the range pH 7.1–7.5. Higher pH values were not used since at pH > 7.5 the amount of the hydrolysed form present exceeds 5% of the total metal concentration.[13]

(*iii*) To the left of the pH minimum the term involving $k_{41}$ in equation (1) is unimportant and the relaxation expression reduces to $\tau^{-1} = (c_Hk_{32}K_2/K_1) + c_{Co}k_{32} + k_{14}$. The plot of $\tau^{-1}$ *vs.* $c_H$ is shown in SUP 57041 and the rate constants derived using the spectrophotometrically determined stability constant $K_1$ are listed in Table 1.

In view of the complexity of the system and the experimental difficulties in studying it, we regard the level of agreement as satisfactory.

Reactions of nsa with the substituted cobalt species [CoL] follow a similar scheme to (1) but in these cases it was only possible to obtain measurable relaxation effects on the high-pH side of the minimum. Method (*ii*) was used to analyse the data, with $c_{Co}$ in equation (2) replaced by $c_{CoL}$, the concentration of [CoL]. In each case the plot of $\tau^{-1}$ *vs.* $c_{CoL}/(1 + K_2c_H)$ gave a single straight line for solutions of widely varying $c_{CoL}$ and pH, indicating that $k_{32} \ll k_{41}/(l + K_2c_H)$ over the available pH

**Table 1** Rate and equilibrium constants for the reaction of $Co^{2+}$ (aq) with $nsa^{2-}$ and $Hnsa^-$ (estimated errors in parentheses)[a]

| Method[b] | $T$/°C | $k_{41}/10^6$ dm$^3$ mol$^{-1}$ s$^{-1}$ | $k_{32}/10^6$ dm$^3$ mol$^{-1}$ s$^{-1}$ | $k_{14}$/s$^{-1}$ | $K_1/10^4$ dm$^3$ mol$^{-1}$ |
|---|---|---|---|---|---|
| (*i*) | 25.0 | 6.5 (0.5) | 2.7 (0.3) | 105 (5) | 6.2 (0.7) |
| (*ii*) | 15.0 | 2.8 (0.3) | 3.1 (1.0) | 61 (4) | 4.6 (0.8) |
| | 20.0 | 3.4 (0.4) | 4.0 (0.5) | 89 (5) | 3.8 (0.7) |
| | 25.0 | 5.0 (0.5) | 6.0 (1.5) | 129 (8) | 3.9 (0.7) |
| | 31.0 | 7.1 (0.6) | 7.5 (2.0) | 201 (16) | 3.5 (0.6) |
| (*iii*) | 25.0 | 8.4 (3.4) | 2.9 (0.7) | 120 (40) | 6.9 (0.3)[c] |

[a] At ionic strength 0.3 mol dm$^{-3}$ ($NaNO_3$). [b] See text for description of methods. [c] Spectrophotometrically determined value.

**Table 2** Rate and equilibrium constants and activation parameters for the reaction of cobalt(II) species with $nsa^{2-}$ (estimated errors in parentheses)[a]

| | $Co^{2+}$ (aq) | $[Co(tp)]^{3-}$ ($n$ = 3) | [Co(ida)] ($n$ = 3) | $[Co(nta)]^-$ ($n$ = 4) |
|---|---|---|---|---|
| $k_f$/dm$^3$ mol$^{-1}$ s$^{-1}$ | [b]$6.5 (0.5) \times 10^6$ | $9.9 (0.8) \times 10^5$ | $7.0 (0.4) \times 10^6$ | $4.3 (0.4) \times 10^6$ |
| $k_f^s$/dm$^3$ mol$^{-1}$ s$^{-1}$ | $6.5 \times 10^6$ | $2.0 \times 10^6$ | $1.4 \times 10^7$ | $1.3 \times 10^7$ |
| $\Delta H_f^{\neq}$/kJ mol$^{-1}$ | [b]42 (4) | | | 32 (3) |
| $\Delta S_f^{\neq (s)}$/J K$^{-1}$ mol$^{-1}$ | [b]+26 (11) | | | 0 (3) |
| $k_d$/s$^{-1}$ | $1.05 (0.05) \times 10^2$ | $9.5 (0.7) \times 10^2$ | $1.3 (0.1) \times 10^3$ | $6.4 (0.4) \times 10^3$ |
| $\Delta H_d^{\neq}$/kJ mol$^{-1}$ | 50 (4) | | | 34 (4) |
| $\Delta S_d^{\neq}$/J K$^{-1}$ mol$^{-1}$ | −38 (13) | | | −59 (11) |
| $K_{kin}$/dm$^3$ mol$^{-1}$ | $6.2 (0.7) \times 10^4$ | $1.0 (0.2) \times 10^3$ | $5.4 (0.7) \times 10^3$ | $6.7 (1.1) \times 10^2$ |
| $10^3$[CoL]/mol dm$^{-3}$ | 4.0–8.0 | 2.0–8.0 | 2.0–5.0 | 2.0–12.0 |
| $10^5$[nsa][c]/mol dm$^{-3}$ | 10 | 10 | 10 | 10 |
| pH | 6.4–7.7 | 8.2–9.1 | 8.4–8.9 | 8.5–9.5 |
| $K_{spec}$/dm$^3$ mol$^{-1}$ | $6.9 (0.3) \times 10^4$ | $1.4 (0.2) \times 10^3$ | | $6.4 (0.8) \times 10^2$ |
| $10^3$[CoL]/mol dm$^{-3}$ | 4.0–8.0 | 2.0–6.0 | | 2.5–7.5 |
| $10^5$[nsa][c]/mol dm$^{-3}$ | 5.0 | 5.0 | | 3.5 |
| pH | 6.9–7.5 | 8.4–9.6 | | 8.6–10.0 |
| | [Co($N$,$N'$-edda)] ($n$ = 4) | [Co($N$,$N$-edda)] ($n$ = 4) | $[Co(dien)]^{2+}$ ($n$ = 3) | $[Co(trien)]^{2+}$ ($n$ = 4) |
| $k_f$/dm$^3$ mol$^{-1}$ s$^{-1}$ | $4.9(0.4) \times 10^5$ | $6.9 (0.5) \times 10^6$ | $1.6 (0.2) \times 10^8$ | $6.2 (0.5) \times 10^7$ |
| $k_f^s$/dm$^3$ mol$^{-1}$ s$^{-1}$ | $1.5 \times 10^6$ | $2.1 \times 10^7$ | $3.2 \times 10^8$ | $1.9 \times 10^8$ |
| $\Delta H_f^{\neq}$/kJ mol$^{-1}$ | 45 (4) | 31 (2) | | 25 (17) |
| $\Delta S_f^{\neq (s)}$/J K$^{-1}$ mol$^{-1}$ | +24 (11) | +1 (5) | | −2 (50) |
| $k_d$/s$^{-1}$ | $3.5 (0.2) \times 10^2$ | $6.8 (0.4) \times 10^3$ | $1.0 (0.1) \times 10^4$ | $2.4 (0.2) \times 10^4$ |
| $\Delta H_d^{\neq}$/kJ mol$^{-1}$ | 49 (8) | 42 (3) | | 38 (8) |
| $\Delta S_d^{\neq}$/J K$^{-1}$ mol$^{-1}$ | −29 (25) | −29 (10) | | −33 (25) |
| $K_{kin}$/dm$^3$ mol$^{-1}$ | $1.4 (0.2) \times 10^3$ | $1.0 (0.2) \times 10^3$ | $1.6 (0.4) \times 10^4$ | $2.6 (0.5) \times 10^3$ |
| $10^3$[CoL]/mol dm$^{-3}$ | 2.5–10.0 | 2.5–10.0 | 2.5–5.0 | 2.5–5.0 |
| $10^5$[nsa][c]/mol dm$^{-3}$ | 12.5 | 12.5 | 12.5 | 12.5 |
| pH | 8.1–8.9 | 8.0–8.8 | 7.8–8.3 | 7.9–9.1 |
| $K_{spec}$/dm$^3$ mol$^{-1}$ | $8.9 (0.3) \times 10^2$ | $9.9 (1.3) \times 10^2$ | | |
| $10^3$[CoL]/mol dm$^{-3}$ | 5.0–10.0 | 5.0–10.0 | | |
| $10^5$[nsa][c]/mol dm$^{-3}$ | 7.5 | 7.5 | | |
| pH | 8.1–9.4 | 7.9–9.2 | | |

[a] The rate and equilibrium constants refer to 25 °C and ionic strength 0.3 mol dm$^{-3}$ ($NaNO_3$); $k_f$, $k_d$ are $k_{41}$, $k_{14}$, respectively, in Scheme 1; $K_{kin}$, $K_{spec}$ are $K_1$ (see text); $n$ 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] Values of $k_f$, $\Delta H_f^{\neq}$ and $\Delta S_f^{\neq}$ for the reaction of $Co^{2+}$ (aq) with $Hnsa^-$ are, respectively, $2.7 (0.3) \times 10^3$ dm$^3$ mol$^{-1}$ s$^{-1}$, 40 (7) kJ mol$^{-1}$ and −37 (21) J K$^{-1}$ mol$^{-1}$. [c] Total weighed-in concentration of nsa species ($nsa^{2-}$, $Hnsa^-$, $H_2nsa$).

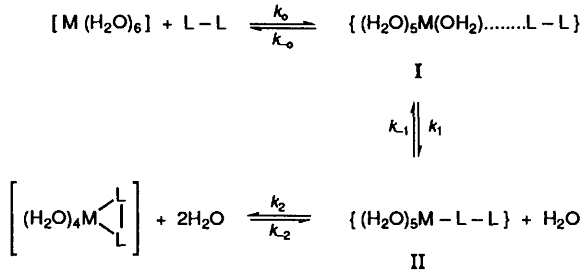
range. The results are shown in Fig. 2, SUP 57041 and Table 2. Stability constants for the $nsa^{2-}$ complexes with $Co^{2+}$ (aq) and with [CoL] (L = $tp^{5-}$, $nta^{3-}$, N,N′- and N,N-$edda^{2-}$) were determined spectrophotometrically[6,14] at 25 °C. The agreement between spectrophotometrically and kinetically determined values (Table 2) is satisfactory.

The $[Co(trien)]^{2+}$ system proved difficult to study as the relaxation effect was fast (τ 20–70 μs) and the amplitude relatively small; we could not obtain reliable data at temperatures higher than 25 °C. Similar difficulties were experienced with the $[Co(trien)]^{2+}$ + pada system.[5] In preliminary experiments with $[Co(tren)]^{2+}$ no relaxation effect attributable to ternary complex formation was observed at pH < 9; a very small effect was seen above pH 9 but suitable conditions for making measurements could not be found.

## Discussion

In this section we will review briefly the mechanism of labile metal complex formation and consider our results for the aqua-ion. We will then discuss the modifying effects of the bound ligands L, with special reference to the electrostatic influence exterted when L carries a negative charge. It is helpful to compare the present results (Table 2) with those obtained under similar conditions for the reaction of nsa with nickel(II)[7] and magnesium(II)[14] species, and for the reaction of the same cobalt(II)[5,15] and nickel(II)[4,6,7] species with the neutral bidentate ligand pada. The dominant position of nickel(II) in mechanistic studies has already been highlighted. The significance of $Mg^{2+}$ is that it is an ion of similar size to $Co^{2+}$ and $Ni^{2+}$ (effective ionic radii 72, 74.5 and 69 pm, respectively[16]) but, in contrast to $Co^{2+}$ and $Ni^{2+}$, forms complexes in water in which the bonding is assumed to be purely electrovalent.

*General*.—Complex formation between a labile bivalent aquametal ion $[M(H_2O)_6]^{2+}$ and a bidentate ligand L–L is generally discussed in terms of Scheme 2, from which charges have been omitted for clarity. In this scheme species **I** is an outer- sphere complex (in the event that the ligand is charged, an ion pair)



**Scheme 2**

and **II** is a singly co-ordinated inner-sphere complex. The formation rate of the outer-sphere complex is diffusion-controlled and for many metals, including cobalt(II), nickel(II) and magnesium(II), the water-loss step (**I** ——→ **II**) is considerably slower than this.

The formation constant for the outer-sphere intermediate, $K_{os}$ ($=k_0/k_{-0}$), can be calculated by the Fuoss equation[17] (3)

$$K_{os} = (4\pi N_0a^3/3000)\exp(-U) \qquad (3)$$

where $U = z_Mz_{L-L}e_0^2/a\varepsilon kT$ and $a$ is the reaction distance between metal M and ligand L–L, $z_M$ and $z_{L-L}$, respectively, are the charges on M and L–L, $N_0$ is Avogadro's number, $e_0$ the electronic charge, ε the permittivity of the solvent, $k$ the Boltzmann constant and $T$ the absolute temperature. If a steady state is assumed for intermediate **II**, the observed rate constant for the formation of the chelate complex is usually given by $k_f = K_{os}k_1$, which is equivalent to $K_{os}k_{ex}$, where $k_{ex}$ is the rate constant for water exchange at the aqua-metal ion. Although this scheme dates from the early days of fast-reaction techniques,[1,2] powerful supporting evidence has come recently[18] from the measurement of activation volumes, and an $I_d$ mechanism[19] can generally be assumed, at least for $Co^{2+}$ and $Ni^{2+}$, and probably $Mg^{2+}$. A possible complication[3] is that chelate ring closure becomes rate limiting.

A similar scheme to Scheme 2 can be written for the formation of the ternary complex between L–L and $[ML(H_2O)_{6-n}]$, where L is a ligand of denticity $n$ and it is assumed that the co-ordination number of the metal remains six. To facilitate comparison of rate constants, it is usual[3] to multiply the measured $k_f$ by a statistical factor $6/(6-n)$ to give $k_f^s$.

*Reaction with* $Co^{2+}$ *(aq)*.—The U-shaped pH profile (Fig. 1) indicates the existence of parallel reaction pathways but it does not identify them unequivocally. The low-pH arm is clearly associated with the reaction of the monoprotonated ligand $Hnsa^-$ with $[Co(H_2O)_6]^{2+}$ but the high-pH arm is subject to proton ambiguity.[20] Owing to the similarity of the $pK_a$ values of $Hnsa^-$ and $Co^{2+}$ (aq) (9.9[14] and 9.4,[13] respectively) it is difficult to decide whether the reactants are $nsa^{2-}$ and $[Co(H_2O)_6]^{2+}$ or $Hnsa^-$ and $[Co(OH)(H_2O)_5]^+$. Similar profiles have been found for the reaction of several salicylic acids with $Co^{2+}$ (aq) or $Ni^{2+}$ (aq) and these have been interpreted[21] in terms of the reaction of $Hnsa^-$ with aqua- and hydroxo-forms of the metal, by comparison with certain tervalent metals. However, a detailed analysis by Chopra and Jordan[22] has shown that it is not necessary to invoke $[M(OH)(H_2O)_5]^+$, and there now seems to be agreement[23] that the high-pH arm is associated with the reaction between $[M(H_2O)_6]^{2+}$ and the fully deprotonated form $nsa^{2-}$, in line with our earlier interpretation.[7,14]

The value of $k_f$ for the reaction of $nsa^{2-}$ with $Co^{2+}$ (aq) (Table 2; log $k_f = 6.81$) compares well with those found[3] for complex formation between cobalt(II) and other dianions (for example, malonate, 6.95; tartrate, 6.70; iminodiacetate, 7.04; cysteine, 6.75). Moreover, the value of $\Delta H_f^{\neq}$ (42 kJ $mol^{-1}$) is comparable to activation enthalpies for water exchange at cobalt(II) (47 kJ $mol^{-1}$)[24] and for complex formation between cobalt(II) and pada (43 kJ $mol^{-1}$).[5] We therefore conclude that the rate-determining step in the $Co^{2+}$ (aq) + $nsa^{2-}$ reaction is replacement of the first water molecule in the inner co-ordination sphere of the metal (rather than ring closure, Scheme 2), as it seems to be for the $Ni^{2+}$ + $nsa^{2-}$ reaction[7] and the reaction of both metals with pada.[5,6,15] The differences in log $k_f$ between $nsa^{2-}$ and pada for cobalt(II) and nickel(II) (1.93 and 1.87, respectively) merely reflect[25] the greater desolvation associated with charge neutralization which occurs on forming the transition state with $nsa^{2-}$. As expected, the differences in $k_f$ are also associated with more positive $\Delta S_f^{\neq}$ values for $nsa^{2-}$ (+26 and +33 J $K^{-1}$ $mol^{-1}$) than for pada (−8 and +4 J $K^{-1}$ $mol^{-1}$, respectively).

Before assessing the agreement between the measured $k_f$ for $nsa^{2-}$ and the value calculated from $K_{os}k_{ex}$, it should be remembered that for charged ligands the generally stated form of the Fuoss equation (3) applies only at infinite dilution. Under the high ionic strength conditions used here ($I = 0.3$ mol $dm^{-3}$) the right-hand side must[17] be multiplied by $f_\pm^2$, where $f_\pm$ is the mean ionic activity coefficient. Since we are well outside the linear region it is necessary[26] to employ the extended form of the Debye–Hückel equation (4) to estimate $f_\pm$, where $A$, $B$ and $b$ are constants.

$$\log_{10}f_\pm = Az_Mz_{L-L}I^{\frac{1}{2}}/(1 + BaI^{\frac{1}{2}}) + bI \qquad (4)$$

In view of the similarity in respective sizes of $Co^{2+}$ (aq) and $Ni^{2+}$ (aq) and of the co-ordinating portions of $nsa^{2-}$ and pada (and therefore in all the values of $a$), a convenient way of testing the Fuoss equation is through the ratio $k_f^s(nsa^{2-})/k_f^s$(pada). This should be equal to the electrostatic component of $K_{os}(nsa^{2-})$, namely $\exp(-U)f_\pm^2$. Using the normal[26] values for $A$, $B$ and $b$ ($\equiv 0.1\,|z_Mz_{L-L}|$) and a reaction distance ($a$) of 420 pm (the typical[27] distance of a second-sphere atom from a $Co^{2+}$ or $Ni^{2+}$ ion in aqueous solution), we calculate a charge increment of 85 $dm^3$ $mol^{-1}$ for $K_{os}(nsa^{2-})$, which is equivalent to a difference [$\log_{10} k_f^s(nsa^{2-}) - \log_{10} k_f^s$(pada)] of 1.9. While this is gratifyingly close to the observed differences in $\log_{10} k_f$ for the two metals, the level of agreement should not be overemphasized.

The value of $k_f$ for the reaction of $Hnsa^-$ with $Co^{2+}$ (aq) (Table 2, log $k_f = 3.43$) is about two orders of magnitude less than those found[3] for many other monoanions. It is similar to that reported[21] for the protonated form of salicyclic acid (log $k_f = 3.70$) and it is likely in both cases that the rate-determining process involves breaking the intramolecular hydrogen bond.[28]

*Reaction with* $[CoL(H_2O)_{6-n}]$.—Not much is known about the effect of partial replacement of the inner hydration sphere of $Co^{2+}$ (aq) on the substitution lability of the remaining waters. With nickel(II) it has been found that $k_f$ and $k_{ex}$ tend to increase with increasing number of (aliphatic) nitrogens co-ordinated to the metal[3] and we have recently found[4] evidence for a small additional labilization if L is pyramidal. Following an indication[29] that similar factors are important for cobalt(II), we compared[5] the values of $k_f^s$ for the reaction of pada with nine cobalt(II) species with those for the corresponding nickel(II) reaction. Although the values range over two orders of magnitude for both metals, in all but two cases (L = $nta^{3-}$ or *N,N'*-$edda^{2-}$) log $k_f^s$ is 1.9 ± 0.4 larger for Co than for Ni. The value 1.9 is the average between Δlog $k$ [$Co^{2+}$(aq) − $Ni^{2+}$(aq)] for water exchange ($k_{ex}$) and complex formation with pada ($k_f$), and can be seen as a measure of the difference in the 'inherent' labilities of the two metals.

Fig. 3 shows that there is a similar pattern of behaviour for the reaction with $nsa^{2-}$. To emphasize the similarity we have added (and connected with a dashed line) the values of log $k_f^s$ for nickel to which we have added 1.9. In this case the observed value for Co is within 0.2 of the nickel-derived value.

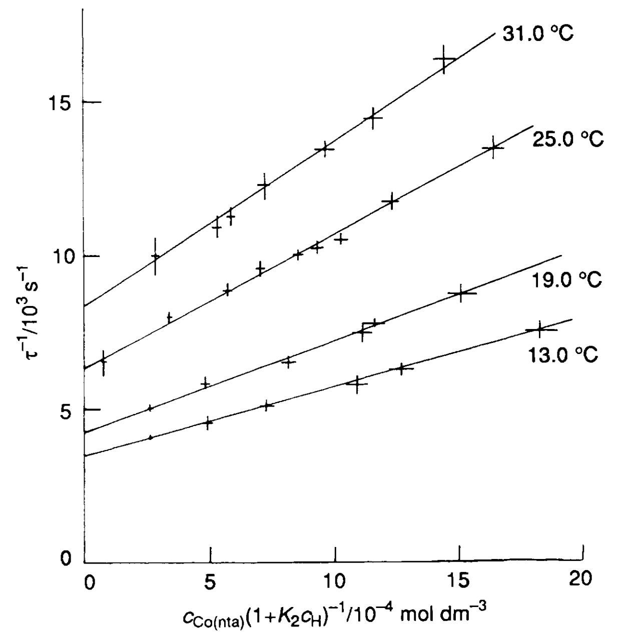


**Fig. 2** Variation of $\tau^{-1}$ with $c_{\text{CoL}}/(1 + K_2c_{\text{H}})$ for the reaction of [Co(nta)]$^-$ with nsa at different temperatures. The lines on each point indicate experimental scatter (representing, on average, five or six experiments)

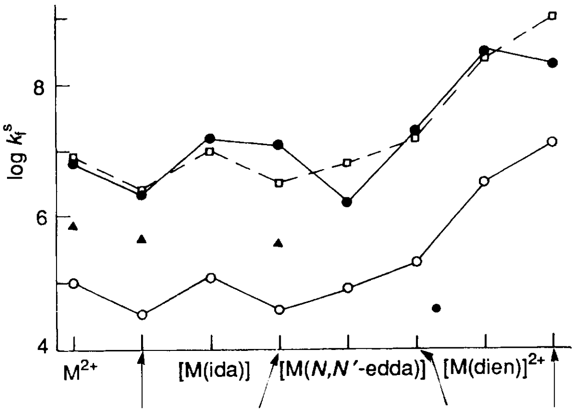


**Fig. 3** Statistically adjusted rate constant (log $k_f^s$) for reaction of cobalt(II) (●), nickel(II) (○) and magnesium(II) (▲) species with nsa$^{2-}$; also (1.9 + log $k_f^s$) for the reaction of the nickel(II) species with nsa$^{2-}$ (□) (see text)

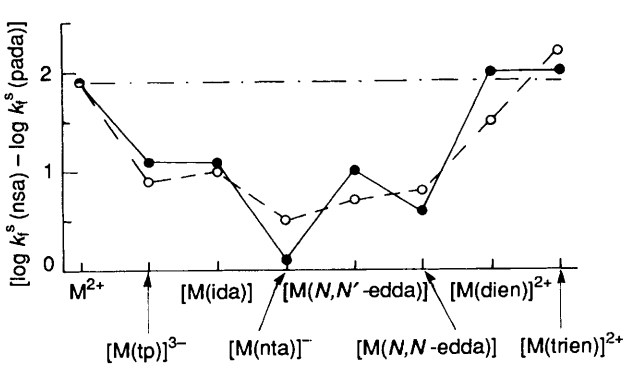


**Fig. 4** Difference in statistically adjusted rate constants (log $k_f^s$) for reaction of cobalt(II) (●) and nickel(II) (○) species with nsa$^{2-}$ and pada (see text)

As with pada, [Co(nta)]$^-$ is more labile and [Co(*N*,*N'*-edda)] less labile than 'predicted'. {The position of [Co(trien)]$^{2+}$ is ambiguous. Although it also is rather less labile than predicted by these comparisons (0.7 towards nsa$^{2-}$ and 0.4 towards pada), the experimental difficulties we experienced with both these systems lead us to be less confident about the size of these differences.} Like pada,[5] nsa$^{2-}$ is apparently unable to enforce an increase in co-ordination number on the metal in [Co(tren)]$^{2+}$ from five to six; in the nickel analogue [Ni(tren)]$^{2+}$ the co-ordination number of the metal is already six and the tendency to form ternary complexes is similar to that with [Ni(trien)]$^{2+}$.

Focusing now on the nsa$^{2-}$ systems in which L is charged, it is immediately apparent that the observed variation in $k_f^s$ cannot be accommodated by the Fuoss equation (3). This may be seen by reference to Fig. 4, in which $\Delta\log k_f^s$ {([ML] + nsa$^{2-}$) − ([ML] + pada)} has been plotted for Co and Ni. The dot-dashed line shows the value predicted by the Fuoss equation (1.9) for the aqua-systems (see above), and others for which L is uncharged (dien or trien). For both metals $\Delta\log k_f^s$ remains positive throughout, while the Fuoss equation would predict values of 0 where [ML] is uncharged (L = ida$^{2-}$, *N*,*N'*- or *N*,*N*-edda$^{2-}$) and $<0$ where [ML] carries a net negative charge (L = tp$^{5-}$ or nta$^{3-}$). Notwithstanding the neutral or unfavourable net charge on the latter [ML] complexes, the incoming nsa$^{2-}$ dianion is evidently attracted to the local positive charge on the metal.

In conclusion, we have found considerable similarity between the reactivity patterns of substituted cobalt(II) species towards nsa$^{2-}$ and pada, and the analogous systems involving nickel(II). For both metals the lability of the remaining water molecules appears to be influenced by the number of bound nitrogens, and the retarding effect of bound negatively charged groups on an incoming anion is substantially less than predicted by the Fuoss equation. The similarity is interesting in the light of the generally held view that, although there are small differences between typical transition states for the two metals,[30] substitution at octahedrally co-ordinated high-spin Ni$^{II}$ requires crystal-field activation energy (c.f.a.e.) while at high-spin Co$^{II}$ it does not.[31] Though the range of [MgL] complexes which can be studied is far narrower than for the transition metals, the two for which reactivity towards nsa$^{2-}$ has been measured[14] (L = tp$^{5-}$ or nta$^{3-}$) conform precisely to the behaviour seen with Co and Ni (Fig. 3). It is difficult to avoid the conclusion that steric (and electrostatic) factors are at least as important as electronic effects in determining the reactivity of nickel(II) in these [ML(H$_2$O)$_{6-n}$] complexes, as they must be for magnesium(II) and cobalt(II).

## Acknowledgements

We thank the SERC for a studentship (to A. R. W.).

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*Received* 22*nd July* 1994; *Paper* 4/04502E