Complex Formation between Nickel(II) and some Pentamine(substituted salicylato)cobalt(III) Ions

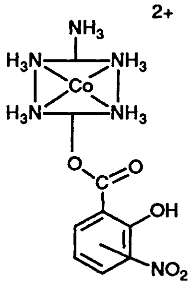
Anadi C. Dash,* Rabindra K. Nanda and Achyuta N. Acharya
Department of Chemistry, Utkal University, Bhubaneswar-751004, India

The kinetics of reversible complexation of Ni^{II} with pentamine(substituted salicylato)cobalt(III) ions, $[Co(N_5)\{O_2CC_6H_3(X)OH\}]^{2+}$ [N_5 = $5NH_3$, $(en)_2(NH_3)$ (*cis* isomer, en = ethane-1,2-diamine) or tetren (tetraethylenepentamine), X = $3-NO_2$; N_5 = $5NH_3$, X = $5-NO_2$], was investigated by the stopped-flow technique at 15–35 °C, pH 5.70–6.90 and $I = 0.30$ mol dm^{-3} (ClO_4^-). The formation of $[(Co(N_5)\{O_2CC_6H_3(X)O\}Ni]^{3+}$ occurs *via* the reaction of $[Ni(OH_2)_6]^{2+}$ with the phenoxide form of the cobalt(III) substrates. The rate and activation parameters have been determined for the formation and dissociation of the binuclear species in which nickel(II) is chelated by the salicylate moiety. The data are consistent with an I_d mechanism. The rate constant for spontaneous dissociation of the binuclear species to the reacting partners is sensitive to the nature of the pentamine moiety and decreases in the sequence tetren > $(en)_2(NH_3)$ ≈ $5NH_3$. The acid-catalysed dissociation of *cis*-$[(en)_2(NH_3)Co\{O_2CC_6H_3(NO_2\text{-}3)O\}Ni]^{3+}$ conforms to a two-step process.

The kinetics of complexing of Ni^{II} with substituted salicylates [1–6] and ligands of biological importance [7,8] has been the subject of several investigations in the recent past. For salicylate the reaction is believed to occur *via* nickel(II)–carboxylate bond formation followed by chelation of the metal ion by the phenol or phenoxide moiety. Recent work of Chopra and Jordan [5] elegantly highlighted the protonation equilibrium of the nickel(II) salicylate $\overline{Ni(O_2CC_6H_4O)}$ as a possible alternative to interpret the pH dependence of the rate profile which was otherwise attributed by Mentasti *et al* [3,4] to the kinetic consequences of both $[Ni(OH_2)_6]^{2+}$ and its hydrolysed species $[Ni(OH_2)_5(OH)]^+$.

The pentamine substituted salicylatocobalt(III) substrates $[Co(N_5)\{O_2CC_6H_3(X)OH\}]^{2+}$ [N_5 = $5NH_3$, $(en)_2(NH_3)$(*cis* isomer, en = ethane-1,2-diamine) or tetren (tetraethylenepentamine; X = 3- or $5-NO_2$)] (see diagrams **1**–**3**) provide an opportunity to examine the complexing abilities towards Ni^{II} when the carboxylate group is already bound to a cobalt(III) centre. Previous equilibrium and kinetic studies have shown that the pentamine substituted salicylatocobalt(III) substrates act as potential chelating agents towards Al^{III}, Fe^{III} and Ga^{III},[9–12] despite the unfavourable electrostatic repulsion between the like charge centres in the binuclear species. To our knowledge similar kinetic and equilibrium studies with Ni^{2+} except for the $[Co(NH_3)_5(C_2O_4)]^+$–Ni^{2+} system [13–15] have not been reported.

The purpose of this study was to determine whether the dipositive pentamine substituted salicylatocobalt(III) substrates $[Co(N_5)\{O_2CC_6H_3(X)OH\}]^{2+}$ react with Ni^{2+} and then to assess the kinetics and mechanism of the reaction. These cationic cobalt(III) substrates present an interesting variation with respect to both electrostatic and non-electrostatic interactions which can influence the kinetics and energetics of the formation and dissociation of the binuclear species. Further, the nitrosalicylates were chosen because of their inertness to aquation and also the low pK_{OH} values (8.0, 29.5 °C, $I = 1.0$ mol dm^{-3}).[10] The latter will favour substantial partitioning of the complexes between the phenoxide and phenol forms under the experimental conditions of pH 5.70–6.90 at which hydrolysis of $[Ni(OH_2)_6]^{2+}$ would be insignificant so that the reactivity of both the phenol and phenoxide species would be unambiguously assessed.



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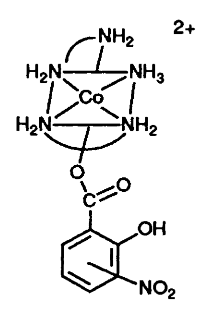

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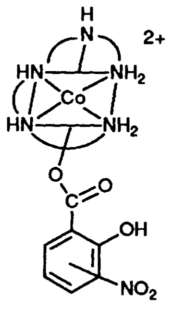

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Experimental

Materials and Methods.—The pentamine(substituted salicylato)cobalt(III) diperchlorates, $[Co(N_5)\{O_2CC_6H_3(X)OH\}][ClO_4]_2$ [N_5 = $5NH_3$, $(en)_2(NH_3)$ (*cis* isomer) or tetren, X = $3-NO_3$; N_5 = $5NH_3$, X = $5-NO_2$] were prepared as reported earlier.[10,12,16] The analytical and UV/VIS spectral data for the samples were in satisfactory agreement with those calculated theoretically and reported earlier respectively. The tetren substrate is a mixture of $\alpha\beta R$ and $\alpha\beta S$ isomers.[16]

The stock solution of nickel(II) chloride was standardised by complexometric titration using Na_2H_2edta [17] (edta = ethylenediaminetetraacetate). 2,6-dimethylpyridine and 2-morpholinoethanesulfonic acid (mes) buffers were used for adjustment of pH. AnalaR grade reagents were used. Solutions were prepared in deionised water distilled from alkaline permanganate in an all-glass apparatus. The ionic strength adjustments were made using $NaClO_4$.

The pH measurements were made with an Elico digital pH meter, model LI 120, equipped with a model CL 51 combination electrode glass–AgCl, NaCl (2.0 mol dm^{-3}). Standard NBS buffers (pH 4.01, 6.86 and 9.20) were used for calibration of the pH meter. The concentration of H^+ ($= a_{H^+}/f_{H^+}$) was calculated from the pH data using the calculated values of the activity coefficient [f_{H^+} = 0.714, 0.709, 0.707 and 0.704 at 15, 25, 30 and 35 °C ($I = 0.3$ mol dm^{-3})].[18] All UV/VIS spectra were recorded on a JASCO model 7800 spectrophotometer with 10 mm matched quartz cells. The rate data was analysed by a non-linear least-squares computer program adapted to a Wipro

Table 1 Values of K_{OH} for $[Co(N_5)\{O_2CC_6H_3(X)OH\}]^{2+}$ and stability constants of the binuclear species $[Co(N_5)\{O_2CC_6H_3(X)O\}Ni]^{3+\,a}$

	$10^8 K_{OH}{}^b$/mol dm^{-3}				$10^{-3}K_M{}^c$/dm^{-3} mol^{-1}
N_5/X	15 ± 0.1	25.0 ± 0.1	30.0 ± 0.1	35.0 ± 0.1 °C	25.0 ± 0.1 °C
$5NH_3/3\text{-}NO_2{}^d$	2.36	1.79 ± 0.07	1.65 ± 0.07	1.38 ± 0.06	4.83 ± 0.15
$5NH_3/5\text{-}NO_2{}^d$	1.83	1.63 ± 0.09	1.50 ± 0.10	1.44 ± 0.10	4.91 ± 0.08
$(en)_2(NH_3)/3\text{-}NO_2{}^d$	2.22	1.76 ± 0.07	1.52 ± 0.10	1.44 ± 0.15	4.05 ± 0.09
tetren/$3\text{-}NO_2{}^{d,e}$	1.90	2.46 ± 0.17	2.72 ± 0.19	3.13 ± 0.24	2.35 ± 0.04

[a] I = 0.30 mol dm^{-3}, $[\text{complex}]_T$ = (1.3–1.6) × 10^{-4} mol dm^{-3}. [b] Values at 15 °C were extrapolated. [c] pH 6.19–6.40 (2,6-dimethylpyridine buffer). [d] ε_i (dm^3 mol^{-1} cm^{-1}) = 156 ± 5, 6977 ± 240, 2630 ± 49 ($5NH_3/3\text{-}NO_2$); 89 ± 3, 10 211 ± 523, 1543 ± 45 ($5NH_3/5\text{-}NO_2$); 181 ± 6, 7375 ± 258, 2704 ± 12 [$(en)_2(NH_3)/3\text{-}NO_2$]; 150 ± 5, 9232 ± 536, 2243 ± 22 (tetren/$3\text{-}NO_2$) for i = 1,2 (400 nm), 3 (387 nm) respectively. [e] For tetren complex, $\varepsilon_1 = (\varepsilon_s A + \varepsilon_r)/(1 + A)$, $\varepsilon_2 = (\varepsilon_s' A + \varepsilon_r')/(1 + A)$ where $A = [\alpha\beta S]_T + [\alpha\beta R]_T$, ε_s and ε_r (ε_s' and ε_r') denote the molar absorption coefficient of the phenol form (phenoxide form) of the $\alpha\beta S$ and $\alpha\beta R$ isomers respectively (ref. 16).

Land Mark 4860 computer available at Utkal University Computer Centre. The kinetic measurements were performed with a fully automated HI-TECH (U.K.) SF-51 stopped-flow spectrophotometer. The drive syringes and cell compartments were thermostatted at the desired temperature with an accuracy of ±0.1 °C.

Kinetic Measurements.—The rate measurements were made under pseudo-first-order conditions at $15.0 \leqslant T \leqslant 35.0$ °C and I = 0.3 mol dm^{-3} ($NaClO_4$) with $[\text{complex}]_T$ = (2–10) × 10^{-5}, $[Ni^{2+}]_T$ = (0.10–5.0) × 10^{-2} mol dm^{-3} and pH 5.70–6.90 (see Table 2). The formation and the acid-catalysed decomposition of the binuclear complex of a given substrate were monitored at any suitable wavelength between 370 and 390 nm (see Tables 3 and 4). For the study of the acid-catalysed dissociation, the binuclear complex was generated by adjusting the mixture containing $[\text{complex}]_T$ = 1.0 × 10^{-4} mol dm^{-3} and $[Ni^{2+}]_T$ = 0.10 mol dm^{-3} (I = 0.3 mol dm^{-3}) with NaOH to pH 6.5. Further details of the experimental procedures were essentially the same as reported earlier.[11] The absorbance *vs.* time data for all substrates displayed as the voltage output on the monitor of an on-line Apple IIGS computer were fitted by a single exponential curve applicable to first-order kinetics by help of a least-squares computer program written in BASIC made available to us by HI-TECH Scientific Ltd. (U.K.). Each rate constant reported is the average from at least seven replicate measurements for a given reaction mixture and the error quoted is the standard deviation.

Results and Discussion

Dissociation Constant (pK_{OH}).—The absorbance of the cobalt(III) substrates at 400 nm increased with increasing pH which is attributed to the formation of the highly absorbing phenoxide form of the substrates.[10] The dissociation constant [see equation (1)] of the unco-ordinated phenol group was

$$[Co(N_5)\{O_2CC_6H_3(NO_2)OH\}]^{2+} \underset{}{\overset{K_{OH}}{\rightleftharpoons}} [Co(N_5)\{O_2CC_6H_3(NO_2)O\}]^{+} + H^+ \quad (1)$$

determined using the absorbance data at 400 nm for $[\text{complex}]_T$ = (1.3–1.6) × 10^{-4} mol dm^{-3} in the range pH 7.00–8.20 [tris(hydroxymethyl)methylamine (Tris) buffer] and in 0.10 mol dm^{-3} $HClO_4$ media (I = 0.3 mol dm^{-3}) using the linearised form of equation (2)[10,*] where ε_{obs}, ε_1 and ε_2 denote the

$$\varepsilon_{obs} = (\varepsilon_1 + \varepsilon_2 K_{OH}[H^+]^{-1})/(1 + K_{OH}[H^+]^{-1}) \quad (2)$$

observed molar absorption coefficient of the complex at a given pH and that of its phenol and phenoxide forms respectively (see footnote *e* of Table 1); $\varepsilon_1 = \varepsilon_{obs}$ at $[H^+]$ = 0.10 mol dm^{-3} was used to fit the data. The values of pK_{OH} and associated thermodynamic parameters and the molar absorption coefficients of the phenoxide and phenol forms of the substrates are collected in Table 1.

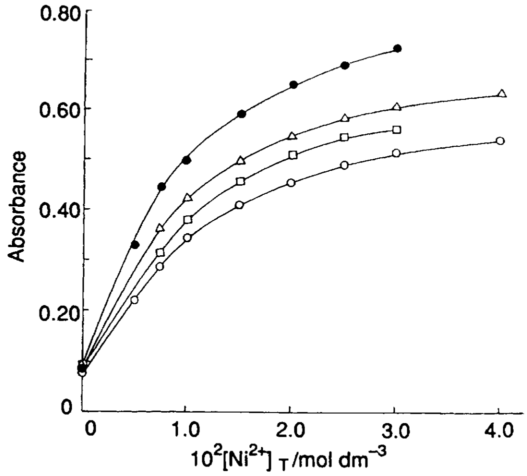

Fig. 1 Variation of $(A_{obs} - A_{Ni})$ with $[Ni^{2+}]_T$ at 387 nm where A_{obs} = absorbance of ($[\text{complex}]_T$ + $[Ni^{2+}]_T$) and A_{Ni} = absorbance of $[Ni^{2+}]_T$ at the same pH, I = 0.30 mol dm^{-3}, cell path = 1.0 cm, 25 °C $[\text{complex}]_T$/mol dm^{-3} (pH): 3.33 × 10^{-4} (6.19), $5NH_3/3\text{-}NO_2$ (□); 6.7 × 10^{-4} (6.29), $5NH_3/5\text{-}NO_2$ (●); 3.2 × 10^{-4} (6.29), $(en)_2(NH_3)/3\text{-}NO_2$ (Δ); and 3.4 × 10^{-4} (6.39), tetren/$3\text{-}NO_2$ (○)

The interaction of Ni^{2+} with the cobalt(III) substrates results in a large absorbance increase around 400 nm. In contrast, no spectral evidence of complex formation between Ni^{II} and *p*- and *o*-nitrophenol under comparable conditions was observed.

Equilibrium Constant.—The equilibrium constant, K_M, for the reaction (3) was calculated at 25 °C (I = 0.30 mol dm^{-3}) from

$$[Co(N_5)\{O_2CC_6H_3(NO_2)O\}]^{+} + Ni^{2+} \overset{K_M}{\rightleftharpoons} [Co(N_5)\{O_2CC_6H_3(NO_2)O\}Ni]^{3+} \quad (3)$$

the absorbance data at 387 nm for solutions containing a fixed $[\text{complex}]_T$ and varying $[Ni^{2+}]_T$ = 0.005–0.040 mol dm^{-3} at a fixed pH after making due allowance for the absorbance of $[Ni^{2+}]_T$ (see Fig. 1). The calculation involved fitting of the $[Ni^{2+}]_T$-corrected absorbance data for the reaction mixtures by the linearised form of equation (4)[9,10] where $\varepsilon'_{obs} = (A_{obs} -$

$$\varepsilon'_{obs} = \frac{\varepsilon_1 + \varepsilon_2 K_{OH}[H^+]^{-1} + \varepsilon_3 K_{OH} K_M [Ni^{2+}]_T [H^+]^{-1}}{1 + K_{OH} K_M [Ni^{2+}]_T [H^+]^{-1}} \quad (4)$$

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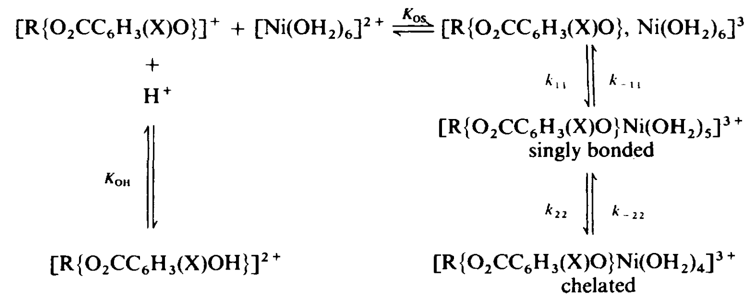
[*] $(\varepsilon_{obs} - \varepsilon_1)^{-1}$ *vs.* $[H^+]$ was plotted where $(\varepsilon_{obs} - \varepsilon_1)^{-1}$ was weighted inversely as its variance which was calculated on the basis of $\sigma(\varepsilon_1)$ (see footnote *d* in Table 1).



Scheme 1 R = $(en)_2(NH_3)Co$, $(NH_3)_5Co$ or (tetren)Co; X = NO_2

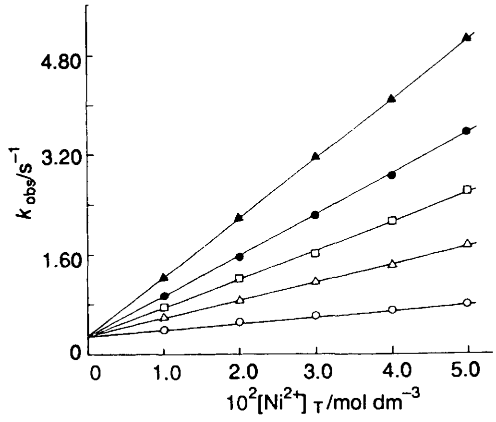


Fig. 2 Plots of k_{obs} *vs.* $[Ni^{2+}]_T$ for *cis*-$[Co(en)_2(NH_3)\{O_2CC_6H_3(NO_2\text{-}3)OH\}]^{2+}$ at 25 °C and pH 5.78 (○), 6.30 (△), 6.52 (□), 6.68 (●) and 6.86 (▲)

$A_{Ni})/[complex]_T$, ε_3 is the molar absorption coefficient of the binuclear species and all other terms have their usual meanings. The values of K_M and ε_3 (387 nm) are collected in Table 1. The values of K_M may be contrasted with the values of the stability constants of 1 : 1 3- and 5-nitrosalicylate complexes of Ni^{II} [log K_{ML} = 5.89 ± 0.04 (3-NO_2), 5.46 ± 0.04 (5-NO_2), I = 0.0037 mol dm^{-3} at 25 °C reported by Sthapak *et al.*[19]] and lack of evidence for the complexation of Ni^{II} with *o*- and *p*-nitro phenolate. The low stability constants of the binuclear species relative to that of the nickel(II) nitrosalicylates are in accord with the inherent coulombic repulsion between the like-charge centres in the former assuming that the binuclear species are essentially chelates.

Formation of Binuclear Salicylates.—Rate data at varying pH and $[Ni^{2+}]_T$ (15–35 °C) are collected in Table 2. Plots of k_{obs} *vs.* $[Ni^{2+}]_T$ for any cobalt(III) substrate at different pH are linear and converge to a common intercept (see Fig. 2). The lack of a pH dependence of the intercept suggests that the dissociation of the binuclear species is not catalysed by H^+ or OH^- in the range pH 5.70–6.90 or the acid or base components of the buffers used. The observed inverse acid dependence of the gradient of such plots under the pH conditions employed cannot arise from the competitive reaction of $[Ni(OH_2)_5(OH)]^+$ with the phenol form of the cobalt(III) substrate considering the high pK of $[Ni(OH_2)_6]^{2+}$ (pK = 9.9 at 25 °C, I = 0).[20] Also earlier studies on the nickel(II) complexation reactions with 2,3-dihydroxybenzoate[6] (pH 6.5–7.0) and peptides[21] (pH 6.43–7.50) did not provide positive evidence for the occurrence of such a path at pH ⩽ 7.0. Consistent with these facts and assuming that the chelated species is formed *via* the singly bonded intermediate the possible reaction pathways are delineated in Scheme 1 for which k_{obs} takes the form (5) (see Appendix), where the overall

$$k_{obs} = k_f\{K_{OH}/([H^+] + K_{OH})\}[Ni^{2+}]_T + k_r \qquad (5)$$

formation rate constant (k_f) and the dissociation rate constant (k_r) of the binuclear species $[Co(N_5)\{O_2CC_6H_3(NO_2)O\}Ni]^{3+}$ are given by equations (6) and (7) respectively. Here k_{ii} and k_{-ii}

$$k_f = \frac{K_{os}k_{11}k_{22}}{k_{22} + k_{-11}} \qquad (6)$$

$$k_r = \frac{k_{-11}k_{-22}}{k_{22} + k_{-11}} \qquad (7)$$

denote the rate constants for the individual steps and K_{os} is the outer-sphere association constant of $[Ni(OH_2)_6]^{2+}$ with the phenoxide form of the cobalt(III) substrate. The values of k_f and k_r in Table 3 were calculated by fitting the rate data by use of equation (5) and a weighted least-squares program which minimised the residuals $\Sigma w_i(k_{calc} - k_{obs})^2$ where $w_i = [1/\sigma(k_{obs,i})]^2$. The values of k_f, k_r and K_{OH} reproduced the observed rate constants satisfactorily.

Comparison of the Rate and Equilibrium Constants (k_f *and* K_M), *and the Mechanism of Reaction.*—It is worth noting that there is no evidence of a reaction path involving $[Ni(OH_2)_6]^{2+}$ and the dipositive phenol form of the complex. Similar observations were made in studies of the kinetics of complexation of $[Co(NH_3)_5(C_2O_4H)]^{2+}$ with $[Ni(OH_2)_6]^{2+}$.[13,15] This must be ascribed to substantial electrostatic repulsion between the dipositive reactants which is unfavourable for the encounter complex formation. The calculated values of K_M ($= k_f/k_r$) from the kinetic data at 25 °C (I = 0.3 mol dm^{-3}) agree excellently with those obtained from equilibrium measurements. For the $[Co(tetren)\{O_2CC_6H_3(NO_2\text{-}3)O\}]^+$ the calculated values of K_M at 15–35 °C range from (2.14 ± 0.08) × 10^3 to (1.4 ± 0.02) × 10^3 dm^3 mol^{-1} decreasing with increasing temperature. These values are lower by a factor of 2–3 than the values for the corresponding pentaammine and $(en)_2(NH_3)$ complexes, presumably indicating that the relatively higher hydrophobicity of the tetren moiety and also the increasing rigidity of the cobalt(III) substrates imposed by the amine ligands* decreased the thermodynamic stability of the corresponding binuclear species. This is also evident from the higher values of k_r for the tetren complex (see Table 3).

Despite the variation of the rigidity and the hydrophobic nature of the N_5 moiety it is important to note that the values of k_f do not reflect any significant variation at 25 °C [k_f (25.0 °C) ≈ 1.1 × 10^3 dm^3 mol^{-1} s^{-1}}. These data may be compared with the analogous rate data for the 5-nitro- and 3,5-dinitro-salicylate monoanions [k_f/dm^3 mol^{-1} s^{-1} = 1.02 × 10^5 (ref. 2) and 1.3 × 10^5 (ref. 5) at 25 °C and I = 0.3 mol dm^{-3}]. The relatively higher values of k_f for the substituted salicylate anions evidently point to a favourable electrostatic effect on the

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* We are thankful to one of the referees for the interpretation of the observed trend in the variation of K_M and k_r in terms of the rigidity of the substrates imposed by the ligands.

Table 2 Rate data for the complexing of Ni^{II}

T/°C (±0.1 °C)	10^2 [Ni^{2+}]/ mol dm^{-3}	k_{obs}/s^{-1}				
(*a*) With $[(NH_3)_5Co\{O_2CC_6H_3(NO_2\text{-}3)OH\}]^{2+}$ [a]						
		(6.89 ± 0.01)[b]	(6.68 ± 0.01)	(6.51 ± 0.01)	(6.32 ± 0.01)	(5.75 ± 0.02)
15.0	1.0	0.58 ± 0.02	0.39 ± 0.02	0.33 ± 0.02	0.26 ± 0.02	0.17 ± 0.01
	2.0	0.99 ± 0.02	0.72 ± 0.02	0.51 ± 0.02	0.40 ± 0.03	0.21 ± 0.02
	3.0	1.43 ± 0.03	0.95 ± 0.03	0.70 ± 0.02	0.55 ± 0.02	0.26 ± 0.02
	4.0	1.87 ± 0.02	1.27 ± 0.03	0.89 ± 0.02	0.69 ± 0.03	0.31 ± 0.03
	5.0	2.30 ± 0.04	1.54 ± 0.08	1.09 ± 0.06	0.83 ± 0.03	0.35 ± 0.02
		(6.88 ± 0.01)	(6.69 ± 0.01)	(6.51 ± 0.01)	(6.32 ± 0.01)	(5.75 ± 0.02)
25.0	1.0	1.35 ± 0.06	1.02 ± 0.04	0.82 ± 0.02	0.64 ± 0.02	0.43 ± 0.02
	2.0	2.33 ± 0.04	1.69 ± 0.03	1.30 ± 0.03	0.98 ± 0.03	0.55 ± 0.02
	3.0	3.34 ± 0.04	2.35 ± 0.04	1.83 ± 0.04	1.32 ± 0.02	0.66 ± 0.02
	4.0	4.36 ± 0.04	3.08 ± 0.02	2.36 ± 0.07	1.62 ± 0.04	0.74 ± 0.03
	5.0	5.40 ± 0.04	3.79 ± 0.03	2.81 ± 0.10	1.90 ± 0.06	0.84 ± 0.03
		(6.85 ± 0.01)	(6.70 ± 0.01)	(6.52 ± 0.01)	(6.32 ± 0.01)	(5.79 ± 0.02)
30.0	1.0	1.95 ± 0.04	1.57 ± 0.03	1.22 ± 0.04	1.00 ± 0.03	0.72 ± 0.02
	2.0	3.35 ± 0.05	2.60 ± 0.04	1.97 ± 0.03	1.43 ± 0.03	0.85 ± 0.03
	3.0	4.75 ± 0.12	3.66 ± 0.03	2.68 ± 0.03	1.96 ± 0.05	1.03 ± 0.02
	4.0	6.22 ± 0.03	4.72 ± 0.02	3.40 ± 0.04	2.43 ± 0.06	1.16 ± 0.02
	5.0	7.65 ± 0.04	5.76 ± 0.10	4.15 ± 0.04	2.94 ± 0.06	1.35 ± 0.04
		(6.88 ± 0.01)	(6.60 ± 0.01)	(6.47 ± 0.01)	(6.11 ± 0.01)	(5.79 ± 0.01)
35.0	0.10	0.88 ± 0.03	0.81 ± 0.02	0.77 ± 0.02	0.73 ± 0.02	0.70 ± 0.02
	0.25	1.24 ± 0.03	1.0 ± 0.02	0.91 ± 0.03	0.80 ± 0.02	0.75 ± 0.02
	0.50	1.80 ± 0.04	1.35 ± 0.02	1.20 ± 0.03	0.96 ± 0.03	0.80 ± 0.03
	0.75	2.36 ± 0.05	1.66 ± 0.02	1.42 ± 0.04	1.07 ± 0.02	0.90 ± 0.03
	1.0	2.92 ± 0.06	1.98 ± 0.04	1.66 ± 0.04	1.20 ± 0.04	1.00 ± 0.04
(*b*) With $[(NH_3)_5Co\{O_2CC_6H_3(NO_2\text{-}5)OH\}]^{2+}$ [c]						
		(6.80 ± 0.01)	(6.67 ± 0.01)	(6.50 ± 0.01)	(6.28 ± 0.01)	(5.76 ± 0.02)
15.0	1.0	0.48 ± 0.02	0.38 ± 0.02	0.31 ± 0.02	0.23 ± 0.02	0.16 ± 0.01
	2.0	0.83 ± 0.02	0.64 ± 0.02	0.50 ± 0.02	0.35 ± 0.02	0.21 ± 0.01
	3.0	1.20 ± 0.06	0.85 ± 0.03	0.69 ± 0.02	0.50 ± 0.02	0.25 ± 0.01
	4.0	1.56 ± 0.02	1.15 ± 0.02	0.88 ± 0.04	0.62 ± 0.03	0.29 ± 0.02
	5.0	1.90 ± 0.04	1.44 ± 0.03	1.07 ± 0.02	0.72 ± 0.03	0.33 ± 0.02
		(6.87 ± 0.01)	(6.70 ± 0.01)	(6.51 ± 0.01)	(6.33 ± 0.01)	(5.77 ± 0.02)
25.0	1.0	1.14 ± 0.06	0.82 ± 0.03	0.69 ± 0.03	0.57 ± 0.02	0.41 ± 0.02
	2.0	1.98 ± 0.07	1.49 ± 0.03	1.10 ± 0.03	0.86 ± 0.03	0.49 ± 0.02
	3.0	2.82 ± 0.04	2.08 ± 0.11	1.51 ± 0.03	1.08 ± 0.04	0.57 ± 0.04
	4.0	3.71 ± 0.04	2.70 ± 0.08	1.92 ± 0.04	1.40 ± 0.03	0.67 ± 0.03
	5.0	4.52 ± 0.04	3.30 ± 0.12	2.34 ± 0.06	1.69 ± 0.03	0.76 ± 0.04
		(6.85 ± 0.01)	(6.67 ± 0.01)	(6.49 ± 0.01)	(6.29 ± 0.01)	(5.77 ± 0.02)
30.0	1.0	1.77 ± 0.04	1.40 ± 0.04	1.09 ± 0.04	0.90 ± 0.02	0.64 ± 0.04
	2.0	3.10 ± 0.02	2.25 ± 0.05	1.70 ± 0.03	1.33 ± 0.02	0.80 ± 0.03
	3.0	4.41 ± 0.04	3.11 ± 0.03	2.34 ± 0.04	1.68 ± 0.05	0.95 ± 0.02
	4.0	5.72 ± 0.04	3.99 ± 0.06	2.92 ± 0.07	2.09 ± 0.04	1.05 ± 0.03
	5.0	6.94 ± 0.04	4.89 ± 0.08	3.56 ± 0.06	2.53 ± 0.10	1.20 ± 0.05
		(6.89 ± 0.01)	(6.68 ± 0.01)	(6.49 ± 0.01)	(6.26 ± 0.01)	(5.77 ± 0.02)
35.0	0.10	0.80 ± 0.04	0.75 ± 0.02	0.70 ± 0.02	0.69 ± 0.03	0.63 ± 0.02
	0.25	1.10 ± 0.04	0.95 ± 0.03	0.86 ± 0.02	0.77 ± 0.02	0.67 ± 0.02
	0.50	1.58 ± 0.03	1.28 ± 0.02	1.10 ± 0.03	0.93 ± 0.02	0.73 ± 0.02
	0.75	2.07 ± 0.04	1.65 ± 0.04	1.30 ± 0.05	1.06 ± 0.04	0.80 ± 0.03
	1.0	2.56 ± 0.06	1.90 ± 0.03	1.57 ± 0.06	1.24 ± 0.06	0.85 ± 0.03
(*c*) With *cis*-$[(en)_2(NH_3)Co\{O_2CC_6H_3(NO_2\text{-}3)OH\}]^{2+}$ [d]						
		(6.88 ± 0.01)	(6.67 ± 0.01)	(6.58 ± 0.01)	(6.27 ± 0.01)	(5.70 ± 0.02)
15.0	1.0	0.55 ± 0.02	0.42 ± 0.03	0.39 ± 0.02	0.27 ± 0.02	0.19 ± 0.02
	2.0	0.98 ± 0.02	0.69 ± 0.02	0.62 ± 0.03	0.39 ± 0.03	0.22 ± 0.02
	3.0	1.39 ± 0.04	0.94 ± 0.04	0.80 ± 0.02	0.51 ± 0.04	0.25 ± 0.02
	4.0	1.71 ± 0.02	1.20 ± 0.05	1.01 ± 0.02	0.60 ± 0.05	0.30 ± 0.02
	5.0	2.11 ± 0.04	1.47 ± 0.03	1.24 ± 0.03	0.70 ± 0.05	0.35 ± 0.02
		(6.86 ± 0.01)	(6.68 ± 0.01)	(6.52 ± 0.01)	(6.30 ± 0.01)	(5.78 ± 0.02)
25.0	1.0	1.24 ± 0.02	0.97 ± 0.02	0.75 ± 0.02	0.60 ± 0.02	0.41 ± 0.02
	2.0	2.21 ± 0.04	1.57 ± 0.02	1.23 ± 0.03	0.87 ± 0.02	0.52 ± 0.02
	3.0	3.14 ± 0.04	2.21 ± 0.02	1.60 ± 0.04	1.15 ± 0.02	0.62 ± 0.02
	4.0	4.08 ± 0.04	2.83 ± 0.05	2.17 ± 0.07	1.42 ± 0.03	0.70 ± 0.03
	5.0	5.05 ± 0.08	3.58 ± 0.03	2.61 ± 0.02	1.73 ± 0.08	0.79 ± 0.02

Table 2 (*continued*)

T/°C (±0.1 °C)	10^2 [Ni^{2+}]/ mol dm^{-3}	k_{obs}/s^{-1}				
		(6.86 ± 0.01)	(6.71 ± 0.01)	(6.52 ± 0.01)	(6.30 ± 0.01)	(5.85 ± 0.02)
30.0	1.0	1.91 ± 0.03	1.52 ± 0.04	1.26 ± 0.03	0.91 ± 0.03	0.68 ± 0.02
	2.0	3.25 ± 0.10	2.49 ± 0.04	1.91 ± 0.03	1.33 ± 0.02	0.84 ± 0.03
	3.0	4.69 ± 0.09	3.50 ± 0.08	2.60 ± 0.04	1.72 ± 0.08	1.0 ± 0.02
	4.0	5.99 ± 0.12	4.52 ± 0.04	3.24 ± 0.05	2.20 ± 0.08	1.17 ± 0.03
	5.0	7.47 ± 0.19	5.69 ± 0.09	3.91 ± 0.06	2.63 ± 0.07	1.33 ± 0.03
		(6.81 ± 0.01)	(6.59 ± 0.01)	(6.49 ± 0.01)	(6.25 ± 0.01)	(5.78 ± 0.02)
35.0	0.10	0.88 ± 0.02	0.79 ± 0.02	0.78 ± 0.02	0.73 ± 0.02	0.70 ± 0.02
	0.25	1.23 ± 0.02	1.0 ± 0.02	0.94 ± 0.02	0.84 ± 0.03	0.73 ± 0.03
	0.50	1.76 ± 0.03	1.35 ± 0.03	1.20 ± 0.04	1.01 ± 0.04	0.81 ± 0.03
	0.75	2.35 ± 0.02	1.77 ± 0.05	1.50 ± 0.03	1.18 ± 0.03	0.86 ± 0.02
	1.0	2.85 ± 0.04	2.11 ± 0.04	1.71 ± 0.06	1.36 ± 0.03	0.97 ± 0.03
(*d*) With [(tetren)Co{$O_2CC_6H_3(NO_2$-3)OH}]$^{2+ e}$						
		(6.86 ± 0.01)	(6.69 ± 0.01)	(6.51 ± 0.01)	(6.32 ± 0.01)	(5.72 ± 0.02)
15.0	1.0	0.78 ± 0.02	0.61 ± 0.02	0.50 ± 0.02	0.41 ± 0.02	0.29 ± 0.02
	2.0	1.26 ± 0.03	0.97 ± 0.03	0.73 ± 0.04	0.61 ± 0.02	0.35 ± 0.02
	3.0	1.78 ± 0.04	1.33 ± 0.04	1.0 ± 0.04	0.82 ± 0.04	0.42 ± 0.02
	4.0	2.27 ± 0.07	1.73 ± 0.04	1.31 ± 0.04	0.98 ± 0.04	0.46 ± 0.02
	5.0	2.79 ± 0.08	2.10 ± 0.03	1.56 ± 0.04	1.15 ± 0.04	0.52 ± 0.03
		(6.83 ± 0.01)	(6.71 ± 0.01)	(6.52 ± 0.02)	(6.34 ± 0.01)	(5.69 ± 0.02)
25.0	1.0	1.70 ± 0.03	1.45 ± 0.02	1.20 ± 0.03	0.98 ± 0.02	0.63 ± 0.02
	2.0	2.85 ± 0.06	2.30 ± 0.09	1.82 ± 0.04	1.44 ± 0.04	0.71 ± 0.03
	3.0	4.02 ± 0.04	3.30 ± 0.04	2.46 ± 0.06	1.80 ± 0.04	0.87 ± 0.02
	4.0	5.15 ± 0.07	4.20 ± 0.04	3.02 ± 0.03	2.20 ± 0.05	0.92 ± 0.02
	5.0	6.40 ± 0.08	5.15 ± 0.05	3.67 ± 0.08	2.67 ± 0.05	1.03 ± 0.03
		(6.86 ± 0.01)	(6.69 ± 0.01)	(6.52 ± 0.01)	(6.37 ± 0.01)	(5.73 ± 0.02)
30.0	1.0	2.48 ± 0.06	2.0 ± 0.03	1.70 ± 0.04	1.40 ± 0.03	0.95 ± 0.02
	2.0	4.24 ± 0.04	3.23 ± 0.03	2.40 ± 0.03	2.12 ± 0.04	1.08 ± 0.02
	3.0	5.92 ± 0.05	4.40 ± 0.05	3.41 ± 0.07	2.70 ± 0.04	1.28 ± 0.02
	4.0	7.53 ± 0.09	5.64 ± 0.08	4.20 ± 0.05	3.30 ± 0.05	1.42 ± 0.02
	5.0	9.23 ± 0.08	6.80 ± 0.05	5.05 ± 0.06	3.90 ± 0.06	1.54 ± 0.04
		(6.86 ± 0.01)	(6.66 ± 0.01)	(6.52 ± 0.01)	(6.34 ± 0.01)	(5.69 ± 0.02)
35.0	1.0	3.98 ± 0.08	2.98 ± 0.06	2.62 ± 0.04	2.18 ± 0.04	1.59 ± 0.03
	2.0	6.41 ± 0.04	4.86 ± 0.08	4.02 ± 0.06	3.16 ± 0.04	1.83 ± 0.05
	3.0	9.07 ± 0.14	6.63 ± 0.04	5.20 ± 0.02	4.05 ± 0.03	2.03 ± 0.04
	4.0	11.54 ± 0.15	8.21 ± 0.12	6.60 ± 0.10	4.97 ± 0.06	2.22 ± 0.04
	5.0	14.18 ± 0.16	10.05 ± 0.05	8.0 ± 0.14	5.91 ± 0.12	2.46 ± 0.10

[a] [complex]$_T$ = (4.0–8.5) × 10^{-5} mol dm^{-3}. [b] Values in parentheses denote pH. [c] [complex]$_T$ = (5.0–10.0) × 10^{-5} mol dm^{-3}. [d] [complex]$_T$ = (2.0–4.5) × 10^{-5} mol dm^{-3}. [e] [complex]$_T$ = (4.0–8.0) × 10^{-5} mol dm^{-3}.

Table 3 Rate and activation parameters for the formation and dissociation of [$Co(N_5)\{O_2CC_6H_3(X)O\}Ni]^{3+}$ *

N_5/X^-	T/°C	k_f/dm^3 mol^{-1} s^{-1}	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}	k_r/s^{-1}	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/ $JK^{-1}mol^{-1}$
$5NH_3/3-NO_2$	15.0	373 ± 32	74.1 ± 3.1	62 ± 10	0.18 ± 0.01	49.8 ± 4.8	−88 ± 16
	25.0	1148 ± 8			0.38 ± 0.02		
	30.0	1866 ± 10			0.58 ± 0.02		
	35.0	3244 ± 48			0.70 ± 0.03		
$5NH_3/5-NO_2$	15.0	457 ± 5	65.7 ± 4.5	34 ± 15	0.14 ± 0.01	55.2 ± 9.1	−69 ± 30
	25.0	1063 ± 7			0.34 ± 0.02		
	30.0	1832 ± 10			0.56 ± 0.02		
	35.0	2701 ± 46			0.64 ± 0.03		
$(en)_2(NH_3)/3-NO_2$	15.0	365 ± 3	80.6 ± 2.6	85 ± 9	0.18 ± 0.01	46.3 ± 7.4	−98 ± 24
	25.0	1132 ± 8			0.33 ± 0.01		
	30.0	1920 ± 15			0.55 ± 0.01		
	35.0	3620 ± 34			0.67 ± 0.01		
tetren/$3-NO_2$	15.0	579 ± 10	40.0 ± 2.1	−53 ± 7	0.27 ± 0.01	62.8 ± 7.1	−39 ± 23
	25.0	1111 ± 10			0.56 ± 0.01		
	30.0	1392 ± 10			0.83 ± 0.01		
	35.0	1885 ± 11			1.39 ± 0.02		

* λ = 390 nm, I = 0.30 mol dm^{-3}.

encounter complex formation as well as its transformation to the final product. Since the values of k_f at 25 °C for all substrates of identical charge type are virtually alike and compare well with that for [$Co(NH_3)_5(C_2O_4)]^+$–Ni^{2+} complexation [(2.98 ± 0.31) × 10^3 dm^3 mol^{-1} s^{-1} at 25 °C, I = 0.3 mol dm^{-3}],[13] we are led to believe that the N_5 moiety and the position of the NO_2 substituent in the aromatic ligand have very little effect on the rate-limiting step of the binuclear complex formation. From the coulombic concept it is reasonable to assume that K_{os} will be invariant of the nature of the cobalt(III) substrate. Hence the invariance of the formation rate constant at 25 °C with respect to the N_5 moiety and the substituent in the benzene ring identifies k_f as $K_{os}k_{11}$ ($k_{22} \gg k_{-11}$) [see equation (6)], *i.e.*. the first bond formation between the nickel(II) centre and the ligand in the encounter complex is rate limiting. This must of course occur at the free phenoxide end and the resulting singly bonded form of the binuclear species will undergo rapid chelation by the vicinal carboxylate moiety despite the inherent electrostatic repulsion between the like-charge centres in the binuclear species. The value of the interchange rate constant k_{11} can be predicted if K_{os} is known. Based on the diffusion-limited ion pairing and purely coulombic concepts, K_{os} can be calculated from relationships (8)–(10), where N = Avogadro

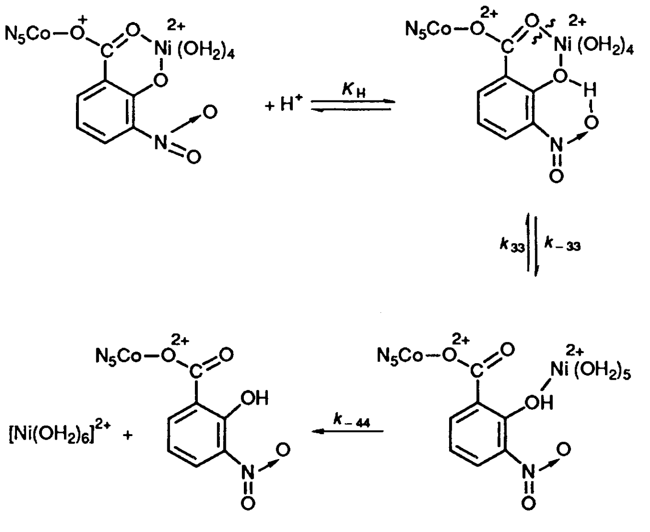
$$K_{os} = \left(\frac{4}{3000}\pi N a^3\right) \exp[-U(a)/k_BT] \qquad (8)$$

$$U(a) = (z_1z_2e_o^2/aD) - z_1z_2e_o^2K/D(1 + Ka) \qquad (9)$$

$$K = (8\pi N e_o^2 I/1000D\,k_BT)^{\frac{1}{2}} \qquad (10)$$

number, a = distance of closest approach of the ions of charge z_1 and z_2, k_B = Boltzmann's constant, e_o = charge of electron, D = bulk relative permittivity, I = ionic strength and T = absolute temperature.[22] At 25 °C, the values of K_{os} were 1.4, 0.3 and 0.07 $dm^3\ mol^{-1}$ for (2+, −1), (2+, 0), and (2+, 1+) ion-pairing processes respectively. Using this conservative estimate of K_{os} = 0.07 $dm^3\ mol^{-1}$, k_{11} (=k_f/K_{os}) was calculated to be $1.6 \times 10^4\ s^{-1}$ at 25 °C irrespective of the cobalt(III) substrates, which compares with the water-exchange rate constant of $[Ni(OH_2)_6]^{2+}$ [k_{ex} = (2.7–3.6) × $10^4\ s^{-1}$ at 25 °C].[23] Hence the first nickel–ligand bond formation within the encounter complex involves essentially dissociative interchange (I_d).[24] Despite this fact it is rather striking that the values of the activation parameters ($\Delta H^‡$ = 40–81 kJ mol^{-1}, $\Delta S^‡$ = −53 to +85 J K^{-1} mol^{-1}, see Table 3) for the complexation reaction are substantially different from those reported for the water-exchange reaction of $[Ni(OH_2)_6]^{2+}$ ($\Delta H^‡$ = 45–51.7 kJ mol^{-1}, $\Delta S^‡$ = 2.5–15.1 J K^{-1} mol^{-1}).[23] The contribution of ΔH° and ΔS° for the encounter complex formation cannot fully account for this divergence. However, this difference presumably indicates that the differential solvation effects of the initial state of the highly charged encounter complex and the corresponding transition state augmented by the hydrophobic/hydrophilic interactions of the N_5 moieties with their solvent cospheres control the magnitude of the activation enthalpies and entropies of formation of the binuclear species.

Spontaneous Dissociation of the Binuclear Species.—The values of the dissociation rate constants (k_r) (see Table 3) are at least ≈10^4 times smaller than that of $[Ni(OH_2)_5(O_2CCH_3)]^+$ (5000 s^{-1} at 25 °C, I = 0)[25] and ≈10^2 times smaller than that of $[(NH_3)_5Co(C_2O_4)Ni]^{3+}$ (58 s^{-1} at 25 °C, I = 0.3 mol dm^{-3}).[13] The destabilising coulomb effect for $[(NH_3)_5Co(C_2O_4)Ni]^{3+}$ is comparable to that for the binuclear species under consideration. Evidently the high stabilities of these binuclear species to dissociation indicate their chelated nature. The condition $k_{-11}/k_{22} \ll 1$ leads to $k_r = k_{-11}Q$ [see equation (7)] where Q (=k_{-22}/k_{22}) denotes the forward equilibrium constant for the chelate $\rightleftharpoons$ singly bonded form of the binuclear species. A rough estimate of Q at 25 °C using $k_{-11} \approx 5 \times 10^3\ s^{-1}$ [*i.e.* the value for k_r of monoacetatonickel(II)[25]] is ≈1×10^{-4} which reflects that the equilibrium is largely driven in the direction of the chelated form. However, the relatively higher values of k_r at all temperatures for the tetren complex (see Table 3) reflect the discriminating effect of the bulky tetren ligand on this thermodynamic equilibrium. The large negative values of $\Delta S^‡$ and its order of variation [(tetren) > $(en)_2(NH_3)$ or $(NH_3)_5$] (see Table 3) for the spontaneous dissociation of the binuclear species reflect the solvation demands of the dissociative transition state which are compensated partly by the same effects for the singly bonded $\rightleftharpoons$ chelated equilibrium. The activation enthalpies and entropies for the spontaneous dissociation reactions of the binuclear species (see Table 3) show little variation with respect to the nature of the N_5 moiety. However, under isoentropic conditions, the dissociation of the binuclear species has a relatively higher activation enthalpy (about ≈20 kJ mol^{-1}) compared to that for its formation reaction.



Scheme 2 $N_5 = (en)_2(NH_3)$

The Acid-catalysed Dissociation of cis-$[(en)_2(NH_3)Co\{O_2CC_6H_3(NO_2\text{-}3)O\}Ni]^{3+}$.—Rate data for the acid-catalysed dissociation of the binuclear species at 15.0 ⩽ T ⩽ 30.0 °C and 0.0050 ⩽ $[H^+]$ ⩽ 0.15 mol dm^{-3} (I = 0.30 mol dm^{-3}) are collected in Table 4. The plots of k_{obs} *vs.* $[H^+]$ tend to show asymptotic behaviour at high $[H^+]$ and extrapolate virtually to zero at $[H^+]$ = 0 consistent with the fast protonation equilibrium of the binuclear species followed by rate-limiting dissociation of Ni^{II} from the protonated intermediate as in Scheme 2. Taking the spontaneous dissociation of the binuclear species into account, the observed pseudo-first-order rate constant in accord with Scheme 2 is given by equation (11)

$$k_{obs} = \frac{k_HK_H[H^+] + k_r}{1 + K_H[H^+]} \qquad (11)$$

where K_H denotes the protonation equilibrium constant of the binuclear species, k_H is the dissociation rate constant of its protonated analogue [equation (12)] and k_r is as defined earlier

$$k_H = \frac{k_{-44}k_{-33}}{k_{33} + k_{-44}} \qquad (12)$$

[see equation (7)]. The values of k_H and K_H were calculated by a non-linear least-squares program which varied the parameters k_HK_H and K_H and minimised $\Sigma w_i(k_{calc,i} - k_{obs,i})^2$ where $w_i = [1/\sigma(k_{obs,i})]^2$. The input values of k_H and K_H were obtained from the intercept and gradients of plots of $(k_{obs} - k_r)^{-1}$ *vs* $[H^+]^{-1}$ (see Fig. 3). Values of k_H, K_H and the associated thermodynamic parameters are collected in Table 4.

The site of protonation is the co-ordinated phenoxide of the binuclear species, as it is the most basic site and extra stability for the protonated species can be achieved *via* intramolecular hydrogen bonding with the proximal nitro group (see Scheme 2). However, the pK (≈0.66) of the protonated binuclear species is substantially lower (by a factor of 7) than that of the phenol

Table 4 Rate data (k^a/s^{-1}) for the acid-catalysed dissociation of *cis*-$[(en)_2(NH_3)Co\{O_2CC_6H_3(NO_2\text{-}3)O\}Ni]^{3+}$ ^{a}

10[HClO$_4$]/ mol dm^{-3}	15.0 ± 0.1 °C Obs.	Calc.^{b}	20.0 ± 0.1 °C Obs.	Calc.^{b}	25.0 ± 0.1 °C Obs.	Calc.^{b}	30.0 ± 0.1 °C Obs.	Calc.^{b}
0.050	9.90 ± 0.20	10.2	14.6 ± 0.30	14.6	19.9 ± 0.3	20.3	28.6 ± 0.60	28.2
0.10	19.70 ± 0.50	19.9	28.6 ± 0.20	28.8	39.6 ± 0.60	39.6	55.1 ± 0.80	54.9
0.20	38.70 ± 0.60	38.0	55.3 ± 0.60	55.2	76.4 ± 1.7	76.3	108 ± 4	106
0.30	55.70 ± 1.50	54.7	80.6 ± 1.80	79.9	114 ± 4	111	152 ± 3	154
0.40	71.90 ± 2.0	70.2	106 ± 3	103	146 ± 5	143	202 ± 7	199
0.50	86.8 ± 3.0	84.6	130 ± 4	124	178 ± 6	173	243 ± 7	241
0.70	113 ± 4	110	169 ± 7	164	224 ± 8	229	318 ± 12	319
0.90	128 ± 6	133	191 ± 9	198	268 ± 8	278	378 ± 17	388
1.0	136 ± 6	143	212 ± 12	214	294 ± 10	301	411 ± 16	421
1.20	156 ± 6	162	223 ± 15	244	328 ± 12	344	473 ± 10	481
1.40	172 ± 8	179	249 ± 16	270	368 ± 14	382	534 ± 10	535
1.50	184 ± 7	186	269 ± 18	282	379 ± 16	400		
k_H/s^{-1}	473 ± 34		775 ± 61		1164 ± 81		1677 ± 61	
K_H/dm^3 mol^{-1}	4.34 ± 0.31		3.82 ± 0.30		3.49 ± 0.24		3.35 ± 0.12	

$\Delta H^{\ddagger c}$/kJ mol^{-1} 57.8 ± 1.9
$\Delta S^{\ddagger c}$/J K^{-1} mol^{-1} 7 ± 6
$\Delta H^{\circ d}$/kJ mol^{-1} = −1 1.8 ± 1.6
$\Delta S^{\circ d}$/J K^{-1} mol^{-1} = −2 9 ± 5

^{a} $[\text{complex}]_T = 5.0 \times 10^{-5}$ mol dm^{-3}, $[Ni^{2+}]_T = 0.05$ mol dm^{-3}, $I = 0.30$ mol dm^{-3}, $\lambda = 400$ nm. ^{b} Values of k_r used to get k_{calc} [see equation (11)] are 0.18, 0.25, 0.33 and 0.55 s^{-1} at 15, 20, 25 and 30 °C respectively. ^{c} Calculated from the temperature dependence of k_H. ^{d} Calculated from the temperature dependence of K_H.

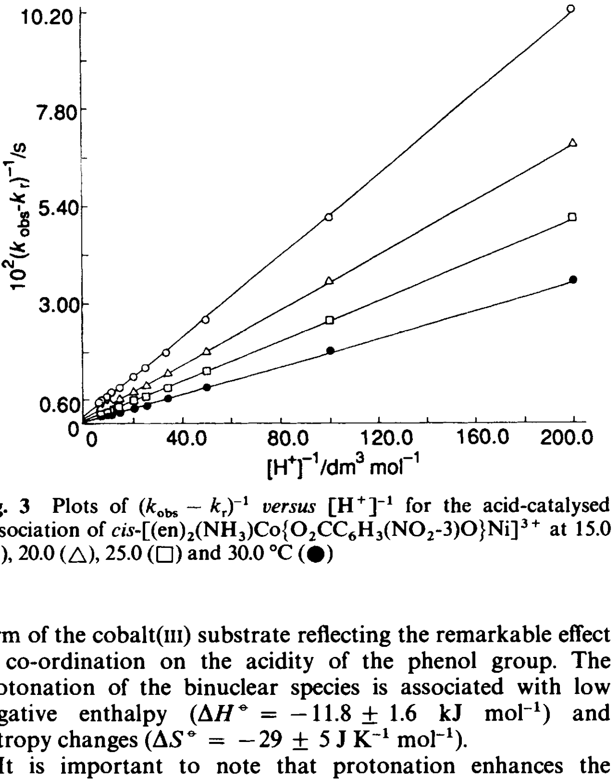


Fig. 3 Plots of $(k_{obs} - k_r)^{-1}$ *versus* $[H^+]^{-1}$ for the acid-catalysed dissociation of *cis*-$[(en)_2(NH_3)Co\{O_2CC_6H_3(NO_2\text{-}3)O\}Ni]^{3+}$ at 15.0 (○), 20.0 (△), 25.0 (□) and 30.0 °C (●)

form of the cobalt(III) substrate reflecting the remarkable effect of co-ordination on the acidity of the phenol group. The protonation of the binuclear species is associated with low negative enthalpy ($\Delta H^\circ = -11.8 \pm 1.6$ kJ mol^{-1}) and entropy changes ($\Delta S^\circ = -29 \pm 5$ J K^{-1} mol^{-1}).

It is important to note that protonation enhances the dissociation rate constant of the binuclear species by a large factor ($k_H/k_r \approx 3000$) despite the fact that the activation enthalpy for the dissociation reaction of the unprotonated species is lower than that of its protonated analogue. A substantially large rate effect arises due to the relatively more favourable value of the activation entropy for the protonated binuclear species (see Tables 3 and 4). This large enhancement can also be rationalised in terms of a large value of the dissociation rate constant of the singly bonded protonated species (k_{-44}) with the limit that the singly bonded $\rightleftharpoons$ chelated equilibrium for such a species is rapidly established on the time-scale of its dissociation. In other words $k_H \approx k_{-44}k_{-33}/k_{33}$ may still be valid and the relatively greater coulombic repulsion between the like-charge centres and weakening of nickel–ligand bond due to protonation presumably make the chelate ring greatly susceptible to reversible cleavage.

Appendix

Assuming that Ni^{2+} and [NiCl]$^+$ are the reacting species, k_{obs} takes the form (A1) where k_f, k_f' denote the formation rate

$$k_{obs} = \left(\frac{k_f + k_f'K[Cl^-]}{1 + K[Cl^-]}\right)[Ni]_T\frac{K_{OH}}{[H^+] + K_{OH}} + k_r \quad (A1)$$

constants for the binuclear species with Ni^{2+} and [NiCl]$^+$ respectively, K is the stability constant of [NiCl]$^+$ and all other terms are as defined in the text. A value of $K \approx 1.03$ dm^3 mol^{-1} (25 °C, $I = 0.3$ mol dm^{-3}) judged from the available data in the literature (ref. 20, vol. 4, p. 105) indicates that $1 + K[Cl^-]$ varies only marginally ($\leqslant 1.1$) in the range of $[Cl^-]_T$ (0.02–0.10 mol dm^{-3}) available in the reaction mixtures due to the use of NiCl$_2$. However, at constant pH, plots of k_{obs} *vs.* $[Ni^{2+}]_T$ are excellent straight lines (correlation coefficient = 0.999), despite the variation of $[Cl^-]_T$. Thus the [Cl$^-$] independence of the slopes of such plots is in keeping with the fact that $k_f \approx k_f'$ or the chloride complexing of Ni^{2+} has no significant effect on the formation/dissociation of the binuclear species. We are thankful to a referee for drawing our attention to the monochloronickel(II) species.

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