Binary and Ternary Complexes of Nickel(II) with 2-Aminomethylbenzimidazole and Salicylaldehyde: Kinetic and Equilibrium Studies†

Anadi C. Dash,* Achyuta N. Acharya and Rama K. Sahoo
Department of Chemistry, Utkal University, Bhubaneswar-751 004, India

The complexation of Ni^{II} with 2-aminomethylbenzimidazole (L) has been investigated at 20–40 °C, $I = 0.30$ mol dm^{-3}. Both monoprotonated and unprotonated ligands bind the metal ion to form $[NiL]^{2+}$, and the rate and activation parameters for the formation and acid-catalysed dissociation of this chelate are calculated. In the presence of salicylaldehyde (Hsal), a mixed-ligand complex, $[NiL(sal)]^+$, is also formed as an intermediate which further condenses to the Schiff-base complex, $[NiL']^+$ [HL′ = *N*-(benzimidazol-2-ylmethyl)salicylideneimine]. The kinetics of the fast ternary complex formation and its slow intramolecular transformation to the Schiff base complex have been investigated at 25 °C. The presence of L in the co-ordination sphere of Ni^{2+} enhances the dissociation of $[NiL(sal)]^+$ to $[NiL]^{2+}$ and sal^- with respect to $[Ni(sal)]^+$, as evidenced by the stability constants of $[NiL(sal)]^+$ and $[Ni(sal)]^+$. Calculations based on the values of ΔS° for the ionisation of H_2L^{2+} and the formation of $[NiL]^{2+}$ combined with $\bar{S}^\circ_{aq}(H^+)$ and $\bar{S}^\circ_{aq}(Ni^{2+})$ data yielded the values $\bar{S}^\circ_{aq}(H_2L^{2+}) - \bar{S}^\circ_{aq}(L) = 110$, $\bar{S}^\circ_{aq}(L) - \bar{S}^\circ_{aq}(HL^+) = -116$ and $\bar{S}^\circ_{aq}([NiL]^{2+}) - \bar{S}^\circ_{aq}(L) = -294$ J K^{-1} mol^{-1}, which presumably reflect the varying solvent-ordering effects of L, HL^+, H_2L^{2+} and $[NiL]^{2+}$.

Metal ions and ligands never exist in pure and isolated forms under biological and environmental conditions. Invariably multiligand–multimetal-ion equilibria predominate leading to mixed-ligand–mixed-metal-ion complexes, the simplest of which is a ternary complex containing one metal ion and two different ligands. Ternary complexes have become increasingly important in analytical chemistry, participating in many metal-ion catalysed reactions,[1,2] and they are used as models for metal-ion–enzyme–substrate complexes.[3,4] This has led to considerable emphasis on kinetic and equilibrium studies involving binary and ternary complexes in recent years.[5–7]

The work reported here comprises kinetic and equilibrium studies of the reversible formation of the nickel(II)–2-aminomethylbenzimidazole complex $[NiL]^{2+}$ and the ternary complex of $[NiL]^{2+}$ with salicylaldehyde (Hsal) together with the transformation of the intermediate, $[NiL(sal)]^+$, by the template condensation of the primary-amine function with the salicylaldehyde moiety, resulting in the nickel(II) complex of the Schiff base *N*-(benzimidazol-2-ylmethyl)salicylideneimine. In addition, the steric, electronic and hydrogen-bonding effects of L and its protonated derivatives (HL^+ and H_2L^{2+}) on the kinetics and mechanism of the formation and dissociation of $[NiL]^{2+}$ are examined. Relevant rate data for the formation of nickel(II)–2-aminoalkylpyridine complexes are available for comparison.[8]

Experimental

Materials and Methods.—2-Aminomethylbenzimidazole dihydrochloride was prepared by the method of Cescon and Dey[9] and recrystallised from 95% ethanol using animal charcoal as a decolourising agent giving a white crystalline compound, m.p. 263 °C (lit.,[9] 263 °C) (Found: C, 40.5; H, 5.7; N, 18.6. Calc. for $C_8H_{11}Cl_2N_3{\cdot}H_2O$: C, 40.3; H, 5.5; N, 17.6%). AnalaR or extrapure quality chemicals were used. Salicylaldehyde was freshly distilled prior to use. Nickel(II) in stock nickel(II) chloride solution was estimated volumetrically by complexometric titration with Na_2H_2edta (edta = ethylenediaminetetraacetate).[10] Elemental analysis was carried out at the Central Drug Research Institute, Lucknow.

The pH measurements were made with an Elico digital pH meter, model LI 120, equipped with a model CL 51 combination glass–Ag–AgCl, NaCl (2.0 mol dm^{-3}) electrode. All rate and equilibrium measurements were carried out at $I = 0.30$ mol dm^{-3} adjusted with $NaClO_4$. The concentration of H^+ ($= 100^{-pH}/f_{H^+}$) was computed from the measured pH values using the activity coefficient of H^+ calculated from the Davies equation ($f_{H^+} = 0.711$, 0.709, 0.704 and 0.701 at 20, 25, 35 and 40 °C respectively). All UV/VIS spectra and kinetic measurements were recorded on a JASCO 7800 spectrophotometer with 10 mm matched quartz cells, calibrated using K_2CrO_4–KOH solution as recommended by Mellon.[11]

Kinetic Measurements.—Rate measurements of the reversible complexation of L with Ni^{II} were obtained in a 2-morpholinoethanesulfonic acid (mes) buffer ($5.60 \leqslant pH \leqslant 6.60$) under pseudo-first-order conditions ($[Ni^{2+}]_T/[L]_T \geqslant 7$) using a fully automated HI-TECH (U.K.) SF 51 stopped-flow spectrophotometer. For the study of the acid-catalysed decomposition of $[NiL]^{2+}$, the substrate was rapidly acidified with $HClO_4$ in a stopped-flow assembly.[12] All measurements were obtained at 280 nm. For each experiment only a single exponential change of absorbance with time was observed which was independent of the rate of measurement indicating that neither forward nor reverse processes of the overall reaction are biphasic. The rate of formation of the ternary complex of $[NiL]^{2+}$ with salicylaldehyde was studied at 370 nm adopting the same procedure. The kinetic traces could be fitted better by a double-exponential equation indicating the reaction is biphasic. However, the rate constant for the slow step was less than the standard deviation of that of the fast step and was also independent of $[Ni^{2+}]_T$, pH and $[L]_T$. Each rate constant reported is the average of 7–10 replicate measurements with a standard deviation $[\sigma(k_{obs})] \leqslant 5\%$.

The relatively slow Ni^{II}-mediated condensation of L with

---

† *Supplementary data available* (No. SUP 57042, 9 pp.): Tables of rate data and absorption spectrum for $[NiL(sal)]^+$. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Values of pK for L and stability constants for $[\mathrm{NiL}]^{2+}$

T/°C	pK_1[a]	pK_2[b]	$10^{-6}K_M$[c]/dm^3 mol^{-1}
20.0	—	—	1.52 ± 0.09
25.0	3.17 ± 0.03	7.83 ± 0.07	1.78 ± 0.29
30.0	3.14 ± 0.06	7.68 ± 0.05	—
35.0	3.10 ± 0.02	7.71 ± 0.05	1.43 ± 0.13
40.0	3.06 ± 0.02	7.74 ± 0.04	1.61 ± 0.14
$\Delta H°$/kJ mol^{-1}	13.4 ± 0.5	3 ± 11	−0.7 ± 3.6
$\Delta S°$/J K^{-1} mol^{-1}	−16 ± 2	−138 ± 35	−121 ± 12

[a] $\lambda = 270$ nm, $[\mathrm{L}]_T = 1 \times 10^{-4}$, $I = 0.30$ mol dm^{-3}, $2.4 \leqslant \mathrm{pH} \leqslant 4.20$ (chloroacetate buffer); $\varepsilon_{\mathrm{H_2L^{2+}}} = 8640 \pm 80$, $\varepsilon_{\mathrm{HL^+}} = 4737 \pm 158$ dm^3 mol^{-1} cm^{-1}. [b] $\lambda = 558$ nm, [Phenol Red] $= 1.0 \times 10^{-5}$, $[\mathrm{HClO_4}]_T = 0.001$–$0.009$, $[\mathrm{L}]_T = 0.010$, $I = 0.30$ mol dm^{-3}; pK_{in} = 7.26, 7.23, 7.31 and 7.40 at 25, 30, 35 and 40 °C ($\varepsilon_{\mathrm{Hin}} = 400 \pm 20$, $\varepsilon_{\mathrm{in}} = 57\,376 \pm 725$ dm^3 mol^{-1} cm^{-1}) where Hin and in$^-$ are the unionised and ionised forms of Phenol Red. [c] $\lambda = 280$ nm, pH 4.48 ± 0.02, $[\mathrm{Ni^{2+}}]_T = 0.005$–$0.02$, $[\mathrm{L}]_T = 1.0 \times 10^{-4}$, $I = 0.30$ mol dm^{-3}, $\varepsilon_{\mathrm{NiL}} = 3688 \pm 180$ dm^3 mol^{-1} cm^{-1}.

salicylaldehyde was studied spectrophotometrically ($\lambda = 375$ nm). Under pseudo-first-order conditions the rate constants were calculated from $\ln(A_\infty - A_t)$ *versus* t plots. Rate measurements were repeated at least once.

Results and Discussion

Equilibrium Constants.—The pK_1 and pK_2 values of $\mathrm{H_2L^{2+}}$ and the stability constants (K_M) of $[\mathrm{NiL}]^{2+}$ [equations (1)–(3)]

$$\mathrm{H_2L^{2+}} \underset{}{\overset{K_1}{\rightleftharpoons}} \mathrm{HL^+} + \mathrm{H^+} \qquad (1)$$

$$\mathrm{HL^+} \overset{K_2}{\rightleftharpoons} \mathrm{L} + \mathrm{H^+} \qquad (2)$$

$$\mathrm{Ni^{2+}} + \mathrm{L} \overset{K_M}{\rightleftharpoons} [\mathrm{NiL}]^{2+} \qquad (3)$$

were determined spectrophotometrically (see Table 1) as described earlier[13] and are collected in Table 1 together with associated thermodynamic parameters. A comparison of $\Delta H^\ddagger$ values shows that the loss of a proton from $\mathrm{H_2L^{2+}}$ is relatively more endothermic than from $\mathrm{HL^+}$. The entropy change associated with proton dissociation from $\mathrm{HL^+}$ taking into account the value $\bar{S}^\circ_{\mathrm{aq}}(\mathrm{H^+}) = -22$ J K^{-1} mol^{-1} (25 °C)[14] yields $\bar{S}^\circ_{\mathrm{aq}}(\mathrm{L}) - \bar{S}^\circ_{\mathrm{aq}}(\mathrm{HL^+}) = -116$ J K^{-1} mol^{-1}, suggesting that $\mathrm{HL^+}$ creates more solvent disorder than L. An analogous calculation for the complexation of nickel(II) with L using $\bar{S}^\circ_{\mathrm{aq}}(\mathrm{Ni^{2+}}) = -173$ J K^{-1} mol^{-1} [14] yields $\bar{S}^\circ_{\mathrm{aq}}([\mathrm{NiL}]^{2+}) - \bar{S}^\circ_{\mathrm{aq}}(\mathrm{H_2L^{2+}}) = -404$ J K^{-1} mol^{-1} and $\bar{S}^\circ_{\mathrm{aq}}([\mathrm{NiL}]^{2+}) - \bar{S}^\circ_{\mathrm{aq}}(\mathrm{L}) = -294$ J K^{-1} mol^{-1}, presumably indicating that both L and $\mathrm{H_2L^{2+}}$ cause greater solvent disorder than $[\mathrm{NiL}]^{2+}$. In addition a value of 110 J K^{-1} mol^{-1} is calculated for $\bar{S}^\circ_{\mathrm{aq}}(\mathrm{H_2L^{2+}}) - \bar{S}^\circ_{\mathrm{aq}}(\mathrm{L})$ showing that L has a greater ordering effect on the solvent than $\mathrm{H_2L^{2+}}$.

Formation of $[\mathrm{NiL}]^{2+}$.—The pseudo-first-order rate constants were obtained in the range $5.60 \leqslant \mathrm{pH} \leqslant 6.61$, $[\mathrm{Ni^{2+}}] = 0.005$–$0.040$ mol dm^{-3} and at 15–35 °C. Preliminary calculations using K_1, K_2 and K_M indicated that complex formation was virtually complete ($\geqslant 96\%$ of $[\mathrm{L}]_T$ at equilibrium at the lowest pH and $[\mathrm{Ni^{2+}}]_T$). However, the dependence of k_{obs} on pH and $[\mathrm{Ni^{2+}}]_T$ indicates that the metal ion binds to both $\mathrm{HL^+}$ and L [see equations (4) and (5)], with k_{obs} taking the form (4)

$$k_{\mathrm{obs}} = k_f^{\mathrm{app}}[\mathrm{Ni^{2+}}]_T \qquad (4)$$

$$k_f^{\mathrm{app}} = (k_f^{\mathrm{L}} + k_f^{\mathrm{HL}}\cdot[\mathrm{H^+}]/K_2)/(1 + [\mathrm{H^+}]/K_2 + [\mathrm{H^+}]^2/K_1K_2) \qquad (5)$$

where k_f^{L} and k_f^{HL} are the formation rate constants for the unprotonated and monoprotonated ligand respectively. The calculated values of k_f^{L} and k_f^{HL} together with the corresponding activation parameters are collected in Table 2.

Table 2 Rate data (k_f/dm^3 mol^{-1} s^{-1}) and activation parameters for the formation of $[\mathrm{NiL}]^{2+}$[a]

	T/°C			
k_f	15.0 ± 0.1	25.0 ± 0.1	30.0 ± 0.1	35.0 ± 0.1
$10^{-3}\,k_f^{\mathrm{L}}$	3.2 ± 0.3	6.3 ± 0.2	7.7 ± 1.8	14.7 ± 5.8
$10^{-2}\,k_f^{\mathrm{HL}}$	1.32 ± 0.2	3.01 ± 0.3	4.1 ± 0.4	4.9 ± 0.9
$\Delta H^\ddagger$/kJ mol^{-1}	45.6 ± 3.4	(56.1 ± 1.5)[b]		
$\Delta S^\ddagger$/J K^{-1} mol^{-1}	−19 ± 11	(−9 ± 5)[b]		

[a] $I = 0.30$ mol dm^{-3}, $\lambda = 280$ nm. [b] Values in parentheses are for k_f^{HL} path.

Comparison of the Rate Constants and the Mechanism of the Reaction.—The rate of formation of $[\mathrm{NiL}]^{2+}$ at 25 °C (6.32×10^3 dm^3 mol^{-1} s^{-1}) is less than that of the 2-aminomethylpyridine nickel(II) complex ($k_f^{\mathrm{L}} = 8.6 \times 10^3$ dm^3 mol^{-1} s^{-1}, 25 °C, $I = 0.30$ mol dm^{-3}),[8] presumably resulting from the increased steric interaction of the bulkier benzimidazolyl group during complexation. The neutral ligand reacts 20 times faster than $\mathrm{HL^+}$ ($k_f^{\mathrm{L}}/k_f^{\mathrm{HL}} \approx 20$ at 25 °C), in strong contrast to the rate observed for 2-aminomethylpyridine (amp) under comparable conditions ($k_f^{\mathrm{L}}/k_f^{\mathrm{HL}} \approx 246$).[8] This difference may be attributed to the much higher rate of formation for monoprotonated aminomethylbenzimidazole ($k_f^{\mathrm{HL^+}}/k_f^{\mathrm{Hamp^+}} \approx 246$ at 25 °C, $I = 0.30$ mol dm^{-3}).

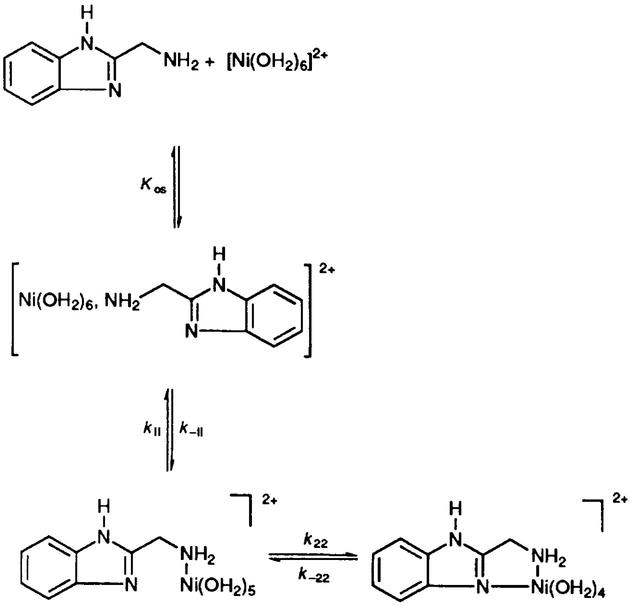
Assuming that the formation of the encounter complex of L and $\mathrm{HL^+}$ with $[\mathrm{Ni(OH_2)_6}]^{2+}$ is diffusion controlled and very low concentrations of the singly bonded intermediates exist in steady-state equilibrium k_f^{L}, k_f^{HL} and the overall dissociation rate constant of $[\mathrm{NiL}]^{2+}$ (k_d) as delineated in Scheme 1 for L are given by equations (6), (7) and (8) respectively, where K_{os},

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

$$k_f^{\mathrm{HL}} = \frac{K'_{\mathrm{os}}k'_{11}k'_{22}}{k'_{-11} + k'_{22}} \qquad (7)$$

$$k_d = \frac{k_{-11}k_{-22}}{k_{-11} + k_{22}} + \frac{k'_{-11}k'_{-22}[\mathrm{H^+}]}{k'_{-11} + k'_{22}} \qquad (8)$$

K'_{os} and $k_{\pm ii}$, $k'_{\pm ii}$ denote the outer-sphere association constants and individual rate constants for L and $\mathrm{HL^+}$ respectively. From Fuoss's theory,[15] and as modified by Rorabacher *et al.*,[16] K_{os} and K'_{os} are 0.30 and 0.01 dm^3 mol^{-1} respectively. If it is assumed that the loss of water from the Ni$^{\mathrm{II}}$ centre in the encounter



Scheme 1 Complexation of L and HL^+ with $[Ni(OH_2)_6]^{2+}$; $K_{os} = K'_{os}$ and $k_{\pm ii} = k'_{\pm ii}$ for HL^+ in which the alkylamine function is protonated

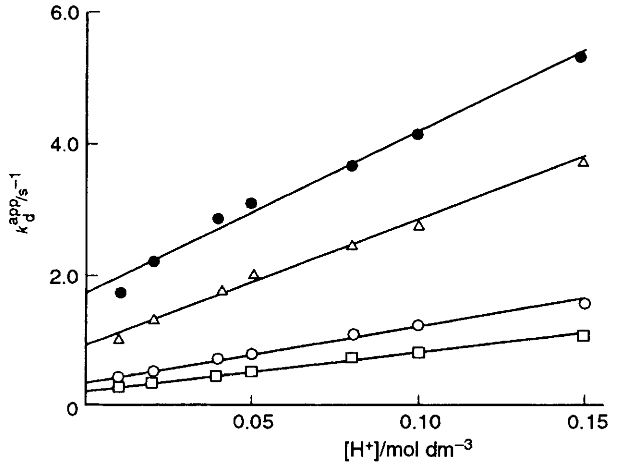


Fig. 1 Plot of k_d^{app} *versus* $[H^+]$ for acid-catalysed aquation of $[NiL]^{2+}$ at λ = 280 nm, $[Ni^{2+}]_T = 0.015$, $I = 0.30$ mol dm^{-3} and 10 (□), 15 (○), 25 (△) and 30 °C (●)

complex is essentially rate controlling then $k_{11} = k'_{11} = f \cdot k_{ex}$, where f is a statistical factor and k_{ex} is the water-exchange rate constant of $[Ni(OH_2)_6]^{2+}$. Using the known value of k_f^L (25 °C), $k_{ex} = 3 \times 10^4$ s^{-1} (25 °C),[17,18] $f = 0.75$,[19] and the estimated value of $K_{os} = 0.3$ dm^3 mol^{-1}, k_{-11}/k_{22} is calculated to be 0.06 from equation (6). An analogous calculation yielded small negative values of k'_{-11}/k'_{22} from equation (7). Therefore the rates of intramolecular chelation (k_{22} and k'_{22}) are faster than the rates of dissociation of the singly bonded species, this effect being prominent when proton loss is also involved in the chelation step for $[Ni(H_2O)_5(HL)]^{3+}$. These rate constants may be compared with the analogous data for the formation of the 2-(2-aminoethyl)benzimidazole nickel(II) complex where the rate of chelation of the singly bonded intermediate species appears to be relatively slow ($k_{-11}/k_{22} = 2.1$ and $k'_{-11}/k'_{22} = 5.1$ at 25 °C).[13] This led us to believe that as the basicity (pK_1 = 4.60 ± 0.01, pK_2 = 7.49 ± 0.01 at 25 °C, $I = 0.30$ mol dm^{-3} for 2-(2-aminoethyl)benzimidazole)[13] and steric interactions are essentially the same for both ligands, the shift in the rate-determining step from intramolecular chelation (for aminoethylbenzimidazole) to formation of the singly bonded species (for L) may be a consequence of chelate-ring size. The activation enthalpy and entropy values for complex formation compare satisfactorily with those (see Table 2) for water exchange in $[Ni(OH_2)_6]^{2+}$ ($\Delta H^{\ddagger}_{ex}$ = 45–53 kJ mol^{-1}, $\Delta S^{\ddagger}_{ex}$ = 2.5–17.2 J K^{-1} mol^{-1})[17,18] indicating that water dissociation from Ni^{II} largely controls the energetics of the process.

Acid-catalysed Aquation of $[NiL]^{2+}$.—For the acid-catalysed aquation of $[NiL]^{2+}$ k_{obs} is given by equation (9) where k_d^{app} is

$$k_{obs} = k_f^{app}[Ni^{2+}]_T + k_d^{app} \qquad (9)$$

the dissociation rate constant of the complex at a given acidity and k_f^{app} is as defined in equation (5). It is also of interest that the values of the spontaneous dissociation rate constant of the complex $\{k_d[NiL^{2+}] = k_f^L/K_M\}$ are *ca.* 0.0035, 0.0048, 0.01 s^{-1} at 25, 30 and 35 °C respectively, which are significantly lower than the errors of k_{obs}. The calculated values of k_d^{app} (= $k_{obs} - k_f^{app}[Ni^{2+}]_T$) showed linear dependence on $[H^+]$ (see Fig. 1) at all temperatures which is consistent with the reaction sequence in Scheme 1 and k_d^{app} is given by equation (8). Equation (8) rearranges to equation (10) when $k_{22} \gg k_{-11}$ and $k'_{22} \gg k'_{-11}$.

$$k_d^{app} = k_{-11}\left(\frac{k_{-22}}{k_{22}}\right) + k'_{-11}\left(\frac{k'_{-22}}{k'_{22}}\right)[H^+] \qquad (10)$$

The values of $k_{-11}(k_{-22}/k_{22})$ and $k'_{-11}(k'_{-22}/k'_{22})$ calculated from the plots of k_d^{app} *versus* $[H]^+$ (see Fig. 1, correlation coefficient = 0.999–0.994) are 0.25 ± 0.01, 0.34 ± 0.02, 0.97 ± 0.08, 1.67 ± 0.09 s^{-1} and 5.9 ± 0.1, 8.7 ± 0.4, 19.4 ± 1.6, 24.9 ± 1.2 s^{-1} at 10.0, 15.0, 25.0 and 30.0 °C respectively.

The terminal amine function of L is less sterically hindered and it is therefore likely that the H^+-assisted chelate-ring opening occurs at this site upon protonation.

Mixed-ligand Complexes.—The UV/VIS spectra indicate that a mixed-ligand complex, $[NiL(sal)]^+$, is formed when salicylaldehyde is added to an equimolar mixture of Ni^{2+} and 2-aminomethylbenzimidazole at pH 6.56 ($[Hsal]_T = 2.0 \times 10^{-4}$, $[Ni^{2+}]_T = [L]_T = 0.006$, $I = 0.30$ mol dm^{-3}, 25 °C). Further slow spectral change with time leading to a small shift of λ_{max} (from 361 to 370 nm) with an isosbestic point at 383 nm indicates the slow transformation of this mixed-ligand complex to the corresponding Schiff-base complex $[NiL']^+$ [HL' = *N*-(benzimidazol-2-ylmethyl)salicylideneimine], the slowness of this process being ascribed to the effect of co-ordination of both the ligands to the same metal ion. The initial fast complexation of salicylaldehyde was studied in solutions where Ni^{2+} was fully complexed by the amine ligand ($[Ni^{2+}]_T$ = 0.002–0.02 mol dm^{-3}, $[L]_T/[Ni^{2+}]_T$ = 1.1–1.25, pH 6.22–7.25, mes buffer). The pseudo-first-order rate constant (k_{obs}) for $[Ni^{2+}]_T \gg [Hsal]_T$ is given by equation (11) where $k_{\pm 1}$ and $k_{\pm 2}$ are the

$$k_{obs} = \frac{(k_1 + k_2K_d/[H^+])[NiL^{2+}]}{1 + K_d/[H^+]} + k_{-1}[H^+] + k_{-2} \qquad (11)$$

rate constants for reactions (12) and (13) respectively. Since the

$$\begin{tikzcd}
{[NiL]^{2+} + Hsal} \arrow[r, shift left, "k_1"] \arrow[d, shift left, "K_d"'] & {[NiL(sal)]^+ + H^+} \arrow[l, shift left, "k_{-1}"] & (12) \\
{[NiL]^{2+} + sal^-} \arrow[u, shift left] \arrow[r, shift left, "k_2"] & {[NiL(sal)]^+} \arrow[l, shift left, "k_{-2}"] & (13)
\end{tikzcd}$$

pK_d value of salicylaldehyde is 8.13 (25 °C, $I = 0.10$ mol dm^{-3}),[20] $K_d/[H^+] \ll 1$ is valid in pH range studied. The weighted least-squares best-fit plot of k_{obs} *versus* $[NiL^{2+}]/[H^+]$ (k_{obs} being weighted inversely as its variance $w = [\sigma(k_{obs})]^2$) is essentially linear (see Fig. 2, correlation coefficient = 0.950) with a positive intercept and gradient, further substantiating

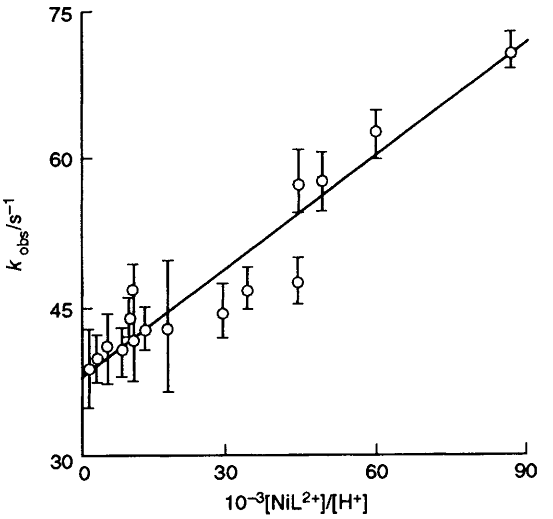
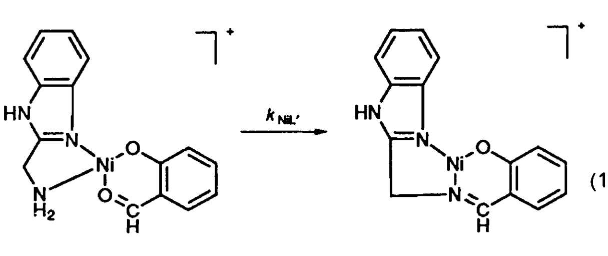


Fig. 2 Plot of k_{obs}/s^{-1} *versus* $[NiL]^{2+}/[H^+]$ for the formation of the mixed-ligand complex $[NiL(sal)]^+$ at 25 °C, λ = 375 nm, I = 0.30 mol dm^{-3}

the insignificance of the terms $k_1[NiL^{2+}]$ and $k_{-1}[H^+]$ in equation (11). The values of k_2 and k_{-2} calculated with K_d taken as 8.3×10^{-9} mol dm^{-3} (I = 0.30 mol dm^{-3} at 25 °C) are $(4.4 \pm 0.2) \times 10^4$ $dm^3 mol^{-1} s^{-1}$ and $38.4 \pm 0.4 s^{-1}$ respectively. It is quite likely that water dissociation from $[NiL(OH_2)_4]^{2+}$ limits the rate of formation of the mixed-ligand complex. The value of k_2 thus indicates that the presence of L in the co-ordination sphere of Ni^{2+} marginally alters the water-exchange rate constant $\{k_{ex} = (2.7\text{–}3.6) \times 10^4$ s^{-1} at 25 °C for $[Ni(OH_2)_6]^{2+}\}$.[17,18] The dissociation rate constant of $[NiL(sal)]^+$ falls in the range observed for several other Ni^{II} chelates.[21–24]

The stability constant of the nickel(II) monosalicylaldehyde complex $[Ni(sal)]^+$ is 3.8×10^4 $dm^3 mol^{-1}$ at 25 °C and I = 0.50 mol dm^{-3};[20] the value obtained for the mixed-ligand complex, $[NiL(sal)]^+$ from the values of k_2 and k_{-2} ($K_{stab} = k_2/k_{-2}$) is $\approx 1.1 \times 10^3$ $dm^3 mol^{-1}$ at 25 °C (I = 0.30 mol dm^{-3}). Thus the primary amine ligand in the co-ordination sphere of Ni^{2+} decreases the propensity of the metal ion to form a complex with salicylaldehyde anion. This is understandable as for steric reasons the salicylaldehyde anion must approach the metal ion on the opposite side to the amine ligand which thus exerts a directive influence on the approach of the secondary ligand.

The mixed-ligand complex is slowly converted to the corresponding Schiff-base complex [equation (14)]. Similar



(14)

behaviour has been reported for the $Cu^{II}L$–Hsal[25] and also for several metal–diamine–salicylaldehyde systems[26–28] simulating the pyridoxal–amino acid condensation mediated by metal ions,[27] an important biochemical reaction. The influence of Ni^{II} on the kinetics of Schiff-base condensation is particularly striking. For example, for $[Ni^{2+}]$ = 0.02 mol dm^{-3} k_{obs} decreased ≈560-fold under comparable experimental conditions $\{k_{obs} = 1.35 \times 10^{-5}$ and 7.6×10^{-3} s^{-1} for $[Ni^{2+}]_T$ = 0.012 and 0 mol dm^{-3} respectively, $[L]_T$ = 0.012, I = 0.30 mol dm^{-3}, pH 6, 25 °C$\}$. The kinetically controlled intramolecular Schiff-base condensation step is preceded by equilibrium (13) hence k_{obs} is given by equation (15). With $K_d = 8.3 \times 10^{-9}$ mol

$$k_{obs} = \frac{k_{NiL'}K_{NiL(sal)}K_d[NiL^{2+}]/[H^+]}{1 + K_d/[H^+] + K_{NiL(sal)}K_d[NiL^{2+}]/[H^+]} \quad (15)$$

dm^{-3} (ref. 20) and $K_{NiL(sal)} = 1.1 \times 10^3$ $dm^3 mol^{-1}$, the rate constant of formation of $[NiL']^+$, $k_{NiL'}$, was calculated to be $(1.8 \pm 0.5) \times 10^{-4}$ s^{-1} at pH 6.1 ± 0.1, I = 0.30 mol dm^{-3}, 25 °C using the values of k_{obs} obtained for $[Ni^{2+}]_T$ = 0.006–0.020 mol dm^{-3} ($[Ni^{2+}]_T = [L]_T$). The validity of equation (14) (*i.e.*, no detectable reverse reaction) further supports the Schiff-base complex being thermodynamically and kinetically stable to dissociation in the neutral pH range. Comparison with similar data on the Cu^{II} system[25] showed that the intramolecular reaction is more facile for Ni^{II}. Thus the propensity of the mixed-ligand complex towards Schiff-base condensation in the co-ordination sphere of the metal ion is invariably related to its thermodynamic stability.

Tables presenting k_{obs} data for complexation of Ni^{2+}, acid-catalysed dissociation of $[NiL]^{2+}$, ternary complex formation between Ni^{2+}, L and salicylaldehyde, and the Schiff-base condensation reaction together with a UV/VIS spectrum showing the formation of the $[NiL']^+$ complex have been deposited as supplementary material (No. SUP 57042).

Acknowledgements

R. K. S. thanks the Department of Higher Education, Government of Orissa, for granting study leave. A. C. D. thanks the Department of Science & Technology, Government of India, for generous funding for the purchase of the stopped-flow and UV/VIS spectrophotometers.

References

1 G. L. Eichhorn and J. C. Bailar, jun, *J. Am. Chem. Soc.*, 1953, **75**, 2905.
2 G. L. Eichhorn and I. M. Trachtenberg, *J. Am. Chem. Soc.*, 1954, **76**, 5183.
3 H. Siegel, R. Griesser and B. Prijs, *Z. Naturforsch., Teil B*, 1972, **27**, 353.
4 H. Siegel, *Inorg. Chem.*, 1975, **14**, 1535; *J. Chin. Acc. Chem. Res.*, 1991, **24**, 145; T. C. Bruice, *Acc. Chem. Res.*, 1991, **24**, 243; E. I. Solomon and Y. Zhang, *Acc. Chem. Res.*, 1992, **25**, 343.
5 D. W. Margerum, G. R. Cayley, D. C. Weatherburn and G. K. Pogenkopf, *ACS Monogr.*, 1978, **2**, 1.
6 S. Chopra and R. B. Jordan, *Inorg. Chem.*, 1983, **22**, 1708; M. J. Sisley and R. B. Jordan, *Inorg. Chem.*, 1992, **31**, 2137; J. E. Bollinger and D. M. Roundhill, *Inorg. Chem.*, 1993, **32**, 2821.
7 D. N. Hague and A. R. White, *J. Chem. Soc., Dalton Trans.*, 1993, 1337; I. Fabion, *Inorg. Chem.*, 1993, **32**, 1184.
8 J. C. Cassatt and R. G. Wilkins, *J. Am. Chem. Soc.*, 1968, **90**, 6045.
9 L. A. Cescon and A. R. Dey, *J. Org. Chem.*, 1962, **27**, 581.
10 A. I. Vogel, *A Text Book of Quantitative Inorganic Analysis*, 3rd edn., Longman, London, 1962, p. 435.
11 M. G. Mellon, *Analytical Absorption Spectroscopy*, 2nd edn., Wiley, New York, 1953, p. 259.
12 A. C. Dash, A. N. Acharya and R. K. Nanda, *J. Chem. Soc., Dalton Trans.*, 1993, 1023.
13 A. C. Dash, A. N. Acharya and R. K. Sahoo, *Transition Met. Chem.*, 1994, in the press.
14 Y. Marcus, *Ion Solvation*, Wiley, New York, 1985, p. 107.
15 R. M. Fuoss, *J. Am. Chem. Soc.*, 1958, **80**, 5059.
16 D. B. Rorabacher, T. S. Turan, J. A. Defever and W. G. Nickels, *Inorg. Chem.*, 1969, **8**, 1498.
17 T. S. Swift and R. E. Connick, *J. Chem. Phys.*, 1962, **37**, 307; R. E. Connick and D. Fiat, *J. Chem. Phys.*, 1966, **44**, 4103; A. G. Desai, H. W. Dodgen and J. P. Hunt, *J. Am. Chem. Soc.*, 1970, **92**, 798.
18 Y. Ducommun, W. L. Earl and A. E. Merbach, *Inorg. Chem.*, 1979, **18**, 2754.
19 J. Neeley and R. E. Connick, *J. Am. Chem. Soc.*, 1970, **92**, 3476.
20 *Critical Stability Constants*, eds. A. E. Martell and R. M. Smith, Plenum, New York, 1977, vol. 3, p. 194.

21 S. Harada, K. Amidaiji and T. Yasunaga, *Bull. Chem. Soc., Jpn.*, 1972, **45**, 1752.

22 H. Hoffmann and E. Yeager, *Ber. Bunsenges. Phys. Chem.*, 1970, **74**, 641.

23 H. Hoffmann and G. Platz, *Ber. Bunsenges. Phys. Chem.*, 1972, **76**, 491.

24 S. Harada, Y. Okuue, H. Khan and T. Yasunaga, *Bull. Chem. Soc., Jpn.*, 1974, **47**, 769.

25 A. C. Dash, D. Panda and B. Dash, *Indian J. Chem., Sect. A*, 1984, **25**, 141.

26 G. L. Eichhorn and N. D. Marchand, *J. Am. Chem. Soc.*, 1956, **78**, 2688.

27 D. Hopgood and D. L. Leussing, *J. Am. Chem. Soc.*, 1969, **91**, 3740; A. E. Martell, *Acc. Chem. Res.*, 1989, **22**, 115.

28 R. S. McQuate and D. L. Leussing, *J. Am. Chem. Soc.*, 1975, **97**, 5117.

Received 5th May 1994; *Paper* 4/02680B