Reactions of Nickel(II) Diphenolate Diamide Complexes with Polydentate Ligands

Sanjukta Tripathy and Sreelekha D. Bhattamisra
Department of Chemistry, Berhampur University, Berhampur-760 007, Orissa, India

(*N,N'*-ethylenedisalicylamidato)nickelate(II), $[NiL]^{2-}$, reacted with ethylenediamine-*N,N,N',N'*-tetraacetate (edta) and *trans*-cyclohexane-1,2-diamine-*N,N,N',N'*-tetraacetate (cdta) in borate buffer with first-order rate constants of 3.39×10^{-4} and 3.44×10^{-4} s^{-1} respectively at pH 9.34. Both the reactions are pH dependent. Kinetic information suggests that the protonated species of $[NiL]^{2-}$ are the reactive species, the reactivity order being $[Ni(H_2L)] > [Ni(HL)]^- > [NiL]^{2-}$. For the edta reaction direct substitution is evident while with cdta steric factors necessitate the formation of an intermediate complex, the decomposition of which in a rate limiting step yields the substituted products. Comparative data for similar reactions involving (*N,N'*-ethylenedisalicylamidato)cuprate(II) are discussed.

Acid dissociation reactions in deprotonated amide complexes of nickel have been studied in detail and are believed to proceed through one of two pathways.[1-4] However, little is known[4] about their reaction with polydentate ligands. The present study deals with the kinetics and mechanism of the reaction of (*N,N'*-ethylenedisalicylamidato)nickelate(II) ($[NiL]^{2-}$) with ethylenediamine-*N,N,N',N'*-tetraacetate (edta) and *trans*-cyclohexane-1,2-diamine-*N,N,N',N'*-tetraacetate (cdta).* The complex $[NiL]^{2-}$ has two phenolate oxygens and two deprotonated amide nitrogens in a square-planar arrangement around Ni^{II} [5,6] and this makes the study important as phenolate groups are known to be effective metal ion carriers in biological systems.[7] Spectral and pH-metric studies also reveal interesting similarities with most nickel peptides.[8]

Experimental

All the chemicals used are of AR grade. Preparative methods for the ligand and the complex are described elsewhere.[5,6] The ligand is a white amorphous solid (m.p. 185 °C) (Found: C, 63.9; H, 4.35; N, 9.20. $C_{16}H_{16}N_2O_4$ requires C, 64.0; H, 5.3; N, 9.3%); ν(O–H) 3406, ν(N–H) 3393, ν(C=O) (amide I) 1640 and ν(C–N) (amide II) 1547 cm^{-1} (Nujol mulls). λ_{max}/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$): 240 ($1.925 \times 10^4$) and 305 ($1.045 \times 10^4$) in ethanol. The hygroscopic complex $K_2[NiL]$ is orange-yellow and soluble in water, m.p. 170 °C. Microanalysis was obtained for a sample dried at 110 °C (Found: C, 44.15; H, 2.80; N, 6.45. $C_{16}H_{12}K_2N_2NiO_4$ requires C, 44.35; H, 2.75; N, 6.45%); ν(C=O) (amide I) 1613 and ν(C–N) (amide II) 1541 cm^{-1}. λ_{max}/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$): pH 7.5, 240 (> 10^4), 390 (4.87), 660 (2.5); pH 8.8, 440 (279), 510–540 (sh) (63). Results from elemental and spectral studies agree well with those reported.[6]

The dissociation constants of the ligand (H_4L) as well as the formation and acid dissociation constants of the nickel complex were determined by pH-titration with carbonate-free KOH under an atmosphere of nitrogen ($I = 0.1$ mol dm^{-3} KNO_3, $T = 30$ °C) using metal : ligand ratios of 1 : 1, 1 : 1.5 and 1 : 2. In each case a single inflection at $a = 4.0$, 3.27 and 2.98 respectively was observed (a = number of moles of base added per mole of the ligand). For the ligand H_4L a single inflection was also observed at $a = 2$. The following equilibrium constants [equations (1)–(5)] were determined using methods described in

$$H_4L \overset{K_1}{\rightleftharpoons} H_3L^- + H^+ \qquad (1)$$

$$H_3L^- \overset{K_2}{\rightleftharpoons} H_2L^{2-} + H^+ \qquad (2)$$

$$Ni^{2+} + H_2L^{2-} \overset{K_3}{\rightleftharpoons} [Ni(H_2L)] \qquad (3)$$

$$[Ni(H_2L)] \overset{K_4}{\rightleftharpoons} [Ni(HL)]^- + H^+ \qquad (4)$$

$$[Ni(HL)]^- \overset{K_5}{\rightleftharpoons} [NiL]^{2-} + H^+ \qquad (5)$$

the references: $K_1 = 5.128 \times 10^{-9}$ mol dm^{-3}, $K_2 = 1.966 \times 10^{-10}$ mol dm^{-3} (ref. 9), $K_3 = 9.12 \times 10^2$ $dm^3\ mol^{-1}$, $K_4 = 1.622 \times 10^{-8}$ mol dm^{-3}, $K_5 = 1.77 \times 10^{-8}$ mol dm^{-3} (refs. 7, 10 and 11). Close similarity for the values for K_4 and K_5 indicates loss of both the protons in a single step and such simultaneous loss of amide protons to form anionic nickel–peptide complexes has been reported earlier.[12]

For kinetic studies, the nickel content in the complex $[NiL]^{2-}$ was determined by titration with edta (pH 7) using murexide as indicator.[13] The ligand cdta was recrystallised as its monosodium salt and standardised against a copper solution.[14] The kinetics of the reaction was monitored spectrophotometrically using an AIMIL spectrophotometer with microprocessor and by following the disappearance of $[NiL]^{2-}$ at 440 nm in ethanol–water (45% v/v) at 30 °C under pseudo-first-order conditions. Borax (sodium tetraborate decahydrate) and boric acid were used as buffering agents (total borate was 0.2 mol dm^{-3} for a typical run). Ionic strength was maintained at 0.125 mol dm^{-3} with KNO_3 and pH variation was accomplished by varying the concentration of boric acid. For the pH range studied the predominant nickel, edta and cdta species were $[NiL]^{2-}$, $Hedta^{3-}$ and $Na(cdta)^{3-}$ respectively.[15,16]

Results

(*a*) *Reaction of* $[NiL]^{2-}$ *with* Na_2H_2edta.—The stoichiometric reaction for the ligand substitution of $[NiL]^{2-}$ by edta in borate buffer is given by equation (6) (n = 0–2). The

$$[Ni(H_nL)]^{n-2} + Hedta^{3-} \longrightarrow [Ni(edta)]^{2-} + HL_{n+1}^{n-3}$$
$$HL^{3-} + H_2O \xrightarrow{fast} H_2L^{2-} + OH^- \qquad (6)$$

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* The abbreviations edta and cdta in this paper are also used in a general sense to encompass all the edta or cdta species present.

Table 1 Rate constant values for the reaction of Na_2H_2edta with (*N,N'*-ethylenedisalicylamidato)nickelate(II); $T = 30$ °C, $I = 0.125$ mol dm^{-3}, [borate] = 0.02 mol dm^{-3}, Solvent, ethanol–water (45:55 v/v)

pH	$10^3[NiL^{2-}]_T$/mol dm^{-3}	$10^2[edta]_T$/mol dm^{-3}	$10^4 k_{obs}/s^{-1}$
9.45 ± 0.03	0.93	1.16	2.319
	1.04		2.204
	1.16		2.287
	1.28		2.305
	1.39		1.806
9.34 ± 0.04	1.18	1.05	2.974
		1.18	3.390
		1.36	3.800
		1.55	4.400
9.45 ± 0.03	1.18	0.82	1.582
		1.16	2.299
		1.28	2.486
		1.55	3.082
9.60 ± 0.04	1.18	1.16	1.388
		1.25	1.566
		1.35	1.720
		1.45	1.842
		1.55	1.946
9.80 ± 0.05	1.18	1.16	0.846
		1.35	0.972
		1.45	1.034
		1.55	1.181
		1.75	1.242
		1.98	1.414

Table 2 Values of rate constants for the reaction of $[NiL]^{2-}$ with edta

Constant	pH	Experimental	Calculated
k_1/dm^3 mol^{-1} s^{-1}			1.228×10^{-3}
k_2/dm^3 mol^{-1} s^{-1}			0.750
k_3/dm^3 mol^{-1} s^{-1}			16.216
$10^2 k'^{a}$/dm^3 mol^{-1} s^{-1}	9.34	2.830	2.808
	9.45	1.997	1.977
	9.60	1.263	1.253
	9.81	0.682	0.688
$10^4 k_{obs}{}^{b}/s^{-1}$	9.04	9.031	9.038
	9.19	5.298	5.316
	9.34	3.390	3.216
	9.45	2.299	2.269
	9.61	1.388	1.408
	9.79	0.846	0.858

[a] $$k'_{calc} = \frac{[H^+]}{[H^+] + K_E} \cdot \frac{k_1 + k_2K_5^{-1}[H^+] + k_3K_5^{-1}K_4^{-1}[H^+]^2}{11 + K_5{}^{-1}[H^+] + K_5^{-1}K_4^{-1}[H^+]^2}$$

[b] Calculated values obtained using equation (20) where $[NiL^{2-}]_T = 1.18 \times 10^{-3}$ mol dm^{-3} and $[edta]_T = 1.16 \times 10^{-2}$ mol dm^{-3}. Protonation constant values $K_5^{-1} = 5.623 \times 10^7$ dm^3 mol^{-1}, $K_4^{-1} = 6.16 \times 10^7$ dm^3 mol^{-1}. k'_{exp} are the slope values of k_{obs} *vs.* $[edta]_T$ plots at different pH (Table 1).

subsequent fast reaction with water has been considered only for $n = 0$. For kinetic studies the concentration of $[NiL]^{2-}$ was varied from 0.93×10^{-3} to 1.39×10^{-3} mol dm^{-3} and edta from 0.82×10^{-2} to 1.55×10^{-2} mol dm^{-3} at pH 9.45. The reaction is consistent with the rate law (7) where k_{obs}, the

$$-\frac{d[NiL^{2-}]}{dt} = k_{obs}[NiL^{2-}]_T \qquad (7)$$

pseudo-first-order rate constant, is a function of both pH and [edta]. Table 1 lists the k_{obs} values at various concentrations of $[NiL]^{2-}$ and edta as well as at a variety of pH values. At constant pH, log k_{obs} *vs.* $[edta]_T$ gives a straight line with positive slope and passing through the origin which precludes the possibility of any complex dependence of rate on $[edta]_T$ or of any parallel reaction[4] being involved in the mechanism. The dependence of rate upon $[edta]_T$ can thus be given by equation (8).

$$k_{obs} = k'[edta]_T \qquad (8)$$

The variation of k_{obs} with pH is presented in Table 2. An inverse proportionality is evident. Also listed in Table 2 are k' values which represent slopes of plots of k_{obs} *vs.* $[edta]_T$ (Table 1) at different pH values. These values fit the empirical equation (9) with $A = 8.283 \times 10^{16}$ dm^9 mol^{-3} s^{-1}, $B = 1.784 \times 10^7$

$$k' = A[H^+]^2 + B[H^+] + C \qquad (9)$$

dm^6 mol^{-2} s^{-1} and $C = 3.041 \times 10^3$ dm^3 mol^{-1} s^{-1}. Combination of equations (8) and (9) reveals the nature of dependence of k_{obs} with $[H^+]$.

Upon mixing the $[NiL]^{2-}$ complex with the reactant solution (buffer + edta) it displays a very small but abrupt decrease in absorbance at 440 nm followed by a rather slow formation of the product. Although at the pH of study, $[NiL]^{2-}$ is calculated to be the predominant species, small concentrations of the other two species $[Ni(HL)]^-$ and $[Ni(H_2L)]$ will be present, their relative amount being determined by equations (10) and (11). Added ligand and changes in solvent composition

$$[NiL]^{2-} + H^+ \xrightleftharpoons{K_5^{-1}} [Ni(HL)]^- \qquad (10)$$

$$[Ni(HL)]^- + H^+ \xrightleftharpoons{K_4^{-1}} [Ni(H_2L)] \qquad (11)$$

or ionic strength have marginal effects on the rate constants. On the basis of the above observations and the kinetic information, the mechanism for the reaction may be represented by equation (12) where $[NiL^{2-}]_T = [NiL^{2-}] + [Ni(HL)^-] + [Ni(H_2L)]$.

$$[NiL^{2-}]_T + Hedta^{3-} \xrightarrow{k''} Products \qquad (12)$$

The rate law (13) arises from the series of reaction steps (14)–(16) and can be rewritten in terms of equations (17) and (18).

$$Rate = k''[NiL^{2-}]_T[Hedta^{3-}] \qquad (13)$$

$$[NiL]^{2-} + Hedta^{3-} \xrightarrow{k_1} [Ni(edta)]^{2-} + HL^{3-} \qquad (14)$$

$$[Ni(HL)]^- + Hedta^{3-} \xrightarrow{k_2} [Ni(edta)]^{2-} + H_2L^{2-} \qquad (15)$$

$$[Ni(H_2L)] + Hedta^{3-} \xrightarrow{k_3} [Ni(edta)]^{2-} + H_3L^- \qquad (16)$$

$$rate = \{k_1[NiL^{2-}] + k_2[Ni(HL)^-] + k_3[Ni(H_2L)]\}[Hedta^{3-}] \qquad (17)$$

$$= (k_1 + k_2K_5^{-1}[H^+] + k_3K_5^{-1}K_4^{-1}[H^+]^2)[NiL^{2-}][Hedta^{3-}] \qquad (18)$$

Since $[NiL^{2-}] = [NiL^{2-}]_T/(1 + K_5^{-1}[H^+] + K_5^{-1}K_4^{-1}[H^+]^2)$ k_{obs} can be written in terms of $[H^+]$ [equation (19)].

$$k_{obs} = \frac{k_1 + k_2K_5^{-1}[H^+] + k_3K_5^{-1}K_4^{-1}[H^+]^2}{1 + K_5^{-1}[H^+] + K_5^{-1}K_4^{-1}[H^+]^2} \cdot [Hedta^{3-}] \qquad (19)$$

In the pH range of study, the concentration of H_2edta^{2-} is negligible (0.09% at pH 9.21). Hence expressing $[edta]_T$ as $[Hedta^{3-}] + [edta^{4-}]$, it follows that $[Hedta^{3-}] = [edta]_T[H^+]/([H^+] + K_E)$ where K_E, the dissociation constant of $Hedta^{3-}$, has a value[13] of 5.01×10^{-11} mol dm^{-3}. Insertion into equation (19) leads to equation (20).

Table 3 Rate constant values for the reaction of $[Na(cdta)]^{3-}$ with (*N*,*N'*-ethylenedisalicylamidato)nickelate(II); $T = 30$ °C, $I = 0.125$ mol dm^{-3}, [borate] = 0.02 mol dm^{-3}, solvent ethanol–water (45:55 v/v)

pH	$10^3[NiL^{2-}]_T$/mol dm^{-3}	$10^2[cdta^{4-}]_T$/mol dm^{-3}	10^4k_{obs}/s^{-1}
9.53 ± 0.02	0.410	1.260	1.720
	0.574		1.517
	0.820		1.218
	1.066		1.264
	1.312		1.240
9.70 ± 0.05	0.820	0.840	0.855
		1.260	1.218
		1.512	1.470
		1.764	1.575
		2.016	1.906
9.35 ± 0.03	0.820	1.020	3.440
		1.243	4.187
		1.512	4.763
		2.016	5.948
9.17 ± 0.03	0.820	1.020	6.749
		1.243	7.750
		1.512	9.120
		2.016	11.150
9.06 ± 0.02	0.820	1.020	10.200
		1.243	11.810
		1.512	13.540
		2.016	16.300

Table 4 Values of rate constants for the reaction of $[NiL]^{2-}$ with cdta *

Constant	$10^2[cdta^{4-}]$/mol dm^{-3}	pH	Exptl.	Calc.
K'/dm^3 mol^{-1}				670.417
K''/dm^3 mol^{-1}				106.859
k'/s^{-1}				4.084 × 10^{-4}
k''/s^{-1}				0.447
10^4k_{obs}/s^{-1}	0.840	9.70	0.855	0.756
	1.260	±0.03	1.218	1.208
	1.512		1.470	1.448
	1.764		1.575	1.601
	2.016		1.906	1.864
	1.243	9.59	1.872	1.655
		9.49	2.948	2.370
		9.35	4.187	4.014
		9.27	5.758	5.483
		9.17	7.750	7.878
		9.11	9.836	9.834
		9.06	11.810	11.810

* Constants K', K'', k' and k'' calculated using equation (26); $[NiL^{2-}]_T = 0.820 \times 10^{-3}$ mol dm^{-3}, other parameters as in Tables 2 and 3.

$$k_{obs} = \frac{[H^+]}{[H^+] + K_E} \cdot \frac{k_1 + k_2K_5^{-1}[H^+] + k_3K_5^{-1}K_4^{-1}[H^+]^2}{1 + K_5^{-1}[H^+] + K_5^{-1}K_4^{-1}[H^+]^2}[edta]_T \quad (20)$$

Analysis of equation (20) with observed rate constant values at various $[H^+]$ yields $k_1 = 1.228 \times 10^{-3}$ dm^3 mol^{-1} s^{-1}, $k_2 = 0.750$ dm^3 mol^{-1} s^{-1} and $k_3 = 16.216$ dm^3 mol^{-1} s^{-1}. Table 2 lists the values of the different rate constants involved in the rate law. There is excellent agreement between (*i*) calculated k' values and the corresponding slope values (Table 1) in the pH range 9.34 to 9.81 and (*ii*) the experimental and calculated [using equation (20)] rate constant values in the pH range 9.04 to 9.79.

(*b*) *Sodium* trans-*Cyclohexane*-1,2-*diaminetetraacetate*.—The stoichiometry of the reaction of cdta with $[NiL]^{2-}$ is similar to that of edta. The pseudo-first-order rate constant values (Table 3) are more or less constant over the concentration range studied. However, upon increasing $[cdta]_T$, the $k_{obs}/[cdta]_T$ values gradually decrease, showing a tendency for the reaction to follow Michaelis–Menten kinetics. The double reciprocal plot of $1/k_{obs}$ *vs.* $1/[cdta]_T$ is linear with finite intercept on the inverse rate axis. Thus a complex formation between $[cdta]^{4-}$ and the nickel complex is suggested. The experimental results conform to the equation (21) where *a* and *b* are functions of

$$k_{obs} = \frac{[cdta^{4-}]}{a + b[cdta^{4-}]} \quad (21)$$

$[H^+]$. The values of *a* and *b* at each pH are obtained respectively from the slope and intercept of the double reciprocal plot.

The k_{obs} values increase with increasing $[H^+]$ as is observed for the edta reaction (Table 4). The order of reaction with respect to $[H^+]$ is 1.5 which indicates that $[N(HL)]^-$ and $[Ni(H_2L)]$ are equally active. This in turn suggests inclusion of equations (10) and (11) in the rate mechanism. Thus the substitution reaction involves an intermediate complex formation of these nickel species with cdta followed by breakdown of the intermediates in rate-limiting steps [equations (22)–(24)] and can be expressed by rate law (25).

$$[Ni(HL)]^- + cdta^{4-} \xrightleftharpoons{K'} \underset{\text{Complex } C_1}{[Ni(HL)\cdots cdta]^{5-}}$$

$$\text{Slow} \downarrow k'$$

$$[Ni(cdta)]^{2-} + HL^{3-} \quad (22)$$

$$[Ni(H_2L)] + cdta^{4-} \xrightleftharpoons{K''} \underset{\text{Complex } C_2}{[Ni(H_2L)\cdots cdta]^{4-}}$$

$$\text{Slow} \downarrow k''$$

$$[Ni(cdta)]^{2-} + H_2L^{2-} \quad (23)$$

$$HL^{3-} + H_2O \xrightarrow{\text{fast}} H_2L^{2-} + OH^- \quad (24)$$

$$\text{Rate} = -\frac{d[NiL^{2-}]}{dt} = \frac{-d[C_1]}{dt} + \frac{-d[C_2]}{dt} =$$

$$k'K'[Ni(HL)^-][cdta^{4-}] + k''K''[Ni(H_2L)][cdta^{4-}] \quad (25)$$

In terms of $[NiL^{2-}]_T$ where $[NiL^{2-}]_T = [NiL^{2-}] + [Ni(HL)^-] + [Ni(H_2L)] + [C_1] + [C_2]$, k_{obs} and $1/k_{obs}$ can be expressed in terms of equations (26) and (27). From the plot of $1/k_{obs}$ *vs.* $1/[cdta^{4-}]_T$, intercept/slope = $AK' + BK''$ (at

$$k_{obs} = \frac{(k'K'K_5^{-1}[H^+] + k''K''K_5^{-1}K_4^{-1}[H^+]^2)[cdta^{4-}]}{1 + K_5^{-1}[H^+] + K_5^{-1}K_4^{-1}[H^+]^2 + K'K_5^{-1}[H^+][cdta^{4-}] + K''K_5^{-1}K_4^{-1}[H^+]^2[cdta^{4-}]} \quad (26)$$

$$1/k_{obs} = \frac{+ K_5^{-1}[H^+] + K_5^{-1}K_4^{-1}[H^+]^2}{(k'K'K_5^{-1}[H^+] + k''K''K_5^{-1}K_4^{-1}[H^+]^2)[cdta^{4-}]} + \frac{K'K_5^{-1}[H^+] + K''K_5^{-1}K_4^{-1}[H^+]^2}{k'K'K_5^{-1}[H^+] + k''K''K_5^{-1}K_4^{-1}[H^+]^2} \quad (27)$$

Table 5 Comparative analysis of the characteristics for the reactions of edta and cdta with $[CuL]^{2-}$ [a] and $[NiL]^{2-}$ [b]

						Dependence on	
Reaction	Condition of study	pH	$10^3[ML^{2-}]_T$/ mol dm^{-3}	10^2[Nucleophile]$_T$/ mol dm^{-3}	k_{obs}	[Nucleophile]	$[H^+]$
$[CuL]^{2-}$–edta	Second order	9.25	1.250	0.125	28.1×10^{-2} dm^3 mol^{-1} s^{-1}	First	Complex
$[NiL]^{2-}$–edta	Pseudo-first order	9.32	1.180	1.180	3.39×10^{-4} s^{-1}	First	Complex
$[CuL]^{2-}$–cdta	Pseudo-first order	9.34	1.050	1.008	3.99×10^{-4} s^{-1}	Complex	2
$[NiL]^{2-}$–cdta	Pseudo-first order	9.35	0.820	1.020	3.44×10^{-4} s^{-1}	Complex	1.5

[a] Refs. 16 and 19. [b] This work.

constant pH). The ratios of intercepts to slopes are 24.68, 16.49 and 7.45 at pH 9.17, 9.35 and 9.70 respectively and from this mean values of K' and K'' of 671 and 106 dm^3 mol^{-1} are obtained.

Discussion

The reaction of $[NiL]^{2-}$ with edta or cdta is pH dependent and the rate constant in either case increases steadily with decrease in pH. In borate buffer the protonation–deprotonation equilibria are reversible [equations (10) and (11)] and all the three forms of the Ni complex *viz.* $[NiL]^{2-}$, $[Ni(HL)]^-$ and $[Ni(H_2L)]$ are present to a meaningful extent. In the pH range of study, $Hedta^{3-}$ and $[Na(cdta)]^{3-}$ are the only predominant forms of the respective nucleophiles. The protonation constant of $Hcdta^{3-}$ is 9.63 in the presence of sodium ion (monosodium salt) instead of the literature value[17] of 11.73. (This is to be expected since cdta strongly complexes with Na^+; $K_{Na(cdta)} = 2.5 \times 10^4$ dm^3 mol^{-1}.)[15] The pH dependence therefore suggests the reactivity order $[Ni(H_2L)] > [Ni(HL)]^- > [NiL]^{2-}$. This inference is supported by (*i*) the sharp, initial decrease in absorbance at 440 nm following the addition of $[NiL]^{2-}$ to the borate buffer and (*ii*) its further but gradual decrease only when the nucleophile is added. Thus the presence of the nucleophile shifts the equilibria in borate buffer [equations (10) and (11)] by reacting with the protonated species of $[NiL]^{2-}$. The anchoring of the nucleophile to the different planar Ni–L species may occur at either of the remaining co-ordination sites (*trans*) for an octahedral orientation, possibly replacing a labile water molecule (water-exchange first-order rate constant in $[Ni(H_2O)_6]^{2+}$ is of the order of 10^4 s^{-1}).[18] The protonated $[NiL]^{2-}$ species favours the substitution process as protonation dissociates the amide nitrogen from the metal, thereby loosening the chelate ring. Obviously, the greater the concentration of the protonated species of $[NiL]^{2-}$, the faster is the substitution process and this explains the observed dependence of reaction rate on pH. This is further supported by the observation that as the pH increases the rate constant for the edta reaction (Table 2) gradually becomes invariant to the H^+ concentration, the value being $\approx 10^{-4}$ s^{-1} at high pH (≈ 9.8). This is to be expected since at high pH tetradeprotonated $[NiL]^{2-}$ is the only species present.

Kinetic results for the edta and cdta reactions with $[NiL]^{2-}$ reveal that the substitution process is dependent on steric factors. The greater steric hindrance for cdta reduces its ability to attack the protonated nickel complex. Consequently the rate determining step shifts to later stages in the mechanism when the nucleophilic attack leads to intermediate complex formation whose decomposition is rate limiting. With edta, on the other hand, the rate limiting step involves direct nucleophilic attack on the different Ni–L species to yield the final product. The $[H^+]$ dependence of the cdta reaction further supports this. The observed order of 1.5 in $[H^+]$ suggests participation of more than one H^+ ion in the mechanism. Thus cleavage of more than one Ni–N amide bond by protonation [equations (10) and (11)] is required to accommodate the bulky cdta ligand.

Comparison with similar substitution reactions[16,19] of $[CuL]^{2-}$ (Table 5) reveals many similarities which are expected on geometrical grounds. However, there are some interesting differences. The substitution reaction of $[CuL]^{2-}$ by edta studied under second-order conditions is ten times faster than that of $[NiL]^{2-}$. Similar differences involving Cu^{II} and Ni^{II} have been reported earlier.[1,2] This could be due to the fact that the water exchange first-order rate constant in nickel(II) complexes is 10^5 times smaller.[18] If the water-exchange reaction is taken as the first step in the substitution mechanism as discussed earlier, the slow initial step in the case of Ni^{II} is reflected in an overall slowing of the process by a factor of approximately 10^{-1}. Further, the cdta reactions of $[CuL]^{2-}$ and $[NiL]^{2-}$ indicate that the order in $[H^+]$ is 2 in the former while with the latter it is 1.5. In either case, steric factors are considered responsible for the high value of the order in $[H^+]$. Although the strain due to the bulky $cdta^{4-}$ undoubtedly exists in the $[NiL]^{2-}$ as in $[CuL]^{2-}$ reactions, the observed order of 1.5 in the former could be due to the initial slower water exchange process which provides the nucleophile with enough time for linking with the metal.

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