The Preparation of *cis*-Folded Macrocyclic Nickel(II) Complexes and the Kinetics of their Base-catalysed Conversion to Planar Species

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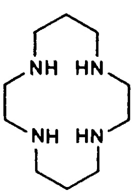
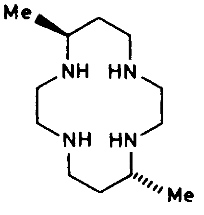
The violet folded *cis*-macrocyclic complexes [NiL(en)][ClO$_4$]$_2$ [L = 1,4,8,11-tetra-azacyclotetradecane (L^1), its C-*meso*-5,12-dimethyl analogue, or 1,4,7,10-tetra-azacyclotridecane] have been prepared. In basic solution these complexes are converted to the yellow planar complexes [NiL]$^{2+}$ which are believed to have the *RSSR* (*SRRS*) chiral nitrogen configuration. Kinetic studies establish that rate = k_{OH}[complex][OH$^-$]. Values of k_{OH} have been obtained at various temperatures and activation parameters determined. Interconversion of the folded *cis* complexes having the *RRRR* (*SSSS*) chiral nitrogen configuration requires the inversion of two chiral *sec*-NH centres to give the *RSSR* (*SRRS*) configuration found in the planar species. The isomerisation of *cis*-[NiL^1(H$_2$O)$_2$]$^{2+}$ shows a first-order dependence on the hydroxide ion concentration up to pH 12.6. Possible mechanisms involving intermolecular attack by hydroxide, or intramolecular attack by co-ordinated hydroxide at the *sec*-NH centres of the complex are considered. The relevance of these studies to the formation of macrocyclic nickel(II) complexes is discussed.

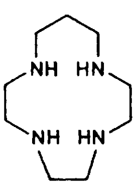
Billo[1] has described the preparation of *cis*-[NiL^1(en)][ClO$_4$]$_2$ (L^1 = 1,4,8,11-tetra-azacycloetradecane and en = ethylenediamine) and has shown that in acidic solution the *cis* isomer isomerises to the *trans* isomer extremely slowly; the half-life at pH 3 is *ca.* 250 d. However, rapid isomerisation occurs in basic solution to give an equilibrium mixture of [NiL^1]$^{2+}$ and *trans*-[NiL^1(H$_2$O)$_2$]$^{2+}$. These two complexes are expected to have the thermodynamically favoured *RSSR* configuration of the *sec*-NH centres. The present paper discusses the synthesis of a number of *cis*-octahedral nickel(II) complexes of the ligands L^1—L^3 and describes kinetic studies of their isomerisation in basic solution over a temperature range.



L^1



L^2



L^3

Experimental

The ligands L^1 (cyclam), L^2 (C-*meso*-5,12-dimethyl-1,4,8,11-tetra-azacyclotetradecane), and L^3 (1,4,7,10-tetra-azacyclotridecane) were prepared by previously described procedures.[2–4]

The planar complex [NiL^2][ClO$_4$]$_2$ was prepared as follows. The ligand (1.5 g) was dissolved in ethanol (25 cm^3) and a solution of Ni[ClO$_4$]$_2$·6H$_2$O (2.4 g) in water (10 cm^3) added dropwise with stirring. The solution was then warmed on a water-bath for *ca.* 30 min. Cooling gave the yellow complex in high yield (1.7 g) (Found: C, 30.0; H, 5.8; N, 11.4. Calc. for $C_{12}H_{28}Cl_2N_4NiO_8$: C, 29.7; H, 5.8; N, 11.5%).

The complex *cis*-[NiL^2(en)][ClO$_4$]$_2$·0.5H$_2$O was prepared as follows. The complex [NiL^2][ClO$_4$]$_2$ (1.5 g) was dissolved in the minimum volume of water. Ethylenediamine (1 g) was added when the solution immediately became violet. The solution was warmed for *ca.* 5 min and then cooled in a refrigerator for 1 h after the addition of a concentrated aqueous solution of NaClO$_4$. The violet crystals of the perchlorate salt were filtered off and dried *in vacuo* (Found: C, 30.0; H, 6.7; N, 15.3. Calc. for $C_{14}H_{37}Cl_2N_6NiO_{8.5}$: C, 30.3; H, 6.7; N, 15.1%).

The complex *cis*-[NiL^{2}Cl$_2$] was prepared similarly using suspension of *cis*-[NiL^2(en)][ClO$_4$]$_2$ in warm methanol with concentrated HBr. On standing, the blue complex *cis*-[NiL^{2}Br$_2$] crystallised (Found: C, 32.6; H, 6.1; N, 12.8. Calc. for $C_{12}H_{28}Br_2N_4Ni$: C, 32.3; H, 6.3; N, 12.5%).

The complex *cis*-[NiL^{2}Cl$_2$] was prepared similarly using concentrated HCl. The complexes *cis*-[NiL^1(en)][ClO$_4$]$_2$ and *cis*-[NiL^{1}Br$_2$] were prepared essentially as previously described,[1] and gave satisfactory analyses. The complex [NiL^3][ClO$_4$]$_2$ was prepared as previously described.[5] Reaction with en in aqueous solution gave the violet *cis*-[NiL^3(en)][ClO$_4$]$_2$ (Found: C, 26.4; H, 6.1; N, 16.9. Calc. for $C_{11}H_{30}Cl_2N_6NiO_8$: C, 26.2; H, 6.0; N, 16.7%).

Kinetics.—Formation of the planar complexes was monitored at 450 nm for the complexes of L^1 and L^2, and 425 nm for that of L^3. All measurements were made using tris(hydroxymethyl)aminomethane (Tris) buffers[6] adjusted to I = 0.1 mol dm^{-3} with Na(ClO$_4$). Plots of log ($A_\infty - A_t$) were linear for at least four half-lives, where A_∞ is the final absorbance and A_t is the absorbance at time t. Additional measurements established that the temperature dependence of the Tris buffer was <0.02 pH unit over the temperature range 25—40 °C. The hydroxide ion concentrations were determined from the pH using the following activity coefficients and ionic products:[7] 25 °C, γ_1 = 0.772, pK_w = 13.996; 30 °C, γ_1 = 0.770, pK_w = 13.833; 35 °C, γ_1 = 0.768, pK_w = 13.680; 40 °C, γ_1 = 0.766, pK_w = 13.535. Activity coefficients were estimated from the Davies equation.[8] The pH measurements were made with a Radiometer PHM64 research pH meter. Interval scan spectra were determined with a Perkin-Elmer Lambda 5 u.v.-visible spectrophotometer. Kinetic monitoring was carried out with a Gilford 2400S spectrophotometer interfaced with an Apple II computing system. Reactions were initiated by the addition of the solid complex to the appropriate temperature-equilibrated buffer solution. Measurements with L^1 and L^2 were made using the dibromo complexes which on dissolving in water give the diaqua complexes. The ethylenediamine complex was used for the studies on L^3 as this complex is sufficiently water soluble for kinetic measurements.

The isomerisation of *cis*-$[NiL^1(H_2O)_2]^{2+}$ in sodium hydroxide solutions was monitored at 450 nm using a Durrum stopped-flow spectrophotometer. The dibromo complex was used in the measurements.

Results and Discussion

Addition of ethylenediamine to a yellow aqueous solution of $[NiL^1]^{2+}$ rapidly gives a violet solution from which the complex *cis*-$[NiL^1(en)][ClO_4]_2$ can readily be isolated. Acidification of the violet solution to pH 2—3 gives a blue solution of *cis*-$[NiL^1(H_2O)_2]^{2+}$. The electronic spectrum of this complex is typical of a *cis*-NiN_4O_2 chromophore, Table 1. Similar behaviour is observed with nickel(II) complexes of L^3 and L^2. A typical visible spectrum is illustrated in Figure 1, which can be assigned to the cation *cis*-$[NiL^2(H_2O)_2]^{2+}$ produced by hydrolysis of the chloride ligands in the complex *cis*-$[NiL^2Cl_2]$. Violet solutions of *cis*-$[NiL^1(H_2O)_2]^{2+}$ isomerise to the yellow $[NiL^1]^{2+}$ in basic solution and similar behaviour is observed with the other diaqua complexes. A typical interval scan spectrum for the isomerisation of *cis*-$[NiL^3(H_2O)_2]^{2+}$ in Tris buffer (pH 7.61) is shown in Figure 2. Tight isobestic points are observed at 365 nm and 510 nm.

The kinetics of isomerisation of *cis*-$[NiL^2(H_2O)_2]^{2+}$, *cis*-$[NiL^1(H_2O)_2]^{2+}$, and *cis*-$[NiL^3(H_2O)_2]^{2+}$ were monitored over the pH range 7.5—8.2 using Tris buffers adjusted to $I = 0.1$ mol dm^{-3}, Tables 2—4. Plots of $k_{obs.}$ (the observed first-order rate constant at constant pH) *versus* the hydroxide ion concentration are linear (Figure 3) with no intercept, confirming a first-order dependence on the hydroxide concentration with rate = k_{OH}[complex]$[OH^-]$ and $k_{OH} = k_{obs.}/[OH^-]$. Values of k_{OH} at various temperatures were determined from the least-squares slope of such plots. Activation parameters for the various isomerisations are summarised in Table 5. The activation parameters for the three complexes are essentially identical (within experimental error) with $\Delta H^‡$ *ca.* 40 kJ mol^{-1} and $\Delta S_{298}^‡$ *ca.* -50 J K^{-1} mol^{-1}.

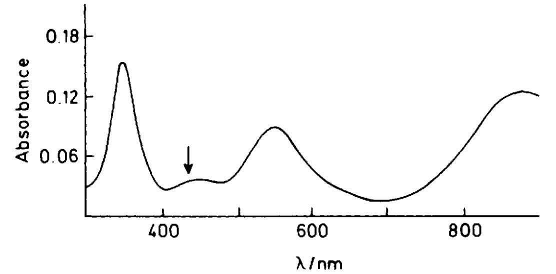


Figure 1. Visible spectrum of *cis*-$[NiL^2Cl_2]$ in aqueous solution, pH 2.4, adjusted with $HClO_4$. The arrow indicates absorption due to the planar species

Table 1. Visible spectra of the complexes

Complex	$\lambda_{max.}$/nm (ε/dm^3 mol^{-1} cm^{-1})
cis-$[NiL^2(en)][ClO_4]_2$[a]	800 (sh) (6), 540 (7), 468 (sh) (5), 348 (10)
cis-$[NiL^2Br_2]$[b]	890 (12), 548 (8), 349 (14)
cis-$[NiL^2Cl_2]$[b]	890 (12), 547 (8), 348 (14)
cis-$[NiL^3(en)][ClO_4]_2$[b]	890 (18), 558 (8), 433 (15), 355 (12)
cis-$[NiL^1Br_2]$[b,c]	890 (10), 546 (7), 348 (16)

[a] Dry methanol as solvent. [b] Aqueous solution, pH adjusted to 2.4 with $HClO_4$ to prevent isomerisation. The complexes give *cis*-$[NiL(H_2O)_2]$ in aqueous solution. [c] For this complex, Billo [1] quotes 890 (14), 548 (8.3), 348 nm (14 dm^3 mol^{-1} cm^{-1}).

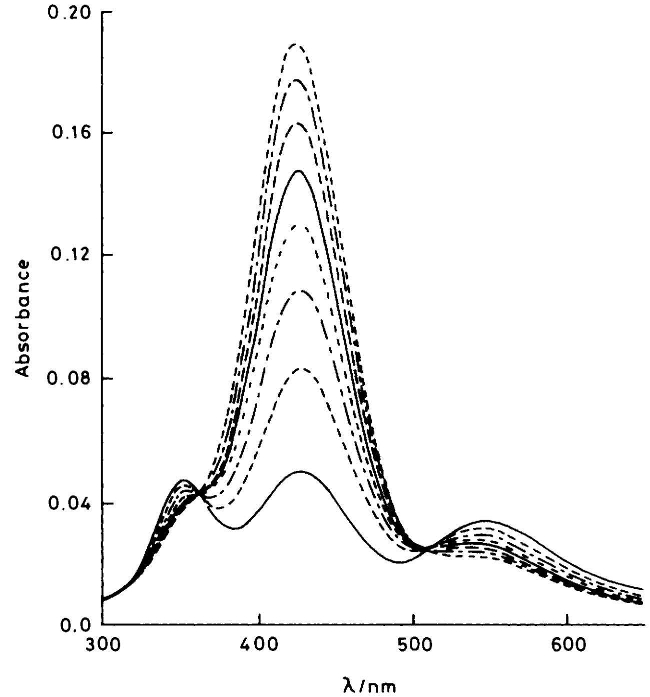


Figure 2. Isomerisation of *cis*-$[NiL^3(H_2O)_2]^{2+}$ in Tris buffer, pH 7.61 at 25 °C. The time interval between scans is 2 min

Table 2. Isomerisation of *cis*-$[NiL^2(H_2O)_2]^{2+}$ at various temperatures and $I = 0.1$ mol dm^{-3}

θ/°C	pH	$10^6[OH^-]$/ mol dm^{-3}	$10^4 k_{obs.}$/ s^{-1}	$10^{-2} k_{OH}$/ dm^3 mol^{-1} s^{-1}
25	7.55	0.46	3.7	8.0
	7.61	0.53	4.6	8.7
	7.71	0.67	5.6	8.35
	7.82	0.86	7.3	8.5
	7.91	1.06	7.45	7.0
	8.05	1.46	10.7	7.3
	8.22	2.17	15.7	7.2
	$k_{OH} = (7.8 \pm 0.4) \times 10^2$ dm^3 mol^{-1} s^{-1}			
30	7.55	0.68	7.6	11.2
	7.61	0.78	9.2	11.8
	7.71	0.98	11.3	11.5
	7.82	1.26	13.9	11.0
	7.91	1.55	16.7	10.8
	$k_{OH} = (11.3 \pm 0.4) \times 10^2$ dm^3 mol^{-1} s^{-1}			
35	7.55	0.97	1.27	13.1
	7.61	1.11	1.55	13.9
	7.71	1.40	1.82	13.0
	7.82	1.80	2.26	12.6
	7.91	2.21	3.01	13.6
	$k_{OH} = (13.2 \pm 0.5) \times 10^2$ dm^3 mol^{-1} s^{-1}			
40	7.55	1.35	2.49	18.4
	7.61	1.55	2.92	18.8
	7.71	1.95	3.55	18.2
	7.82	2.52	4.67	18.5
	7.91	3.09	5.67	18.3
	$k_{OH} = (18.4 \pm 0.4) \times 10^2$ dm^3 mol^{-1} s^{-1}			

Table 3. Isomerisation of *cis*-$[NiL^1(H_2O)_2]^{2+}$ at various temperatures and I = 0.1 mol dm^{-3}

θ/°C	pH	$10^6[OH^-]$/ mol dm^{-3}	$10^4k_{obs.}$/ s^{-1}	$10^{-2}k_{OH}$/ dm^3 mol^{-1} s^{-1}
25	7.55	0.46	0.36	7.8
	7.71	0.67	0.38	5.7
	7.82	0.86	0.55	6.4
	7.91	1.06	0.81	7.6
	8.05	1.46	0.89	6.1
	8.22	2.17	1.39	6.4
	8.54	4.53	2.48	5.5
	k_{OH} = (6.5 ± 0.5) × 10^2 dm^3 mol^{-1} s^{-1}			
30	7.55	0.68	0.60	8.8
	7.61	0.78	0.78	10.0
	7.71	0.98	0.88	9.0
	7.82	1.26	1.04	8.3
	8.05	2.14	1.82	8.5
	k_{OH} = (8.9 ± 0.5) × 10^2 dm^3 mol^{-1} s^{-1}			
35	7.55	0.97	1.14	11.8
	7.61	1.11	1.47	13.2
	7.71	1.40	1.68	12.0
	7.81	1.76	2.09	11.9
	7.91	2.21	2.48	11.2
	k_{OH} = (11.9 ± 0.5) × 10^2 dm^3 mol^{-1} s^{-1}			
40	7.55	1.35	1.86	13.8
	7.61	1.55	2.15	13.9
	7.71	1.95	2.65	13.6
	7.82	2.52	3.47	13.8
	7.91	3.09	4.33	14.0
	k_{OH} = (13.8 ± 0.2) × 10^2 dm^3 mol^{-1} s^{-1}			

Table 4. Isomerisation of *cis*-$[NiL^3(H_2O)_2]^{2+}$ at various temperatures and I = 0.1 mol dm^{-3}

θ/°C	pH	$10^6[OH^-]$/ mol dm^{-3}	$10^4k_{obs.}$/ s^{-1}	$10^{-2}k_{OH}$/ dm^3 mol^{-1} s^{-1}
25	7.55	0.46	1.1	2.4
	7.71	0.67	1.75	2.6
	7.82	0.86	2.2	2.6
	7.91	1.06	2.5	2.4
	8.22	2.17	5.1	2.4
	k_{OH} = (2.4 ± 0.2) × 10^3 dm^3 mol^{-1} s^{-1}			
35	7.55	0.97	4.2	4.3
	7.61	1.11	4.8	4.3
	7.71	1.40	6.0	4.3
	7.82	1.80	7.7	4.3
	7.91	2.21	9.7	4.4
	k_{OH} = (4.3 ± 0.1) × 10^3 dm^3 mol^{-1} s^{-1}			
40	7.55	1.35	8.0	5.0
	7.61	1.55	9.1	5.9
	7.71	2.95	11.5	5.9
	7.82	2.52	15.0	5.95
	7.91	3.09	18.4	5.95
	k_{OH} = (5.9 ± 0.1) × 10^3 dm^3 mol^{-1} s^{-1}			

Billo[1] has studied the isomerisation of *cis*-$[NiL^1(H_2O)_2]^{2+}$ at 25 °C over a wide pH range (1—10), and has established that a minimum occurs in the pH–rate profile at pH 3 where $t_{\frac{1}{2}}$ is *ca.* 250 d. An acid-catalysed isomerisation sets in below pH 3. The base-catalysed isomerisation is likely to proceed by a conjugate-base pathway in which hydroxide ion deprotonates a *sec*-NH group of the macrocyclic ligand. The initial folded macrocycles are expected to have the *RRRR* (*SSSS*) configuration of the chiral nitrogen centres (I) as this allows two folding axes. This view is supported by recent crystallographic work.[9] The complex *cis*-diaqua[(7*S*,14*S*)-5,5,7,12,12,14-hexamethyl-

Table 5. Activation parameters for the conversion of *cis*-$[NiL(H_2O)_2]^{2+}$ to $[NiL]^{2+}$

Ligand	$\Delta H^‡$/ kJ mol^{-1}	$\Delta S^‡$/ J K^{-1} mol^{-1}	k_{OH}^{25}/ dm^3 mol^{-1} s^{-1}
L^1	37 ± 4	−66 ± 13	6.5 × 10^2
L^2	40 ± 4	−56 ± 14	7.8 × 10^2
L^3	44 ± 2	−34 ± 5	2.4 × 10^3
L^5*			4.5 × 10^2

* Data of J. D. Vitiello and E. Billo, *Inorg. Chem.*, 1980, **19**, 3477 (L^5 = 1,9-diamino-3,7-diazanonane).

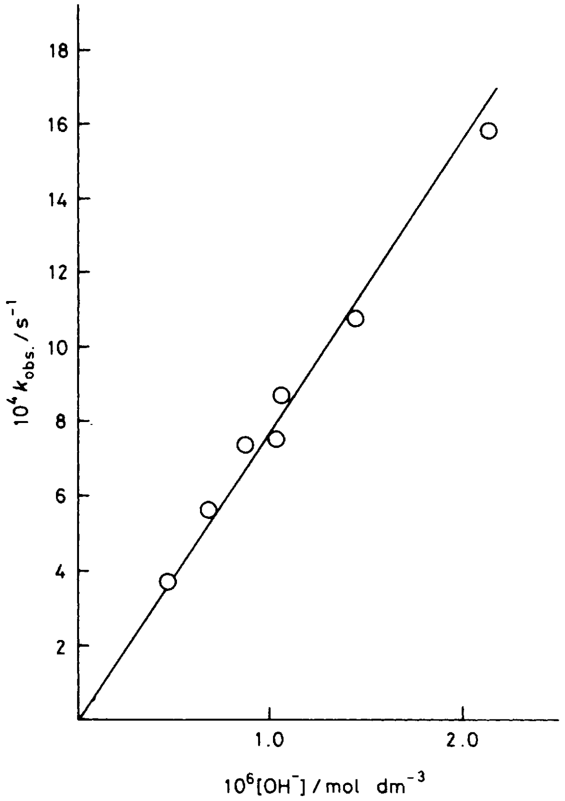
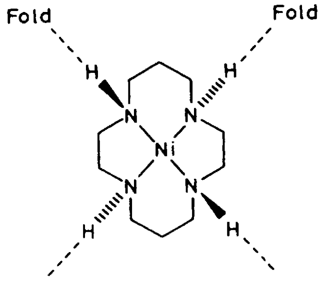
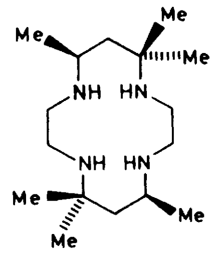


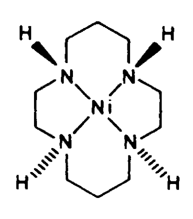
Figure 3. Isomerisation of *cis*-$[NiL^2(H_2O)_2]^{2+}$ at 25 °C and I = 0.1 mol dm^{-3} ($NaClO_4$) as a function of the hydroxide ion concentration in Tris buffer



(I)



rac - L^4



(II)

1,4,8,11-tetra-azacyclotetradecane]nickel(II) chloride, *cis*-$[Ni(S,S\text{-}L^4)(H_2O)_2]Cl_2$ has the *RRRR* configuration at the *sec*-NH centres. (The ligand *S,S*-L^4 is the *S,S*-enantiomer of C-racemic-L^4, *rac*-L^4.) In this complex the ligand L^4 is folded about N(4)–Ni–N(11) as in crystals of $[Ni(rac\text{-}L^4)(O_2CMe)][ClO_4]$[10] and $[\{Ni(S,S\text{-}L^4)\}_2(H_2O)(tart)][ClO_4]_2\cdot 2H_2O$ (tart = D-tartrate).[11] Each chelate ring adopts the most strain-free conformation. Both six-membered rings are of chair conformation, with the single methyl groups in equatorial positions and the five-membered rings *gauche*.

The most thermodynamically stable chiral nitrogen configuration in planar stereochemistry is believed to be the *RSSR* configuration (**II**), and this configuration will be obtained on equilibration under basic conditions. Conversion of the folded *cis* complex to the planar species will involve the inversion of two chiral *sec*-NH centres in the ligand.

The present results are relevant to the mechanism of incorporation of nickel(II) into macrocyclic tetra-aza ligands. The formation reaction would be expected to proceed by initial co-ordination of the ligand in a folded configuration as this would allow the sequential replacement of co-ordinated water molecules. Previous stopped-flow studies[12,13] have shown that the rates of formation of macrocyclic nickel(II) complexes in dipolar aprotic solvents are similar to those for linear tetramines. In addition, some evidence[12] was obtained in the macrocyclic reactions for intermediates which are likely to be the folded *cis* complexes. The reaction of copper(II) with *rac*-L^4 (C-racemic-L^4) is also known to give initially a folded blue complex which slowly converts to the planar red species in basic solution.[14] The incorporation of nickel(II) into a 14-membered tetra-aza ligand such as cyclam (L^1) can be represented by the series of reactions shown in the Scheme. Wu and Kaden[15] have recently studied reaction (1) in some detail. In the pH range 7—8 the only kinetically significant process is equation (4), with

$$[Ni(H_2O)_6]^{2+} + HL^+ \longrightarrow cis\text{-}[NiL(H_2O)_2]^{2+} + H^+ \quad (4)$$

$k = 58\ dm^3\ mol^{-1}\ s^{-1}$ at 25 °C. The analogous reaction with $[Ni(H_2O)_4(en)]^{2+}$ has $k = 75\ dm^3\ mol^{-1}\ s^{-1}$. For cyclam, reaction (2) has $k_{OH} = 6.5 \times 10^2\ dm^3\ mol^{-1}\ s^{-1}$, and at pH 8.05 the half-life of reaction (2) is *ca.* 10.7 min. Reaction (3) involves the equilibrium octahedral $\rightleftharpoons$ planar where $K = 2.45$, and there is 29% of the *trans*-octahedral complex at equilibrium at 25 °C.[16] For *trans*-$[NiL^1(H_2O)_2]^{2+}$ the water-exchange rate $(2.1 \pm 0.4) \times 10^7\ s^{-1}$ per water molecule corresponds to a minimum relaxation time of the equilibrium planar $\rightleftharpoons$ octahedral of 80 ± 30 ns.[17] This estimate is within the experimental error of the minimum of 10^{-7} s observed in recent ultrasonic experiments.[18] It has been suggested[18] that nearly concerted loss and addition of two water molecules occurs with NiL^1, with rate constants k_f and $k_r > 10^7\ s^{-1}$.

$$[Ni(H_2O)_6]^{2+} + H_nL^{n+} \longrightarrow cis\text{-}[NiL(H_2O)_2]^{2+} + nH^+ \quad (1)$$

$$cis\text{-}[NiL(H_2O)_2]^{2+} \xrightarrow[k_{OH}]{OH^-} trans\text{-}[NiL(H_2O)_2]^{2+} \quad (2)$$

$$trans\text{-}[NiL(H_2O)_2]^{2+} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \underset{\text{planar}}{[NiL]^{2+}} + 2H_2O \quad (3)$$

Scheme. Reactions involved in the formation of the planar nickel(II) complex of cyclam (n = 0 or 1)

Table 6. Isomerisation of *cis*-$[NiL^1(H_2O)_2]^{2+}$ in sodium hydroxide solutions at 25 °C and I = 0.1 mol dm^{-3} ($NaClO_4$)

$[OH^-]$/ mol dm^{-3}	pH[a]	$k_{obs.}$[b]/ s^{-1}	$10^{-2}k_{OH}$/ $dm^3\ mol^{-1}\ s^{-1}$
0.01	11.89	6.1	6.1
0.02	12.19	11.7	5.9
0.025	12.28	15.1	6.0
0.03	12.36	18.0	6.0
0.035	12.43	21.1	6.0
0.04	12.49	23.9	6.0
0.045	12.54	27.1	6.0
0.05	12.59	30.0	6.0

[a] pH Estimated using an activity coefficient of 0.77 and pK_w = 14.00.
[b] Average values of at least six kinetic runs.

Table 7. Isomerisation of *cis*-$[NiL^1(H_2O)_2]^{2+}$ in sodium hydroxide solutions at 25 °C and I = 1.0 mol dm^{-3} ($NaClO_4$)

$[OH^-]$/ mol dm^{-3}	$k_{obs.}$/ s^{-1}	$10^{-2}k_{OH}$/ $dm^3\ mol^{-1}\ s^{-1}$
0.01	5.9	5.9
0.02	11.8	5.9
0.03	17.7	5.9
0.04	23.8	5.9
0.05	29.5	5.9

Mechanistic Considerations.—The reaction of *cis*-$[NiL(H_2O)_2]^{2+}$ (L = L^1—L^3) to give the *trans* isomer is catalysed by base. The reaction could occur by either an intermolecular pathway or by an intramolecular pathway involving a hydroxo complex. An intramolecular pathway has been observed in the base-catalysed isomerisation of $[Cu(rac\text{-}L^4)]^{2+}$ (blue) to $[Cu(rac\text{-}L^4)]^{2+}$ (red)[14] and in the analogous blue to red isomerisation of the copper(II) *meso*-L^4 complex.[19] The pK_a values of aqua nickel(II) complexes probably lie in the range *ca.* 10—12 {*e.g.* pK_a = 9.86 for $[Ni(H_2O)_6]^{2+}$}.[20] The concentration of any hydroxo complex in the pH range 7—8 will thus be directly proportional to the hydroxide ion concentration and isomerisation *via* a hydroxo complex will display a first-order dependence on the hydroxide ion concentration. At higher pH where the hydroxo complex is fully formed the intermolecular reaction will become independent of the hydroxide ion concentration. For this reason the base-catalysed isomerisation of *cis*-$[NiL^1(H_2O)_2]^{2+}$ was studied using sodium hydroxide solutions in the pH range 11.9—12.6, using stopped-flow techniques, Table 6. At high pH the reaction also displays a clean first-order dependence on the hydroxide ion with $k_{OH} = 600\ dm^3\ mol^{-1}\ s^{-1}$ at 25 °C and I = 0.1 mol dm^{-3}. This rate constant may be compared with $k_{OH} = 650 \pm 50\ dm^3\ mol^{-1}\ s^{-1}$ obtained using buffer solutions in the pH range 7.5—8.5. The stopped-flow measurements do not exclude an intramolecular process involving attack of co-ordinated hydroxide at the *sec*-NH centres, but indicate that if it applies, there must be less than 10% conversion to the active hydroxo species at pH 12.6.

The intermolecular reaction of hydroxide ion with the *sec*-NH centres of the dication *cis*-$[NiL^1(H_2O)_2]^{2+}$ would be expected to display a substantial negative salt effect. For this reason, the stopped-flow studies were also carried out at the higher ionic strength of 1.0 mol dm^{-3}, Table 7. The value of k_{OH} = 590 dm^3 mol^{-1} s^{-1} at 25 °C and I = 1.0 mol dm^{-3} and is essentially identical to that obtained at I = 0.1 mol dm^{-3}. There is no significant ionic strength effect in the reaction. This result is consistent with an intramolecular process.

In basic solution it is necessary to consider the possible equilibria (5) and (6). If significant quantities of the hydroxo

$$cis\text{-}[NiL^1(H_2O)_2]^{2+} \rightleftharpoons cis\text{-}[NiL^1(H_2O)(OH)]^+ + H^+ \quad (5)$$

$$cis\text{-}[NiL^1(H_2O)(OH)]^+ \rightleftharpoons cis\text{-}[NiL^1(OH)_2]^0 + H^+ \quad (6)$$

complexes are present in the pH range 11.9—12.6 used in the stopped-flow measurements, the intermolecular process would require that hydroxide ion attacks the *sec*-NH function of all three species at the same rate. Such a result is possible, but rather unlikely. In addition, significant negative salt effects would be expected if the diaqua or aqua hydroxo complexes were present in appreciable amounts at pH 12. In the absence of the requisite pK data it is difficult to come to definitive conclusions regarding the mechanism, but an intramolecular process may well occur. Negative values of $\Delta S^\ddagger$ would be expected in both reaction pathways, and this parameter is probably not diagnostic of mechanism in this system.

Acknowledgements

We thank the S.E.R.C. for financial support.

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Received 18*th December* 1984; *Paper* 4/2141