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LETTER

Base catalysed isomerisation of *cis*-$[Ni(cyclam)(OH_2)_2]^{2+}$ in strongly basic solution. Evidence for an intramolecular isomerisation process

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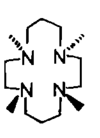
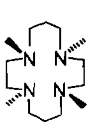
Planar yellow $[Ni(cyclam)]^{2+}$ will readily fold on addition of ethylenediamine to an aqueous solution of the complex to give the violet *cis*-$[Ni(cyclam)(en)]^{2+}$ which can be [1] characterised as the perchlorate salt. Addition of HBr to *cis*-$[Ni(cyclam)(en)]^{2+}$ gives the bromide *cis*-$[Ni(cyclam)Br_2]$ which rapidly hydrolyses to *cis*-$[Ni(cyclam)(OH_2)_2]^{2+}$ in aqueous solution. The *cis* complexes have the *cis*-V configuration (**1**) while the most stable configuration of the *trans* complexes is *trans*-III (**2**)**. The V configuration gives higher energy *trans* structures having two twist boat six-membered rings (T) and two gauche (g) five-membered rings (**3**). However the V configuration can readily fold to give *cis* complexes (**4**). The III configuration gives the most thermodynamically stable *trans* complexes (**5**) with two chair six-membered rings and two gauche five-membered rings. However this configuration cannot 'fold' to give *cis* complexes as this requires the diagonal N–H groups to both lie above or below the plane of the macrocycle.



1

V configuration
(+ − + −)



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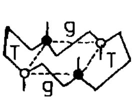
III configuration
(+ − − +)



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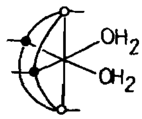

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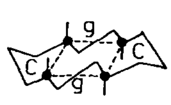

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At pH 8–9 *cis*-$[Ni(cyclam)(OH_2)_2]^{2+}$ slowly converts to planar $[Ni(cyclam)]^{2+}$ which is in equilibrium with some 30% of the octahedral *trans*-$[Ni(cyclam)(OH_2)_2]^{2+}$ with the III configuration. The *trans*-III isomer has been shown to be in rapid diamagnetic ⇌ paramagnetic equilibrium by ^{17}O NMR [3]. Recent investigations by Connolly and Billo indicate that the *trans*-III(planar) ⇌ *trans*-I(planar) equilibrium does occur to a limited extent (15% at 25 °C) with $\Delta H° = 1.2 \pm 0.3$ kcal mol^{-1} and $\Delta S° = 1.0 \pm 0.3$ cal K^{-1} mol^{-1} [4]. The base catalysed isomerisation of *cis*-$[Ni(cyclam)(OH_2)_2]^{2+}$ follows the rate law, rate $= k_{OH}[complex][OH^-]$ [1]. Such a rate law could arise due to attack by 'external' hydroxide on the *sec*-NH groups or intramolecular attack by coordinated hydroxide. Nickel(II) complexes of a number of N_4 macrocycles are known to form brown hydroxo complexes at high pH [5–7] and such complexes could be involved in the isomerisation process. The isomerisation of $[Cu(tet\ b)(blue)]^{2+}$ which involves *sec*-NH inversion has been shown to occur by an intramolecular process involving coordinated hydroxide [8]. The rate of isomerisation becomes independent of the hydroxide ion concentration above pH 12 due to complete formation of the reactive hydroxo complex.

For this reason we have studied the base catalysed isomerisation *cis*-$[Ni(cyclam)(OH_2)_2]^{2+} \rightarrow [Ni(cyclam)^{2+}]$(planar) in the pH range 7–8, and in very basic solution ($[OH^-] = 5 \times 10^{-3}$ M to 0.05 M) in an attempt to define the mechanism of the reaction.

Experimental

Cyclam and $Ni(cyclam)(ClO_4)_2$ were prepared as described by Barefield *et al.* [3].

cis-[Ni(cyclam)(en)](ClO$_4$)$_2$

Excess ethylenediamine (five-fold) was added dropwise to an aqueous solution of $[Ni(cyclam)](ClO_4)_2$ to give a violet solution. Sodium perchlorate was added to give crystals of the violet *cis*-$[Ni(cyclam)(en)](ClO_4)_2$. *Anal.* Calc. for Ni-

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**The five possible planar conformers of cyclam(1,4,8,11-tetra-azacyclotetradecane) are *trans*-I(+ + + +), *trans*-II(+ − + +), *trans*-III(+ − − +), *trans*-IV(+ + − −) and *trans*-V(+ − + −) where + indicates the hydrogen of the NH group is above the plane of the macrocycle and − indicates that it is below [2].

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$C_{12}H_{32}N_6Cl_2O_8$: C, 27.8; H, 6.2; N, 16.2. Found: C, 27.8; H, 6.1; N, 16.1%.

cis-[Ni(cyclam)Br$_2$]

A suspension of [Ni(cyclam)(en)]$(ClO_4)_2$ in boiling methanol was acidified with conc. HBr, giving blue *cis*-[Ni(cyclam)Br_2].

Stopped flow measurements were made with a HI-TECH instrument interfaced with a transient recorder and Apple II microcomputer. Kinetic measurements in the pH range 7–8 were monitored at 450 nm using a Phillips 8256 spectrophotometer. The pH was controlled by tris-HCl buffers adjusted to $I = 0.1$ M. The hydroxide ion concentrations were derived from the pH using $pK_W = 13.9965$ at 25 °C and an activity coefficient of 0.772 derived from the Davies' equation [9].

Results and discussion

The isomerisation of *cis*-$[Ni(cyclam)(OH_2)_2]^{2+}$ to planar $[Ni(cyclam)]^{2+}$ was monitored at 450 nm which is λ_{max} for the planar complex. Plots of $\ln(A_\infty - A_t)$ versus time were linear for several half lives and values of k_{obs} (the observed first order rate constant at constant pH) were obtained from the slope of such plots. The rate constants obtained as a function of pH are summarised in Table 1. A plot of k_{obs} versus $[OH^-]$ is linear (Fig. 1), with a positive intercept indicating that a spontaneous solvolytic isomerisation also occurs in addition to the base catalysed reaction.

A similar observation was also made by Billo [1]. The slope of the plot gives $k_{OH} = 390 \pm 20$ M^{-1} s^{-1} at 25 °C and $I = 0.1$ M. This rate constant is somewhat lower than the constant $k_{OH} = 560$ M^{-1} s^{-1} reported by Billo, but the discrepancy appears to be primarily due to the different methods employed to calculate the hydroxide ion concentrations from the buffer pH.

TABLE 1. Isomerisation kinetics of *cis*-[Ni(cyclam)-$(OH_2)_2]^{2+}$ in the pH range 7.3–8.3 at $I = 0.1$ M (tris buffer) and 25 °C

pH	$10^7 \times [OH^-]$ (M)	$10^4 \times k_{obs}$ (s^{-1})
7.35	2.92	1.62
7.54	4.53	2.31
7.72	6.85	3.30
7.90	10.37	4.76
8.06	15.00	6.37
8.26	23.76	9.79
8.31	26.66	10.34

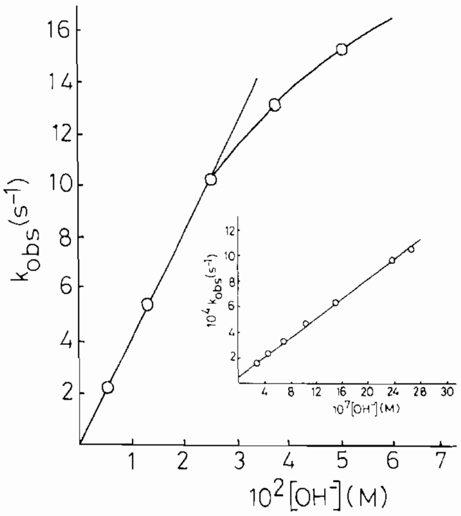


Fig. 1. Plot of k_{obs} vs. the hydroxide ion concentration at low and high base concentrations (25 °C and $I = 0.1$ M).

TABLE 2. Stopped flow kinetics for the base catalysed isomerisation of *cis*-$Ni(cyclam)(OH_2)_2^{2+}$ at $I = 0.1$ M and 25 °C

[NaOH] (M)	k_{obs} (s^{-1})
0.005	2.25
0.0125	5.39
0.025	10.25
0.0375	13.10
0.05	15.30

The complex concentration employed in the kinetic runs was 5×10^{-3} M. The quoted values of k_{obs} are the average of at least five kinetic experiments. For example, at $[OH^-] = 0.05$ M, the values of k_{obs} obtained were 15.35, 15.34, 15.25, 15.18 and 15.39 s^{-1}.

Stopped flow measurements were made using hydroxide solutions in the concentration range 0.005–0.05 M and the values of the rate constants obtained are summarised in Table 2. A plot of k_{obs} versus $[OH^-]$ is initially linear, but beyond an hydroxide ion concentration of 0.025 M pronounced curvature is observed (Fig. 1). The slope of the initial linear portion of the plot gives $k_{OH} = 410 \pm 20$ M^{-1} s^{-1} in good agreement with the constant 390 ± 10 M^{-1} s^{-1} determined in buffer solutions at 25 °C and $I = 0.1$ M.

The curvature at high hydroxide ion concentrations can be rationalised in terms of the reaction scheme

$$cis\text{-}[Ni(cyclam)(OH_2)_2]^{2+} + OH^- \xrightleftharpoons{K} cis\text{-}[Ni(cyclam)OH]^+ + 2H_2O$$

$$cis\text{-}[Ni(cyclam)OH]^+ \xrightarrow{k} \text{planar } [Ni(cyclam)]^{2+} + OH^-$$

The resulting rate expression is given by eqn. (1)

$$\mathrm{d[planar\ Ni(cyclam)^{2+}]}/\mathrm{d}t = k_{\mathrm{obs}}[\mathrm{Ni(cyclam)}]_{\mathrm{total}} = \frac{kK[\mathrm{OH^-}][\mathrm{Ni(cyclam)}]_{\mathrm{total}}}{(1+K[\mathrm{OH^-}])} \qquad (1)$$

so that $k_{\mathrm{obs}} = kK[\mathrm{OH^-}]/(1+K[\mathrm{OH^-}])$ (2)

where $[\mathrm{Ni(cyclam)}]_{\mathrm{total}} = [cis\text{-}[\mathrm{Ni(cyclam)(OH_2)^{2+}}] + [cis\text{-}[\mathrm{Ni(cyclam)OH}]^+$.

Using eqn. (2) it can readily be shown that

$$\frac{1}{k_{\mathrm{obs}}} = \frac{1}{k} + \frac{1}{kK} \times \frac{1}{[\mathrm{OH^-}]}$$

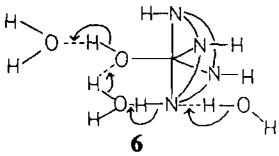
A plot of $1/k_{\mathrm{obs}}$ versus $1/[\mathrm{OH^-}]$ should be linear of slope $1/kK$ and intercept $1/k$. Such a plot is indeed linear (Fig. 2), giving $k = 40\ \mathrm{s^{-1}}$ (the limiting value of k_{obs}) and $k = 12\ \mathrm{M^{-1}}$ at 25 °C. The equilibrium constant of $12\ \mathrm{M^{-1}}$ indicates that with a complex concentration of 5×10^{-3} M used in the stopped flow measurements and $[\mathrm{OH^-}] = 0.025$ M some 20% conversion to the hydroxo complex occurs. In 1 M hydroxide the hydroxo complex is essentially completely formed (92%).

Hydroxo complexes of nickel(II) macrocycles are considered to be five-coordinate [5, 6], and the formation of green nickel(II) complexes as a result of the equilibrium

$$\underset{\text{blue}}{[\mathrm{NiL(H_2O)_2}]^{2+}} + \mathrm{OH^-} \rightleftharpoons \underset{\text{green}}{[\mathrm{NiL(OH)}]^{2+}} + 2\mathrm{H_2O}$$

has previously been observed with a variety of tetraazamacrocyclic ligands [5–7].

The base catalysed conversion of *cis*-$[\mathrm{Ni(cyclam)(OH_2)_2}]^{2+}$ to the planar complex probably occurs by a similar mechanism to that previously reported for the base catalysed conversion of [Cu(tet *b*)(blue)]$^{2+}$ to [Cu(tet *b*)(red)]$^{2+}$ (tet *b* = C-*rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane). This latter reaction involves coordinated hydroxide and the conversion of the folded tet *b* ligand in the *trans*-V configuration to the planar *trans*-III configuration. Margerum and co-workers [8] have suggested that the conversion involves a mechanism of the type shown in **6** and this process seems quite appropriate for the present system.



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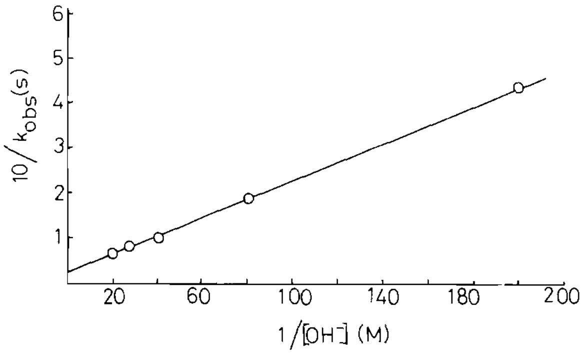

Fig. 2. Double reciprocal plot for the base catalysed isomerisation at high hydroxide ion concentrations.

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