In memory of S. M. Nelson

Synthetic and Equilibrium Studies on Copper(II), Nickel(II), and Palladium(II) Complexes of *N,N′,N″,N‴*-Tetrakis(2-hydroxyethyl)-1,4,8,11-tetra-azacyclotetradecane (L); Kinetics of the Acid Dissociation of the Copper(II) Complex and *X*-Ray Structural Characterisation of the Nickel(II) Complex $[NiLH_{-1}][ClO_4]$†

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The preparation of the macrocyclic ligand *N,N′,N″,N‴*-tetrakis(2-hydroxyethyl)-1,4,8,11-tetra-azacyclotetradecane (L) by reaction of ethylene oxide with cyclam (1,4,8,11-tetra-azacyclotetradecane) is described. The pK_a values of L at 25 °C and $I = 0.1$ mol dm^{-3} ($NaClO_4$) are $pK_1 = 8.83$, $pK_2 = 8.30$, $pK_3 = 2.65$, $pK_4 < 2$. The ligand forms very stable complexes with copper(II) and palladium(II) of the type $[ML]^{2+}$ with log $\beta_{110} = 16.20$ for copper(II) and 18.32 for palladium(II). The equilibria with nickel(II) can be represented by (i)—(iii), as follows.

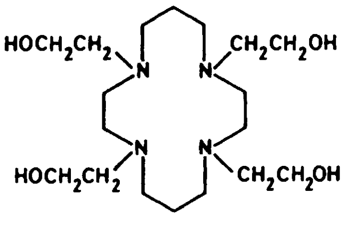
$$Ni^{2+} + L \rightleftharpoons [NiL]^{2+}; \quad \log \beta_{110} = 7.45(1) \qquad (i)$$

$$Ni^{2+} + L \rightleftharpoons [NiLH_{-1}]^{+} + H^{+}; \quad \log \beta_{11-1} = -1.42(1) \qquad (ii)$$

$$Ni^{2+} + L \rightleftharpoons [NiLH_{-2}] + 2H^{+}; \quad \log \beta_{11-2} = -12.39(2) \qquad (iii)$$

The p*K* values of $[NiL]^{2+}$ are 8.87 and 10.97 at 25 °C. The complex $[NiLH_{-1}][ClO_4]$ ($C_{18}H_{39}ClN_4NiO_8$) has been characterised in the solid state and its crystal structure determined. In 0.1 mol dm^{-3} sodium hydroxide solution $E_{\frac{1}{2}}$ for the nickel(III)–nickel(II) couple is +0.28 V, one of the lowest values recorded for a macrocyclic complex. Unlike complexes of cyclam, complexes of L are rapidly formed and dissociate readily in acidic solution. Stopped-flow studies of the dissociation of the copper(II) complex in the acidity range 0.015—0.50 mol dm^{-3} $HClO_4$ establish that rate = $k_H[CuL^{2+}][H^+]$ with $k_H = 3.44$ dm^3 mol^{-1} s^{-1} at 25 °C and $I = 1.0$ mol dm^{-3}. The copper(II) and nickel(II) complexes $[ML][ClO_4]_2$ have been characterised in the solid state and their spectral properties are reported.

The macrocyclic ligand *N,N′,N″,N‴*-tetrakis(2-hydroxyethyl)-1,4,8,11-tetra-azacyclotetradecane (L) was first characterised in 1984,[1,2] and displays many novel properties. For example, L reacts rapidly with metal ions such as copper(II) and nickel(II) and the resulting complexes dissociate readily in acidic solution. The parent ligand 1,4,8,11-tetra-azacyclotetradecane (cyclam) equilibrates extremely slowly with the very labile copper(II) ion and $[Cu(cyclam)]^{2+}$ is not decomposed in 6 mol dm^{-3} HCl over a period of several weeks.[3] The half life of $[Ni(cyclam)]^{2+}$ in 1 mol dm^{-3} $HClO_4$ has recently been shown by Billo[4] to be *ca.* 30 years. Since the initial work of Barefield and Wagner[5] on complexes of *N,N′,N″,N‴*-tetramethyl-1,4,8,11-tetra-azacyclotetradecane (L′) it has been recognised that N-alkylation of cyclam leads to increased lability of the complexes in both formation and dissociation reactions, although this aspect of their chemistry has not been pursued in detail. Enhanced kinetic lability will be of considerable importance in the commercial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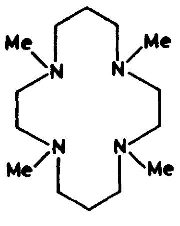
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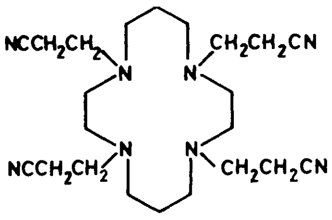
L″

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii–xx.

development of macrocyclic ligands in areas such as hydrometallurgy and metal detoxification.

We have previously shown[6] that the copper(II) complex of N,N',N'',N'''-tetrakis(2-cyanoethyl)-1,4,8,11-tetra-azacyclotetradecane (L″) dissociates readily in acidic solution, although interestingly the ligand only equilibrates very slowly with copper(II).[2]

The present paper discusses various aspects of the co-ordination chemistry of copper(II), nickel(II), and palladium(II) with L.

Experimental

Cyclam was prepared using previously described procedures.[7]

N,N',N'',N'''-Tetrakis(2-hydroxyethyl)-1,4,8,11-tetra-azacyclotetradecane monohydrate was prepared as follows. Cyclam (1g) was dissolved in water (*ca.* 25 cm^3) and the solution cooled to 0 °C in an ice-bath. Ethylene oxide (6 cm^3) was added and the mixture stirred at 0 °C for 2 h. The initially formed solid hydrate or clathrate of ethylene oxide dissolved during this period to give a clear solution. The solvent was removed on a rotary evaporator to give a yellowish oily residue. The oil crystallised on stirring with the minimum quantity of cold water followed by refrigeration, m.p. 111—112 °C (Found: C, 54.7; H, 10.35; N, 14.4; H_2O, 4.8. Calc. for $C_{18}H_{40}N_4O_4{\cdot}H_2O$: C, 54.8; H, 10.2; N, 14.2; H_2O, 4.6%). The water content was determined by thermogravimetric analysis. The i.r. spectrum (KBr disc) lacks the ν(NH) bands which occur in cyclam at 3 182 and 3 265 cm^{-1},[7] but gives a sharp band at 3 420 cm^{-1} assigned to ν(OH). The ^{13}C n.m.r. spectrum is fully consistent with the expected structure ($CDCl_3$ solvent and $SiMe_4$ reference) with signals at δ 25.49 (–CH_2–*C*H_2–CH_2–), 49.50 (–*C*H_2–CH_2–), 52.18 (–*C*H_2–CH_2–CH_2), 55.98 (*C*H_2–N), and 59.55 (*C*H_2–N). The latter four signals are of approximately equal intensity and are roughly twice the intensity of the signal at δ 25.49.

Recrystallisation of the ligand from propan-2-ol gives the anhydrous material, m.p. 121—122 °C (Found: C, 57.1; H, 10.8; N, 14.6: Calc. for $C_{18}H_{40}N_4O_4$: C, 57.3; H, 10.7; N, 14.8%).

Synthesis of Metal Complexes of L.—The copper(II) complex $[CuL][ClO_4]_2$ was prepared as follows. Copper(II) perchlorate hexahydrate (0.2 g) in ethanol (5 cm^3) was added to a solution of the ligand (0.2 g) in ethanol (5 cm^3). The mixture was heated on a steam-bath for *ca.* 15 min. On cooling the blue complex crystallised. It was filtered off, washed with diethyl ether–ethanol (1:1), then diethyl ether and air dried (yield 0.2 g) (Found: C, 34.1; H, 6.4; N, 8.7. Calc. for $C_{18}H_{40}Cl_2CuN_4O_{12}$: C, 33.8; H, 6.3; N, 8.9%). Replacing copper(II) perchlorate with copper(II) chloride gave deep green crystals of $CuLCl_2$.

The nickel(II) complex $[NiL][ClO_4]_2$ was prepared essentially as described for the copper(II) derivative using nickel(II) perchlorate hexahydrate (0.2 g). The complex was recrystallised from methanol to give large blue crystals on slow evaporation.

Slow evaporation of an aqueous solution containing equimolar amounts of $Ni(ClO_4)_2$, L, and sodium hydroxide gave blue prismatic crystals of $[NiLH_{-1}][ClO_4]$. One crystal of approximate dimensions 0.44 × 0.48 × 0.73 mm was used for the *X*-ray structure analysis.

Crystal-structure Determination.—Crystal data. $C_{18}H_{39}ClN_4NiO_8$, $M = 530.65$, triclinic, $a = 12.243\,0(10)$, $b = 9.571\,7(9)$, $c = 11.037\,3(7)$ Å, $\alpha = 104.532(6)$, $\beta = 102.496(7)$, $\gamma = 107.072(8)^\circ$, $U = 1\,136.6$ Å^3 (by least-squares refinement on diffractometer angles for 40 automatically centred reflections, $\lambda = 0.710\,69$ Å), space group $P\bar{1}$, $Z = 2$, $D_c = 1.56$ g cm^{-3}, $\mu = 10.25$ cm^{-1}.

Data collection and processing. Philips PW 1 100 diffractometer, ω–2θ mode, scan width = 1.8°, scan speed = 3.6° min^{-1}, graphite-monochromated Mo-K_α radiation; 6 687 reflections measured with profile analysis[8] ($2 \leqslant \theta \leqslant 30^\circ$) giving 4 764 with $I \geqslant 5\sigma(I)$. Empirical absorption correction using ψ scans[9] was applied (max, min. transmission factors = 1.00, 0.93). No significant variation was observed in three standard reflections monitored at 4 h intervals.

Structure analysis and refinement. The structure was solved by the heavy-atom method and anisotropically refined by full-matrix least squares with a modified version of the computer program ORFLS.[10] All the hydrogen atoms were located in a difference Fourier synthesis and were included in the refinement with isotropic thermal parameters; they all converged to very reasonable co-ordinates and isotropic thermal parameters, with the exception of two out of the three hydrogens belonging to the hydroxyl groups which were therefore excluded from the final least-squares cycle. The electron density around the position of these two hydrogen atoms was in fact greatly smeared, very likely as a result of some positional disorder. Final R and R' values are 0.034, 0.037; the function minimized was $\Sigma w(F_o - F_c)^2$ with $w = 1/\sigma^2(F_o)$, with $\sigma(F_o)$ from counting statistics. The scattering factors used were taken from ref. 11. Final fractional co-ordinates for the non-hydrogen atoms are given in Table 1; selected interatomic distances and angles are collected in Table 2.

Potentiometric Measurements.—The potentiometric titrations of the ligand (L) in the presence and in the absence of metal ions (as perchlorate salts for Cu^{II} and Ni^{II}, nitrate salt for Pd^{II}) were carried out in an automatic system controlled by an Apple IIe computer and consisting of: (*i*) a Radiometer PHM84 research pH meter, using a Beckman Futura glass electrode and an Ingold saturated sodium chloride–calomel reference

Table 1. Fractional atomic co-ordinates with estimated standard deviations in parentheses for the non-hydrogen atoms of $[NiLH_{-1}][ClO_4]$

Atom	*x*	*y*	*z*
Ni(A)	0.500 0	0	0.500 0
Ni(B)	0	0	0
Cl	0.664 1	0.477 8(1)	0.197 9(1)
O(1)	0.646 0	0.398 5(4)	0.068 7(3)
O(2)	0.743 4(3)	0.424 1(3)	0.276 6(3)
O(3)	0.562 8(3)	0.450 2(3)	0.241 0(3)
O(4)	0.726 4(2)	0.641 1(2)	0.231 3(2)
N(1A)	0.429 8(1)	0.018 7(2)	0.668 4(2)
C(2A)	0.480 0(2)	0.189 3(3)	0.739 9(2)
C(3A)	0.608 4(2)	0.261 5(2)	0.742 0(2)
N(4A)	0.618 2(1)	0.229 6(2)	0.605 8(2)
C(5A)	0.744 1(2)	0.246 9(3)	0.612 5(2)
C(6A)	0.767 1(2)	0.201 1(3)	0.479 6(2)
C(7A)	0.703 2(2)	0.032 4(3)	0.391 9(2)
C(8A)	0.581 4(2)	0.336 4(2)	0.543 5(2)
C(9A)	0.445 6(2)	0.277 1(3)	0.476 1(2)
O(10A)	0.396 2(1)	0.112 8(2)	0.426 5(1)
C(11A)	0.450 5(2)	−0.066 6(3)	0.762 8(2)
C(12A)	0.573 6(2)	−0.010 0(3)	0.865 1(2)
O(13A)	0.666 8(1)	−0.021 9(2)	0.812 0(1)
N(1B)	−0.001 5(2)	0.108 2(2)	0.201 1(2)
C(2B)	0.047 8(2)	0.030 4(3)	−0.239 7(2)
C(3B)	−0.007 3(2)	0.147 4(3)	−0.192 7(2)
N(4B)	0.021 1(1)	0.201 5(2)	−0.047 4(2)
C(5B)	−0.064 8(2)	0.274 0(3)	−0.011 2(3)
C(6B)	−0.056 8(2)	0.319 4(3)	0.134 0(3)
C(7B)	−0.088 4(2)	0.188 8(3)	0.190 4(2)
C(8B)	0.147 2(2)	0.315 3(3)	0.016 9(2)
C(9B)	0.239 6(2)	0.239 7(3)	0.043 5(2)
O(10B)	0.185 5(1)	0.095 8(2)	0.059 9(1)
C(11B)	0.118 3(2)	0.214 8(3)	0.298 7(2)
C(12B)	0.121 9(3)	0.309 3(5)	0.434 8(3)
O(13B)	0.090 3(3)	0.225 8(4)	0.509 3(3)

Table 2. Selected bond distances (Å) and angles (°) with estimated standard deviations in parentheses for $[NiLH_{-1}][ClO_4]$

	Subunit A	Subunit B
Ni-O(10)	2.059(2)	2.063(1)
Ni-N(4)	2.098(2)	2.081(2)
Ni-N(1)	2.201(2)	2.207(2)
N(1)-C(2)	1.491(3)	1.487(3)
C(2)-C(3)	1.512(4)	1.511(4)
C(3)-N(4)	1.495(3)	1.483(3)
N(4)-C(5)	1.485(3)	1.490(3)
C(5)-C(6)	1.533(4)	1.525(4)
C(6)-C(7)	1.518(3)	1.520(4)
C(7)-N(1)	1.495(3)	1.489(4)
N(1)-C(11)	1.500(3)	1.496(2)
C(11)-C(12)	1.522(3)	1.530(4)
C(12)-O(13)	1.411(3)	1.323(6)
N(4)-C(8)	1.487(3)	1.492(2)
C(8)-C(9)	1.529(3)	1.528(4)
C(9)-O(10)	1.416(3)	1.417(3)
N(4)-Ni-O(10)	81.3(1)	81.0(1)
N(1)-Ni-O(10)	90.1(1)	91.0(1)
N(1)-Ni-N(4)	94.4(1)	93.7(1)
C(2)-N(1)-C(7)	108.8(2)	111.0(2)
C(2)-N(1)-C(11)	110.3(2)	109.4(2)
C(7)-N(1)-C(11)	107.3(2)	111.2(2)
C(3)-N(4)-C(5)	109.0(2)	109.2(2)
C(3)-N(4)-C(8)	111.0(2)	110.4(2)
C(5)-N(4)-C(8)	110.4(2)	110.2(2)

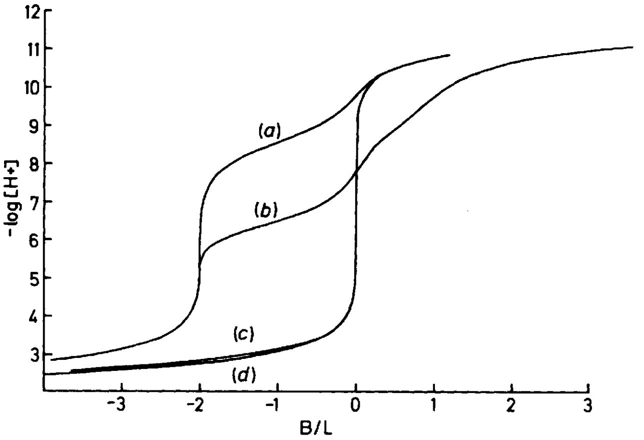

Figure. 1. Titration curves for (*a*) L + H^+, (*b*) L + H^+ + Ni^{2+}, (*c*) L + H^+ + Cu^{2+}, and (*d*) L + H^+ + Pd^{2+}. B/L is the ratio of moles of standard base added, B, to the moles of ligand, L. Negative values indicate excess of acid (*e.g.* -1 = 1 equivalent of standard acid)

electrode fitted in an Ingold cell system; (*ii*) a Radiometer ABU80 autoburette; (*iii*) a Metrohm thermostatted cell; and (*iv*) a Huber MINISTAT digital thermostat.

The temperature was maintained at 25.0 ± 0.1 °C. Each titration was performed on a 50 cm^3 solution adjusted to 0.1 mol dm^{-3} ionic strength with $NaClO_4$. Direct measurements of the hydrogen ion concentration were made.[12a] Typical concentrations of the ligands and metal ions (in a 1:1 molar ratio) were in the range (0.5—1.0) × 10^{-3} mol dm^{-3}. The details of the experimental procedure have been extensively described elsewhere.[13] The data were processed on a VAX 11/780 computer using the MINIQUAD[14] and SUPERQUAD[15] programs and the constants expressed in terms of concentration quotients.[12b] Typical titration curves are shown in Figure 1.

Table 3. pK_a values of some 14-membered tetra-aza macrocycles at 25 °C

	cyclam[a]	L′[b]	L[c]
pK_1	11.59	9.34	8.83
pK_2	10.62	8.99	8.30
pK_3	1.61	2.58	2.65
pK_4	2.42	2.25	<2

[a] M. Micheloni, A. Sabatini, and P. Paoletti, *J. Chem. Soc., Perkin Trans. 2*, 1978, 828. [b] B. S. Nakani, J. J. B. Welsh, and R. D. Hancock, *Inorg. Chem.*, 1983, **22**, 2956. [c] This work; the constants quoted in ref. 2 are pK_1 = 8.80, pK_2 = 8.24, pK_3 = 2.69, and pK_4 ~ 1.2 at 25 °C in 0.1 mol dm^{-3} $NaNO_3$.

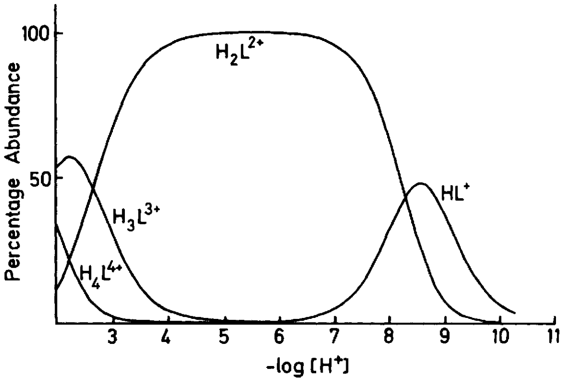

Figure 2. Speciation curves for ligand protonation

Spectrophotometric Titrations.—The spectrophotometric titrations of the Ni^{II} complex with L were run on a Perkin-Elmer Lambda 5 instrument. The initial solution was a 25-cm^3 aliquot of 2 × 10^{-3} mol dm^{-3} L and 2 × 10^{-3} mol dm^{-3} Ni^{II} (perchlorate salt) adjusted to I = 0.1 mol dm^{-3} with $NaClO_4$. Measurements were made at 25 °C and spectra scanned from 300 to 900 nm. The pH measurements were made using a Radiometer PHM26 instrument. The pH was adjusted by the dropwise addition of 6 mol dm^{-3} NaOH to the 25-cm^3 aliquot.

Kinetic Measurements.—Kinetic studies of the acid dissociation of $[CuL]^{2+}$ were carried out using $HClO_4$ solution adjusted to I = 1.0 mol dm^{-3} with $NaClO_4$. Measurements were made at 25 °C with a Durrum stopped-flow spectrophotometer equipped with a Datalab DL901 transient recorder on line with a Commodore computer. Rate constants were calculated on line as pseudo-first-order rates. The reaction was monitored using the absorbance decrease at 627 nm.

Electrochemistry.—Cyclic voltammetry experiments were performed using a PAR 170 electrochemistry system. The concentration of the metal complexes was 1 × 10^{-3} mol dm^{-3}. Measurements with $[Ni(cyclam)]^{2+}$ were made using 0.1 mol dm^{-3} $NaClO_4$ or 0.5 mol dm^{-3} Na_2SO_4 as the supporting electrolyte. Measurements with $[NiLH_{-2}]$ were made on solutions 0.1 mol dm^{-3} in NaOH using a glassy carbon working electrode. Ill defined, poorly reversible profiles were obtained using a platinum working electrode. On glassy carbon, absorption phenomena were observed on multiple scans with $[NiLH_{-2}]$. A saturated calomel electrode (s.c.e.) was used as a reference electrode in all cases.

Results and Discussion

The ligand L is readily prepared by the reaction of cyclam with ethylene oxide in aqueous solution at 0 °C. The compound was

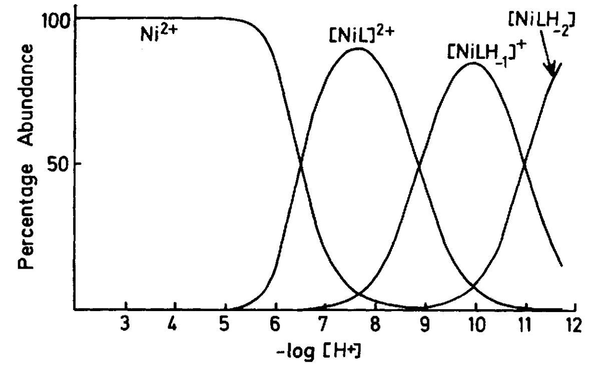

Figure 3. Speciation curves for nickel(II) complexes

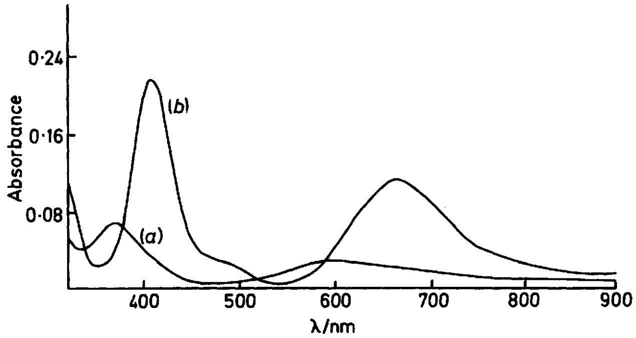

Figure 4. Visible spectra of the nickel(II) complex of L at (*a*) pH 7.72, $\lambda_{max.}$ 366 and 595 nm; (*b*) pH 10.03, $\lambda_{max.}$ 407 and 663 nm

isolated as a monohydrate by this procedure. Vacuum drying at 50 °C or recrystallisation from propan-2-ol gives the anhydrous material. The ligand behaves as a tetraprotic base, and the stepwise protonation equilibria were studied by potentiometric titration [equations (1)—(4)] at 25 °C and $I = 0.1$ mol dm^{-3}. The speciation curve is shown in Figure 2. A comparison of the p*K* data with that of cyclam and L′, Table 3, indicates that conversion of the secondary NH groups to tertiary groups by alkylation significantly lowers the basicity of the nitrogen atoms. A similar effect is observed with simple aliphatic amines,

$$H^+ + L \rightleftharpoons HL^+; \quad \log K_1 = 8.83(1) \qquad (1)$$

$$H^+ + HL^+ \rightleftharpoons H_2L^{2+}; \log K_2 = 8.30(1) \qquad (2)$$

$$H^+ + H_2L^{2+} \rightleftharpoons H_3L^{3+}; \log K_3 = 2.65(1) \qquad (3)$$

$$H^+ + H_3L^{3+} \rightleftharpoons H_4L^{4+}; \log K_4 < 2 \qquad (4)$$

thus the base strength of the methylamines in water follows the order $Me_2NH > MeNH_2 > Me_3N$ the appropriate pK_a values being 10.77, 10.64, and 9.80 respectively.[16] Secondary amines are normally somewhat stronger bases than primary amines while the introduction of a third alkyl group to give a tertiary amine markedly decreases the base strength. The base strength of an amine in water is determined not only by the electron availability at the nitrogen atom, but also by the extent to which the cation produced by protonation can undergo solvation by hydrogen bonding.

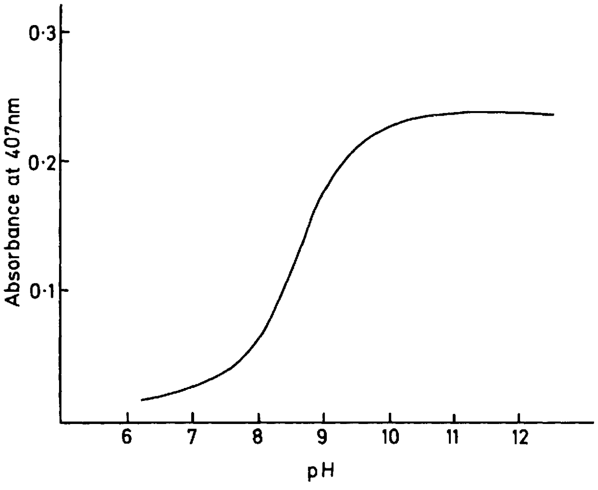

Figure 5. Spectrophotometric titration of [NiL]$^{2+}$ (2 × 10^{-3} mol dm^{-3}) at $I = 0.1$ mol dm^{-3} and 25 °C. Measurements at 407 nm. The estimated pK_a is 8.75

$$M^{2+} + L \rightleftharpoons [ML]^{2+} \qquad (5)$$

$$Ni^{2+} + L \rightleftharpoons [NiL]^{2+}; \qquad \log \beta_{110} = 7.45(1) \qquad (6)$$

$$Ni^{2+} + L \rightleftharpoons [NiLH_{-1}]^+ + H^+; \log \beta_{11-1} = -1.42(1) \qquad (7)$$

$$Ni^{2+} + L \rightleftharpoons [NiLH_{-2}] + 2H^+; \log \beta_{11-2} = -12.39(2) \qquad (8)$$

Formation Constants.—Potentiometric titrations were carried out using 1 : 1 ratios of the ligand to the metal ion. In the case of copper(II) and palladium(II) the titration data could be fitted to the single equilibrium (5) with $\log \beta_{110} = 16.20(2)$ for Cu^{2+} and 18.32(3) for Pd^{2+}. For Ni^{2+}, in the pH range 2—10, the titration data can be fitted to the equilibria (6) and (7). At pH values > 10 a further equilibrium (8) occurs. The $\beta_{l,m,h}$ values are the corresponding formation constants (where *l* is the stoicheiometric coefficient of the ligand, *m* that of the metal, and *h* that of the hydrogen ion in the complex). The distribution curve for the nickel(II) complexes is shown in Figure 3.

It is likely that deprotonation of hydroxyethyl side arms occurs in the complexes [NiLH$_{-1}$]$^+$ and [NiLH$_{-2}$] rather than deprotonation of co-ordinated water molecules, and this view is supported by crystallographic data (see later). Formation of the deprotonated nickel(II) complexes is accompanied by pronounced changes in the visible spectrum, the initial blue solution becomes brown-green, the colour change being reversed on addition of acid, Figure 4. At pH 10 the solution has well defined bands at 407 and 663 nm. Using equations (6)—(8) it can readily be shown that the pK_a values of [NiL]$^{2+}$ are pK_1 = 8.87 and pK_2 = 10.97 at 25 °C, as $\log K_1 = \log \beta_{11-1} - \log \beta_{110}$ and $\log K_2 = \log \beta_{11-2} - \log \beta_{11-1}$. Spectrophotometric titration of the nickel(II) complex using the 407 nm band, Figure 5, gave pK_1 = 8.75, at 25 °C and $I = 0.1$ mol dm^{-3}, in good agreement with the potentiometric data.

The formation constant study also establishes that the selectivity of the L complexes for Cu^{II} over Ni^{II} ($\Delta \log \beta_{ML} = 8.65$) is one of the highest yet recorded for any ligand system in the literature.[17] A further interesting property of L is its ability to complex rapidly with transition-metal ions. Equilibration of L with metal ions is essentially instantaneous on the time scale of potentiometric titrations, except for Ni^{II} where equilibrium was established within two minutes of each addition of acid.* In a recent study of the formation constants of

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* In the B/L scale -2 to $+2$, the equilibrium with Ni^{II} is quite slow and 20—30 min are required for attainment of equilibrium.

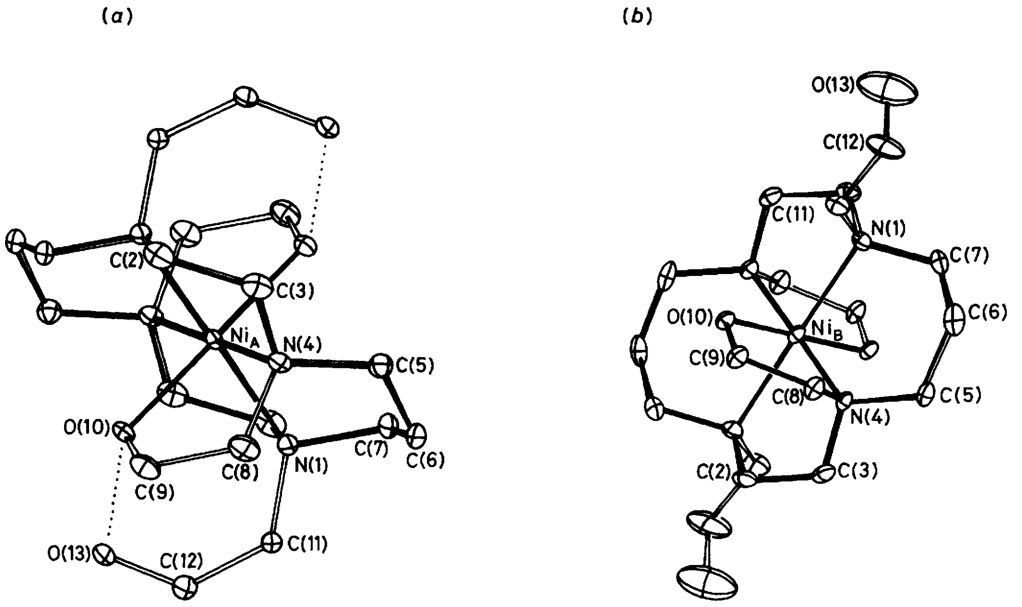
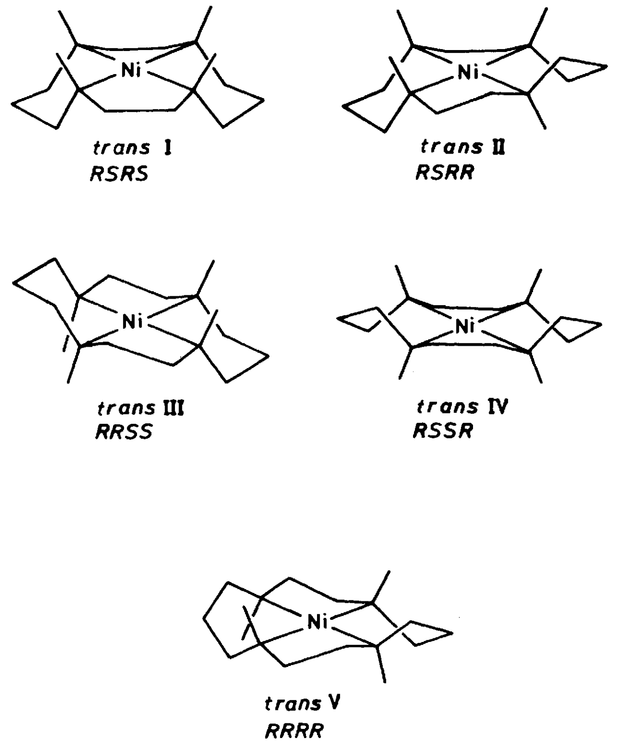


Figure 6. The molecular structure of the two independent centrosymmetric subunits A (*a*) and B (*b*) with atom labelling and thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Open bonds correspond to the hydroxyethyl side arms. Intra-subunit hydrogen bonds are shown by dotted lines



trans I
RSRS

trans II
RSRR

trans III
RRSS

trans IV
RSSR

trans V
RRRR

Figure 7. Configurational isomers of planar [Ni(cyclam)]$^{2+}$

the L′ complexes[18] it was found necessary to allow several hours between each addition of acid in potentiometric titrations with metal ions such as Co^{II}, and up to one week for equilibration with Ni^{II}. Significantly tetrakis(2-cyanoethyl)-1,4,8,11-tetra-azacyclotetradecane (L″), which has lower p*K* values than L, Table 3, equilibrates very slowly even with Cu^{II}.[2]

Decreasing the basicity of the ligand is, in itself, insufficient to cause rapid complexation with transition-metal ions. It must be concluded that the hydroxyethyl side arms aid the metallation reaction by providing points of attachment outside the macrocyclic ring for the incoming metal ion. Previous kinetic work has established that the slow incorporation of metal ions into macrocyclic tetra-aza ligands is due to the slow rate of reaction of the metal ion with the protonated forms of the ligand.[19] This effect results from electrostatic repulsive interactions between the metal ion and the protonated ligand. For cyclam it is known that the only kinetically significant complexation reactions occur between M^{2+} and the HL^{+} and free base (L) forms of the ligand.[20]

Macrocycles with donor atoms in suitable pendant arms will provide an initial co-ordination site where electrostatic repulsion with protons in the central cavity will not be so severe. Transfer of the metal ion to the primary ring site will then become a rapid intramolecular process. Such effects have also been observed in the field of porphyrin chemistry. The attachment of acetate pendant arms to porphyrins has been shown to lead to faster metal incorporation rates.[21]

Crystal Structure of [NiLH$_{-1}$][ClO$_4$].—Slow evaporation of an aqueous solution containing Ni(ClO$_4$)$_2$, L, and NaOH in equimolar amounts gave blue prismatic crystals of [NiLH$_{-1}$]-[ClO$_4$] suitable for *X*-ray analysis. The *X*-ray work established the presence of two independent centrosymmetric subunits (A and B) in the unit cell, Figure 6, with the Ni ions occupying the $\bar{1}$ symmetry sites 0.5,0,0.5 and 0,0,0 respectively. The co-ordination around nickel is almost regular octahedral with four equatorial N atoms and two axial O atoms of two centrosymmetric hydroxyethyl side arms. The macrocyclic ligand adopts the *trans* III stereochemistry[22,*] unlike complexes of L′ which have been shown to adopt the *trans* I stereochemistry with a single unidentate ligand (water, azide, chloride,[23] or acetonitrile[24]) occupying the axial co-ordination site to give a square-

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[*] The five possible diastereoisomeric forms of the metal complexes are designated I—V with *cis* or *trans* forms indicated as such. It should be noted that the *trans* III diastereoisomer is sometimes referred to as the *RSSR* isomer. However, the nitrogen configurations should be designated according to their number in the compound 1,4,8,11-tetra-azacyclotetradecane giving the designation *RRSS* (or *SSRR* for the other enantiomer). The correct designations are given in Figure 7.

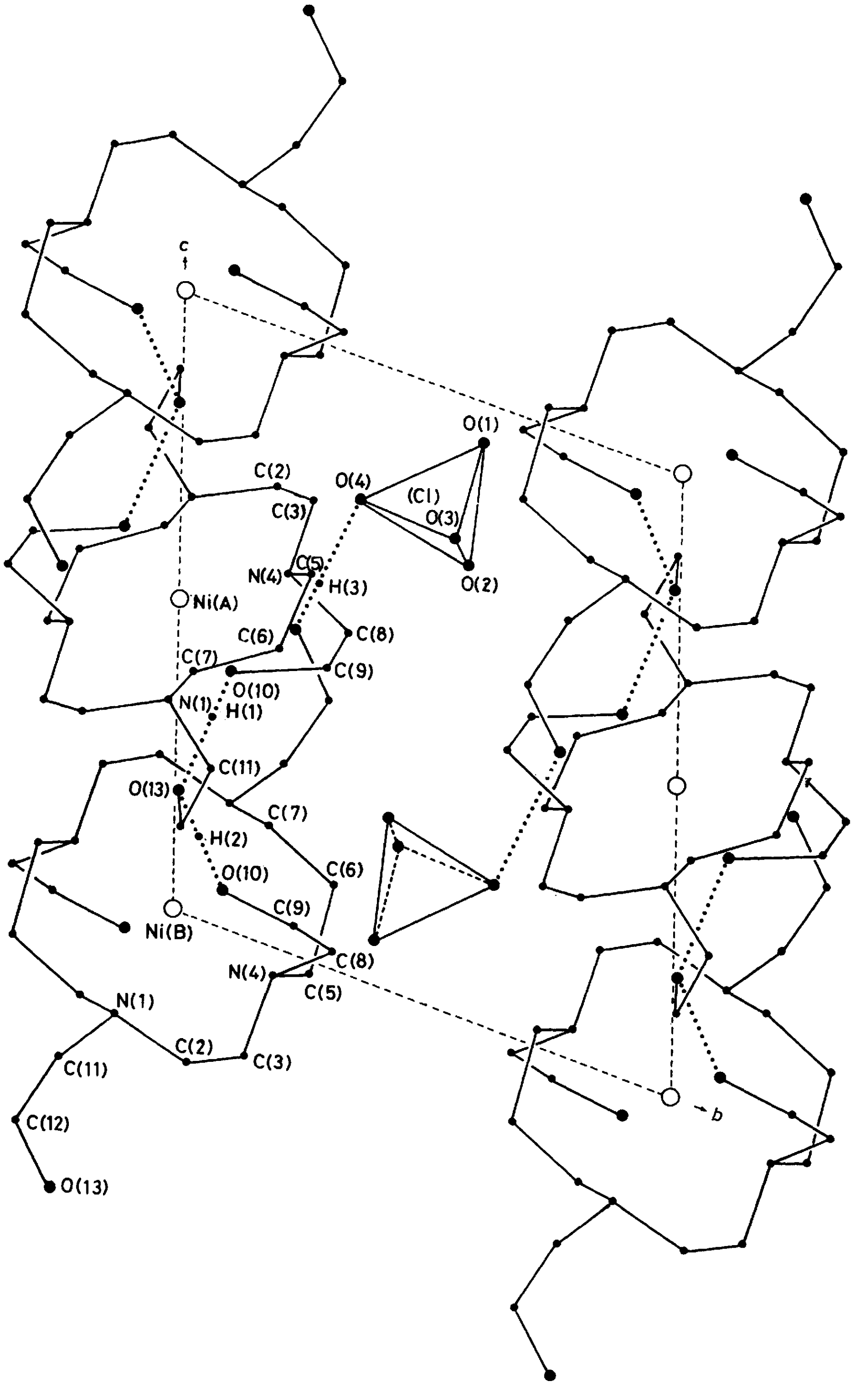


Figure 8. Projection of the structure of $[NiLH_{-1}][ClO_4]$ along [100] showing the atom numbering scheme; the aliphatic hydrogen atoms have been omitted for clarity

pyramidal structure. Barefield and co-workers[25] have recently characterised two isomeric forms (α and β) of the nickel(II) complexes of the ligands *N,N′,N″,N‴*-tetrakis(2-cyanoethyl)-1,4,8,11-tetra-azacyclotetradecane (L″) and *N,N′,N″,N‴*-tetrakis(2-carbamoylethyl)-1,4,8,11-tetra-azacyclotetradecane. In each case the kinetically controlled product (α isomer) obtained by reaction of a nickel salt with the free ligand was converted to the β isomer by heating in an appropriate solvent (water or acetonitrile). The α isomer has the *trans* I stereochemistry and the β isomer the *trans* III stereochemistry. Five possible stereoisomers can exist for a planar complex of the ligand L, Figure 7.

The thermodynamically most stable diastereoisomer has the *trans* III structure in which the five-membered and six-membered rings adopt their most stable conformations. The *trans* V chiral nitrogen configuration which allows ready folding of the ligand occurs in *cis* complexes such as *cis*-$[Ni(cyclam)(OH_2)_2]Cl_2{\cdot}2H_2O$.[26]

Table 4. Kinetics of the acid dissociation of $[CuL]^{2+}$ in perchloric acid solutions at I = 1.0 mol dm^{-3} ($NaClO_4$) and 25 °C*

$[HClO_4]$/mol dm^{-3}	$k_{obs.}/s^{-1}$	$[HClO_4]$/mol dm^{-3}	$k_{obs.}/s^{-1}$
0.015	0.062	0.15	0.63
0.03	0.12	0.30	1.12
0.05	0.20	0.50	1.72

* Reaction monitored at 627 nm.

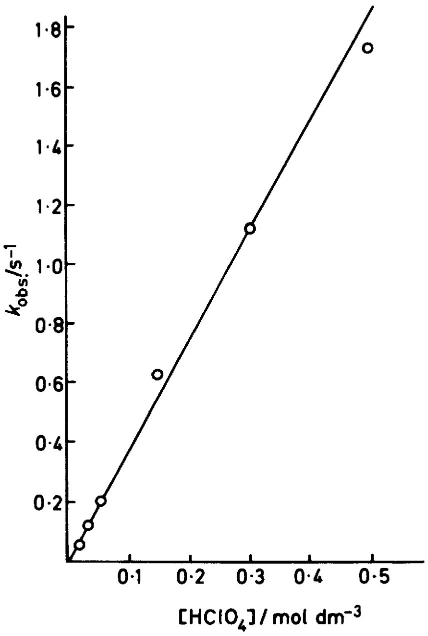


Figure 9. Acid dependence of the dissociation of $[CuL]^{2+}$ in perchloric acid solutions at 25 °C and I = 1.0 mol dm^{-3}

The two subunits have very similar bond distances and angles, all lying within the expected values (Table 2). The only significant difference between the two subunits refers to the mutual orientation of the hydroxyethyl side arms. In the A subunit [Figure 6(*a*)] the N(1)–C(11)–C(12) bonds of the side arms which are not involved in co-ordination to Ni are nearly parallel to the corresponding N(4)–C(8)–C(9) bonds, thus allowing the formation of intra-subunit hydrogen bonds between adjacent hydroxyl groups. In the B subunit [Figure 6(*b*)] the hydroxyethyl side arm C(11)–C(12)–O(13) moves away from the macrocyclic ring by rotation about the N(1)–C(11) bond, thus allowing the formation of hydrogen bonds with the ClO_4^- anions. The different mutual orientations of the hydroxyethyl side arms in the two subunits allows the molecular packing in the crystalline state shown in Figure 8. The O(13) oxygen atoms of the A subunit are involved in very strong intra-subunit [O(13A)–O(10A) = 2.420 Å] and inter-subunit [O(13A)–O(10B) = 2.433 Å] hydrogen bonding. The ClO_4^- anions, which are sandwiched between the chains, provide a linkage along [010] *via* weak hydrogen bonds with the O(13) oxygen atoms of the B subunits. The weakness of this hydrogen bond arises both from the relatively long O ··· O separation [O(13B)–O(4) = 2.927 Å] and from the strong orientational disorder which characterises the ClO_4^- anions.

The different bonding environments of the O(13) hydroxyl groups in the two subunits accounts for the large difference in their thermal motion [the isotropic thermal parameters of the O(13) oxygen atoms are 2.8 and 11.4 Å^2 in the A and B subunits, respectively] and hence for the large difference in their bond distance from the C(12) carbon atom [the C(12)–O(13) bond distance in the two subunits becomes very similar after correction for riding motion].

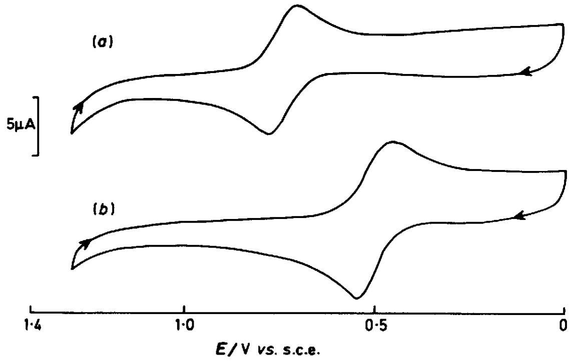


Figure 10. Cyclic voltammograms for the Ni^{III}–Ni^{II} redox couple of nickel complexes of cyclam; (*a*) pH 1.45, 0.1 mol dm^{-3} $NaClO_4$, scan rate 100 mV s^{-1}, $E_{\frac{1}{2}}$ 0.75 V, ΔE_p = 70 mV; (*b*) pH 2, 0.5 mol dm^{-3} Na_2SO_4, scan rate 100 mV s^{-1}, $E_{\frac{1}{2}}$ = 0.51 V, ΔE_p = 90 mV

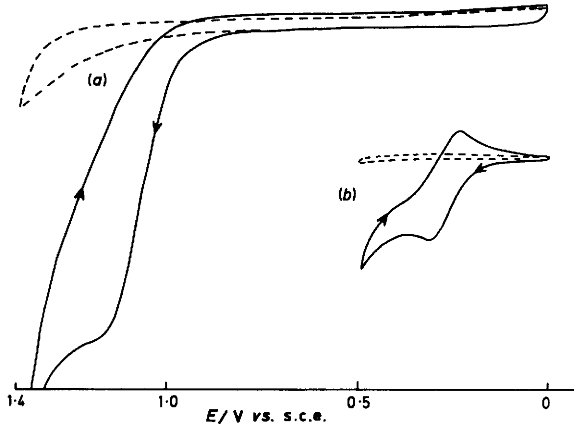


Figure 11. Cyclic voltammograms for (*a*) $[NiL]^{2+}$ in 0.1 mol dm^{-3} $NaClO_4$ and (*b*) $[NiLH_{-2}]$ in 0.1 mol dm^{-3} NaOH. [Complex] = 8.8 × 10^{-4} mol dm^{-3}, scan rate 100 mV s^{-1} with a glassy carbon working electrode. The dotted line is the blank in the absence of the complex. In 0.1 mol dm^{-3} NaOH, $E_{\frac{1}{2}}$ = 0.28 V, ΔE_p = 80 mV

Although the two hydrogen atoms H(1) and H(2) involved in strong hydrogen bond formation appear from the structural analysis to belong mainly to the Ni-bonded oxygens O(10) of both subunits, the very short O ··· O separation and the great smearing of electron density observed in the difference Fourier synthesis in the proximity of the hydrogen positions could suggest a partial disordered distribution of the two hydrogen atoms. That is, almost equal deprotonation could affect all three hydroxyl groups involved in the hydrogen bonding system which connects the subunits. Therefore, in the crystalline state, the deprotonated complex must be considered as a linear polymer of the cation $[Ni_2L_2H_{-2}]^{2+}$.

In solution stepwise deprotonation of $[NiL]^{2+}$ occurs to give initially $[NiLH_{-1}]^+$. However, on formation of the crystal lattice disproportionation can take place producing the A $\{[NiLH_{-2}]\}$ and B $\{[NiL][ClO_4]_2\}$ subunits, although the crystallographic data suggest that one oxygen atom of both the A and B subunits is involved, at least partially (or statistically) in the deprotonation.

$[CuL][ClO_4]_2$.—The blue copper(II) complex was readily characterised by reaction of the ligand with copper(II)

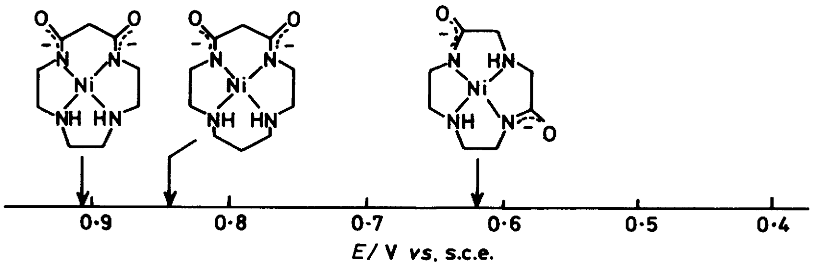


Figure 12. The Ni^{III}–Ni^{II} redox couple potentials for nickel complexes of various dioxo macrocycles (3.0 mol dm^{-3} $NaClO_4$, 25 °C)

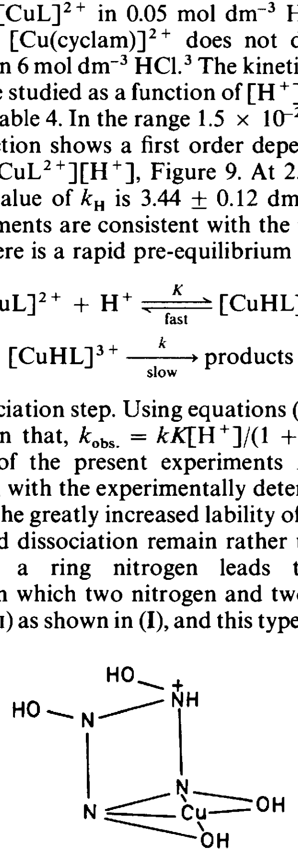
perchlorate hexahydrate in ethanol. The complex displays a single broad band in the *d–d* spectrum with $\lambda_{max.}$645 nm (water solvent). A 1×10^{-3} mol dm^{-3} solution in nitromethane has $\Lambda_M = 160$ S cm^2 mol^{-1} at 25 °C consistent with a 2:1 electrolyte. However, the i.r. spectrum (KBr disc) displays some splitting of the ν_3 perchlorate band at 1 100 cm^{-1} possibly indicative of perchlorate co-ordination in the solid state.

The copper(II) complex dissociates readily in acidic solution. The half-life of $[CuL]^{2+}$ in 0.05 mol dm^{-3} $HClO_4$ is 3.5 s at 25 °C, although [Cu(cyclam)]$^{2+}$ does not dissociate over a period of weeks in 6 mol dm^{-3} HCl.[3] The kinetics of dissociation of $[CuL]^{2+}$ were studied as a function of $[H^+]$ using perchloric acid solutions, Table 4. In the range 1.5×10^{-2}—0.50 mol dm^{-3} $HClO_4$, the reaction shows a first order dependence on $[H^+]$ with rate = $k_H[CuL^{2+}][H^+]$, Figure 9. At 25 °C and $I = 1.0$ mol dm^{-3}, the value of k_H is 3.44 ± 0.12 dm^3 mol^{-1} s^{-1}. The kinetic measurements are consistent with the reactions (9) and (10) in which there is a rapid pre-equilibrium protonation step

$$[CuL]^{2+} + H^+ \underset{fast}{\overset{K}{\rightleftharpoons}} [CuHL]^{3+} \qquad (9)$$

$$[CuHL]^{3+} \xrightarrow[slow]{k} \text{products} \qquad (10)$$

and a slow dissociation step. Using equations (9) and (10) it can be readily shown that, $k_{obs.} = kK[H^+]/(1 + K[H^+])$. Under the conditions of the present experiments $K[H^+] \ll 1$ and $k_{obs.} = kK[H^+]$, with the experimentally determined $k_H = kK$. The reasons for the greatly increased lability of the L complexes in acid promoted dissociation remain rather unclear. Possibly protonation of a ring nitrogen leads to a molecular rearrangement in which two nitrogen and two oxygen donors bond to copper(II) as shown in (I), and this type of species occurs



(I)

as an intermediate in the dissociation process. Copper complexes having the N_2O_2 donor set have been isolated and characterised by *X*-ray crystallography using the ligand 1,4,8,11-tetra-azacyclotetradecane-*N*,*N*′,*N*″,*N*‴-tetra-acetic acid.[27]

$[NiL][ClO_4]_2$.—This complex was obtained as blue crystals on recrystallisation from methanol. The complex is a 2:1 electrolyte in $MeNO_2$ with $\Lambda_M = 159$ S cm^2 mol^{-1} at 25 °C, and below pH 7 gives a typical octahedral *d–d* spectrum, $\lambda_{max.}$595 ($\varepsilon = 13.5$) and 366 nm ($\varepsilon = 34$ dm^3 mol^{-1} cm^{-1}). The *d–d* spectrum is typical of an octahedral N_4O_2 donor set. Employing the rule of average environment[28] suggests that the $^3A_{1g} \longrightarrow {}^3T_{1g}(F)$ transition for an N_4O_2 chromophore should occur near 588 nm and the $^3A_{2g} \longrightarrow {}^3T_{1g}(P)$ transition near 355 nm.

At pH 10 the complex is brown-green with $\lambda_{max.}$663 (ε 55) and 407 nm (ε 110 dm^3 mol^{-1} cm^{-1}) which may be indicative of a square-pyramidal stereochemistry in solution.*

The potentiometric and crystallographic work confirm that the colour changes are due to stepwise deprotonation of hydroxyethyl side arms ($pK_1 = 8.87$ and $pK_2 = 10.97$ at 25 °C and $I = 0.1$ mol dm^{-3}). Such deprotonations are not observed in the copper(II) and palladium(II) complexes which favour tetragonal and square-planar stereochemistries respectively.

The formation of the deprotonated complex $[NiLH_{-2}]$ above pH 12 suggests that the ligand may be useful in stabilising nickel(III). Previous work[29,30] has shown that axial ligation of sulphate and other anions to several tervalent nickel complexes increases the thermodynamic stability and considerably extends the lifetime of the nickel(III) species. The effect with [Ni(cyclam)]$^{3+}$ is illustrated in the cyclic voltammograms, Figure 10. In 0.1 mol dm^{-3} $NaClO_4$ (pH 1.45), $E_{\frac{1}{2}}$ for the Ni^{III}–Ni^{II} couple is 0.75 V [*versus* saturated calomel electrode (s.c.e.)] but in 0.5 mol dm^{-3} Na_2SO_4 (pH 2.03) the $E_{\frac{1}{2}}$ value is reduced to 0.51 V, corresponding to an increase in thermodynamic stability of the Ni^{III} oxidation state by two orders of magnitude.

A similar anionic interaction occurs in $[NiLH_{-2}]$ which might be expected to stabilise the corresponding nickel(III) species. Cyclic voltammetry on $[NiLH_{-2}]$ in 0.1 mol dm^{-3} NaOH (s.c.e. reference) showed pseudo-reversible behaviour for the Ni^{III}–Ni^{II} couple with $E_{\frac{1}{2}} = 0.28$ V and $\Delta E_p = 80$ mV at 100 mV s^{-1} using a glassy carbon electrode, Figure 11. This potential is one of the lowest recorded for a nickel polyazamacrocyclic complex. A redox process is not observed in aqueous solution at pH values where only $[NiL]^{2+}$ occurs, Figure 11.

The electrochemistry of Ni^{III}–Ni^{II} complexes of dioxo tetra-aza macrocycles which form deprotonated complexes with nickel(II) has recently been studied in considerable detail;[31–34] a typical complex is shown in (II). The Ni^{II}–Ni^{III} redox change, judged from the shape of the cyclic voltammogram profiles, shows quasi-reversible behaviour only at relatively high concentrations of supporting electrolyte. Figure 12 illustrates the potentials for the Ni^{III}–Ni^{II} redox couple for a series of dioxo tetra-aza macrocyclic complexes.[34] These potentials (0.62—0.91 V) are considerably greater than that observed with $[NiLH_{-2}]$ establishing the very much greater thermodynamic

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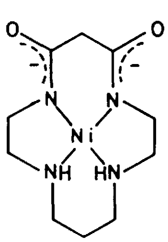
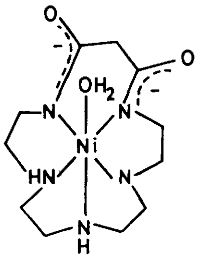
* The formation of green nickel(II) complexes as a result of the equilibrium

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

has been previously observed with a variety of tetra-azamacrocyclic ligands. The green complexes are believed to be five-co-ordinate; see, for example, N. Jubran and D. Meyerstein, *Inorg. Chim. Acta*, 1986, **122**, 149; N. Herron and P. Moore, *Inorg. Chim. Acta*, 1979, **36**, 89.



(II)



(III)

stability of the L complex. Oxidation of the octahedral d^8 Ni^{II} to octahedral low-spin d^7 Ni^{III} appears to be particularly favoured by dianionic quinquedentate and sexidentate macrocycles. Thus, Kimura *et al*,[35] have recently shown that the Ni^{II} complex (**III**) can be oxidised to the Ni^{III} complex by O_2. The $E_{\frac{1}{2}}$ value for the Ni^{III}–Ni^{II} couple in this case is 0.24 V *versus* s.c.e. in aqueous solution.

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