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Synthetic and Kinetic Studies on Copper(II), Nickel(II) and Cobalt(III) Complexes of 1,4,7,11,14-Penta-azacycloheptadecane([17]aneN$_5$)

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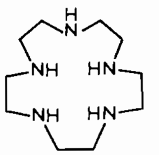
The preparation of the pentadentate macrocyclic ligand L (= II, *4,7,11,14-penta-azacycloheptadecane) is described. The complexes* $[CuL](ClO_4)_2$, $[NiL(H_2O)](ClO_4)_2$, $[CoClL](ClO_4)_2$, $[CoL(CO_3)]ClO_4$, $[Co([15]aneN_5)CO_3]ClO_4$, $[CoL(DMF)](ClO_4)_3$, $[CoL(OOCH)](ClO_4)_2$ *and* $[CoL(OH_2)](ClO_4)_2$ *have been prepared and characterised. The copper(II) complex appears to be square pyramidal on the basis of its d–d spectrum and the nickel(II) complex is octahedral. The copper and nickel complexes dissociate in acidic solution and the reactions have been studied kinetically. For the copper(II) derivative, rate* $= k_H[\text{Complex}][H^+]^2$ *with* $k_H = 1.2 \times 10^3$ M^{-2} s^{-1} *at 25 °C and* $I = 0.1$ M (NaClO$_4$) ($\Delta H^{\ddagger} = 29.8$ kJ mol^{-1} *and* $\Delta S_{298}^{\ddagger} = -86$ JK^{-1} mol^{-1}*). Dissociation rates of the copper complexes increase in the order* [15]aneN$_5$ < [16]aneN$_5$ < [17]aneN$_5$*. For the dissociation of the nickel(II) complex, rate* $= k_H[\text{Complex}][H^+]$ *with* $k_H = 0.23$ M^{-1} s^{-1} *at 25 °C* ($\Delta H^{\ddagger} = 44.0$ kJ mol^{-1}, $\Delta S_{298}^{\ddagger} = -109$ JK^{-1} mol^{-1}*). Mechanisms for these reactions are considered. The nickel(II) complex is oxidised to nickel(III) in acetonitrile solvent in a pseudo-reversible process* ($E_{1/2} = +1.11$ V *with reference to S.C.E.).*

Mercury(II) catalysed aquation of $[CoClL]^{2+}$ *has been studied* ($k_{Hg} = 1.4 \times 10^{-2}$ M^{-1} s^{-1} *at 25 °C). Potentiometric titration of the aqua-complex gives pKa = 6.2 for the aqua* $\rightleftharpoons$ *hydroxo equilibrium. The hydroxo complex* $[CoL(OH)]^{2+}$ *reacts rapidly with* CO_2 *to give the monodentate carbonato complex* $[CoL(CO_3)]^+$*. Decarboxylation of the carbonato complex occurs in acidic solution and the reaction has been studied kinetically,* $k = 0.43$ s^{-1} *at 25 °C* ($\Delta H^{\ddagger} = 48.4$ kJ mol^{-1}; $\Delta S_{298}^{\ddagger} = -90$ JK^{-1} mol^{-1}*). Similar studies on* $[Co([15]aneN_5)CO_3]^+$ *are also reported. The base hydrolysis of the monodentate formato complex* $[CoL(OOCH)]^{2+}$ *has also been investigated* ($k_{OH} = 3.0 \times 10^4$ M^{-1} s^{-1} *at 25 °C,* $\Delta H^{\ddagger} = 41.1$ kJ mol^{-1}; $\Delta S_{298}^{\ddagger} = -20$ JK^{-1} mol^{-1}*).*

Introduction

The preparation of penta-aza macrocycles using the Richman and Atkin's procedure [1] is now relatively straightforward [2, 3]. In a previous paper we have described synthetic and kinetic studies on copper(II), nickel(II) and cobalt(III) complexes of 1, 4, 7, 10, 13-penta-azacyclopentadecane (*I* = [15]-aneN$_5$). The present paper discusses various aspects of the coordination chemistry of 1,4,7,11,14-penta-azacycloheptadecane (*II*) (one of the possible isomers of [17]aneN$_5$). The nickel(II) complex of (*II* = L) has previously been characterised and the electrochemistry of the $[NiL]^{2+}/[NiL]^{3+}$ redox system studied using acetonitrile as solvent [2, 5].



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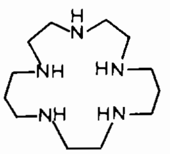

(II) = L

Experimental

N,O,O′-Tritosyldiethanolamine was prepared as previously described [4]; N,N′,N″,N‴-Tetratosyl-1,10-diamino-4,7-diazadecane (the tetratosylate of 3, 2, 3-tet) was prepared by a procedure which has subsequently been described [2]. Condensation of the two tosylates in DMF using sodium hydride, and hydrolysis of the pentatosylate with sulphuric acid was carried out by previously described procedures [2, 4]. The ligand pentahydrochloride L·5HCl was prepared by literature procedures [2, 4].

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$CuL(ClO_4)_2$

The ligand pentahydrochloride (0.5 g) was dissolved in water (20 cm^3) and copper(II) carbonate (0.2 g) added. The mixture was heated on a water bath for *ca.* 0.5 hr, and the solution cooled and filtered to remove unreacted copper(II) carbonate. The filtrate was concentrated to *ca.* 5 cm^3 and treated with $NaClO_4 \cdot 6H_2O$ (0.2 g). On cooling blue needle-like crystals of the copper complex crystallised as the perchlorate salt. *Anal.* Calcd. for $C_{12}H_{29}N_5Cl_2O_8Cu$: C, 28.5; H, 5.8; N, 13.9. Found: C, 28.6; H, 5.8; N, 14.0%. The complex has Λ_M = 243 ohm^{-1} cm^2 in water and Λ_M = 144 ohm^{-1} cm^2 in nitromethane.

$NiL(ClO_4)_2H_2O$

This complex was prepared essentially as described above using nickel(II) carbonate or the basic carbonate. Violet crystals of the perchlorate salt were obtained: *Anal.* Calcd. for $C_{12}H_{29}N_5Cl_2O_8NiH_2O$: C, 27.8; H, 6.0; N, 13.6. Found: C, 27.7; H, 6.1; N, 13.9%. The complex has Λ_M = 235 ohm^{-1} cm^2 in water and Λ_M = 145 ohm^{-1} cm^2 in nitromethane.

$[CoLCl](ClO_4)_2$

The ligand pentahydrochloride (0.5 g) was dissolved in water (20 cm^3) and treated with freshly prepared $Na_3[Co(CO_3)_3] \cdot 3H_2O$ (0.2 g). The mixture was heated on a steam bath for *ca.* 1 hr then cooled and filtered. To the filtrate was added $NaClO_4 \cdot 6H_2O$ (0.2 g) and the solution concentrated to *ca.* 5 cm^3. On cooling the pink complex crystallised. The complex was filtered off and washed with 2-propanol then ether and air dried. *Anal.* Calcd. for $C_{12}H_{29}N_5Cl_3O_8Co$: C, 26.9; H, 5.5; N, 13.0. Found: C, 27.0; H, 5.4, N, 12.8%.

$[CoLCO_3]ClO_4$

The complex $[CoLCl](ClO_4)_2$ (0.2 g) was dissolved in water (25 cm^3) and treated with excess AgOH. The mixture was heated on a steam bath for *ca.* 15 min, then cooled and filtered. To the filtrate was added $LiCO_3$ (0.1 g) and the mixture heated for *ca.* 1 hr on a steam bath. The solution was cooled and filtered. The filtrate was reduced in volume to *ca.* 5 cm^3 (steam bath). Addition of $LiClO_4$ (0.05 g) and cooling gave the pink complex which was filtered off, washed with ethanol then ether and dried *in vacuo*. *Anal.* Calcd. for $C_{13}H_{29}N_5O_7ClCo$: C, 33.8; H, 6.3; N, 15.1. Found: C, 33.8; H, 6.0; N, 15.0%.

$[Co([15]aneN_5)CO_3]ClO_4$

The complex $[Co([15]aneN_5)H_2O](ClO_4)_3$ (0.2 g) prepared as previously described [3] was dissolved in water (20 cm^3) and treated with Li_2CO_3 (0.1 g). The mixture was heated on a steam bath for *ca.* 0.5 hr and then slowly taken to dryness. The residue was extracted with water (10 cm^3) and the aqueous extract treated with $LiClO_4$ (0.05 g). The solution was warmed for *ca.* 10 min to 60 °C, then cooled and filtered. The filtrate was reduced in volume to *ca.* 3 cm^3 (steam bath) and the carbonato complex precipitated by the addition of excess ethanol. The complex was filtered off and washed with ethanol then ether and dried *in vacuo*. *Anal.* Calcd. for $C_{11}H_{25}N_5ClO_7Co$: C, 30.5; H, 5.8; N, 16.15. Found: C, 30.8; H, 5.9; N, 16.1%.

$[CoL(H_2O)](ClO_4)_3$

The chloro-complex $[CoLCl](ClO_4)_2$ (0.54 g) was dissolved in water (20 cm^3) and the solution warmed to *ca.* 50 °C. Silver perchlorate (0.21 g) was added and the solution warmed for a further 15 min to complete precipitation of AgCl. After cooling, the precipitated AgCl was filtered off and the filtrate concentrated to *ca.* 3 cm^3. Cooling in ice followed by the addition of a few drops of 70% $HClO_4$ gave the red complex which was filtered off and washed with ethanol then ether and dried *in vacuo*. *Anal.* Calcd. for $C_{12}H_{29}N_5Cl_3O_{12}Co$: C, 23.3, H, 5.05, N. 11.3. Found: C, 23.05; H, 4.9; N, 11.2%.

$[CoL(DMF)](ClO_4)_3$

The chloro-complex $[CoLCl](ClO_4)_2$ (0.27 g) was dissolved in DMF (1 cm^3) and $AgClO_4$ (0.11 g) added. The mixture was heated for *ca.* 10 min at about 50 °C, then cooled and filtered to remove AgCl. To the filtrate was added ethanol (10 cm^3) followed by excess ether, which on standing gave an oil. Trituration of the oil with ethanol gave a pink solid which was filtered off, washed with ethanol, then ether and dried *in vacuo*. *Anal.* Calcd. for $C_{15}H_{34}N_6Cl_3O_{13}Co$: C, 26.7; H, 5.4; N, 12.5. Found: C, 26.5; H, 5.3; N, 12.6%. The DMF ligand is bonded *via* the oxygen donor with a νC=O band at 1660 cm^{-1}. The ^1H NMR spectrum has two methyl signals at 2.74 and 2.98 (due to the non-equivalent methyl groups) and a formyl singlet at 7.96δ.

$[CoL(OOCH)](ClO_4)_2 \cdot H_2O$

The complex $[CoLCl](ClO_4)_2$ (0.27 g) was suspended in formic acid (2 cm^3) and mixed with $AgClO_4$ (0.11 g). The mixture was heated for *ca.* 10 min at 50 °C, then cooled and the precipitated AgCl filtered off. Addition of ethanol to the filtrate gave the pink complex which was filtered off, washed with ethanol, then ether and air dried. *Anal.* Calcd. for $C_{13}H_{30}N_5Cl_2O_{11}Co$: C, 26.7; H, 5.4; N, 12.4. Found: C, 27.2; H, 5.6; N, 12.5%.

Kinetics

The kinetics of the acid catalysed dissociation of $CuL(ClO_4)_2$ were monitored at 300 nm. Measurements were made using $HClO_4$ solutions adjusted to I = 0.1 *M* with sodium perchlorate. The kinetics of dissociation were followed on a Durrum D110 stopped-flow spectrophotometer. The signal was stored by a Datalab 901 transient recorder on line to a CBM 3016 computer. The acid dissociation of $NiL(ClO_4)_2 \cdot H_2O$ was monitored at 220 nm using a Gilford 2400S spectrophotometer interfaced with an Apple II computing system. Measurements were made with $HClO_4$ solutions adjusted to I = 0.1 *M* with $NaClO_4$. Activation parameters were calculated by least-squares analysis of Eyring plots.

Mercury(II) catalysed aquation of $[CoClL]^{2+}$ was studied spectrophotometrically using a total ionic strength of 0.49 *M*. Mercury(II) solutions were prepared using the nitrate salt.

Decarboxylation of the monodentate carboxylato complexes $[Co([15]aneN_5)CO_3]^+$ and $[Co([17]aneN_5)CO_3]^+$ was monitored by stopped flow measurements at 490 nm using HCl solutions (0.05 *M*). Base hydrolysis of [CoL(OOCH)] was monitored spectrophotometrically at 280 nm. Measurements were made using acetate and citrate buffers adjusted to I = 0.1 *M*. Hydroxide ion concentrations were determined from the pH using listed values of the ionic product of water and a molar activity coefficient of 0.77 estimated from the Davies equation.

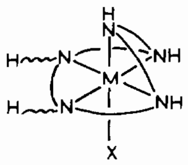
General

Infrared spectra were determined as KBr discs using a Perkin-Elmer 457 instrument. Conductivity measurements were made with a Portland Electronics Model P310 conductivity meter using 10^{-3} *M* solutions at 25 °C. All pH measurements were made with a Radiometer PHM64 Research pH meter, which was standardised using 0.05 *M* potassium hydrogen phthalate (pH 4.008) and phosphate buffer (0.025 *M*), pH 6.86 at 25 °C.

Electrochemistry was carried out with a PAR 170 electrochemistry system. Measurements were made using 1 × 10^{-3} *M* solution in acetonitrile with 0.1 *M* $Bu_4N^+ClO_4^-$ as the supporting electrolyte. Potentials are expressed *versus* S.C.E., using a platinum electrode.

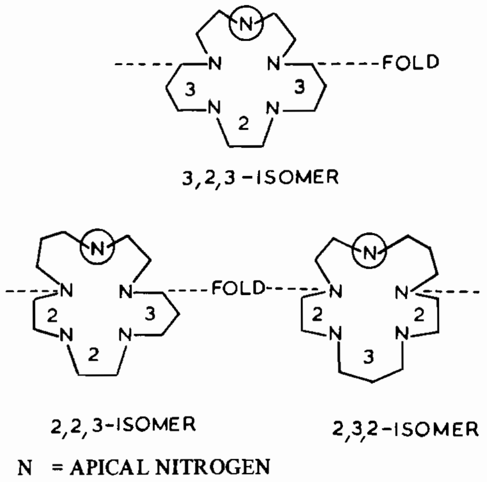
Results and Discussion

The ligand 1,4,7,11,14-penta-azacycloheptadecane is readily prepared by the reaction of the disodium salt of the tetratosylate of 1,10-diamino-4,7-diazadecane with the tritosylate of diethanolamine in N,N-dimethylformamide solution, followed by cleavage of the tosyl groups with concentrated sulphuric acid. The ligand is expected to act as a pentadentate, giving rise to complexes of type (*III*) with metal ions favouring six coordination. Complexes of this type contain two chiral nitrogen centres indicated by the slashed lines.



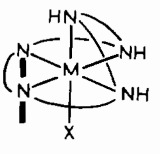
(III)

The unsymmetrical 1,4,7,11,14-penta-azacycloheptadecane presents further scope for isomerism depending upon the nitrogen adopted as the apical donor (Scheme)



Scheme. Possible isomers of complexes of 1,4,7,11,14-penta-azacycloheptadecane.

As a result of the two chiral nitrogen centres, each of these gives rise to three diastereoisomeric species, the *meso*-syn (IV), the *meso*-anti (*V*) and the racemate (*VI*)



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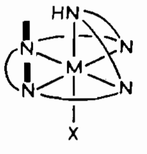

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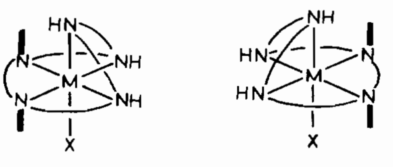
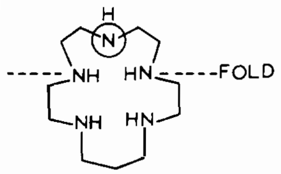


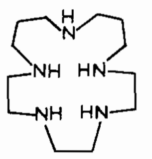
RACEMATE (VI)

Crystallographic work on $[Co([16]aneN_5)Cl](ClO_4)_2$ [6] has indicated that the single 6-membered chelate ring assumes a chair conformation while all five membered rings are gauche. The ligand has the 2,3,2-configuration (*VII*) and the chiral nitrogens have opposite chirality giving the *meso*-syn diastereoisomer.



(VII)

Crystallographic work has also been carried out [7], on the cobalt(III) complex $[CoL_1Cl](ClO_4)_2$ where L_1 = 1,4,7,10,14-penta-azacycloheptadecane (*VIII*) which is the second possible isomer of [17]aneN_5. In this complex the configuration of the ligand is as



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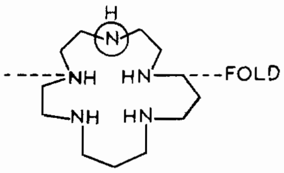


(IX)

in (*IX*), *i.e.* the 2,3,3-isomer with an N-*racemic* arrangement of the chiral nitrogen centres. The available evidence on the 16- and 17-membered ring systems indicates that the six-membered chelate ring occurs in the 'backbone' of the complex so that the 2,3,2-isomer of complexes of 1,4,7,11,14-penta-azacycloheptadecane may be favoured.

The copper(II) complex of [17]aneN_5, $[CuL](ClO_4)_2$ is readily isolated by the reaction of L• 5HCl with copper(II) carbonate, followed by addition of sodium perchlorate. The complex gives a somewhat low conductivity in the non-coordinating solvent nitromethane with Λ_M = 144 ohm^{-1} cm^2 mol^{-1} at 25 °C possibly indicating ion association, but it is a 2:1 electrolyte in water (Λ_M = 243 ohm^{-1} cm^2 mol^{-1} at 25 °C). The visible spectrum in acetonitrile solvent has λ max 590 nm (ϵ = 180 M^{-1} cm^{-1}) Table I, which may be compared with λ max 585 nm (ϵ = 200 M^{-1} cm^{-1}) for the analogous complex of [15]aneN_5. Both complexes also display an additional weaker band, red shifted from the major d–d absorption band. For $[Cu[15]aneN_5](ClO_4)_2$ in water this band occurs at 825 nm ($\epsilon \sim 70$) while for $[CuL](ClO_4)_2$ in acetonitrile the band occurs at 840 nm ($\epsilon \sim 65$). This additional d–d absorption is indicative of axial interaction in a five coordinate system [8, 9]. A five coordinate square-pyramidal structure can be proposed on the basis of the observation of two bands in the visible and near infrared region [8–10]. The CuN_6 chromophores in complexes such as $[Cu(haco)]^{2+}$ (haco = 1,4,7,10,13,16-hexa-azacyclooctadecane) and $[Cu(dien)_2]^{2+}$ absorb at 615 and 640 nm, respectively [11]. The former complex lacks any band in the near infrared region, Fig. 1.

TABLE I. Electronic Spectra of the Complexes.

Complex	λ_{max} (nm)	ϵ (M^{-1} cm^{-1})
$CuL(ClO_4)_2$	582	180
	840	65 (acetonitrile)
$[NiL(H_2O)](ClO_4)_2$	820	5.6
	780	4.6
	540	4.6
	355	8
$[CoLCl]ClO_4$	550	132
	380	174
$[CoL(CO_3)]ClO_4$[a]	510	180
$[Co([15]aneN_5)CO_3]ClO_4$[a]	505	280
$[CoL(OH_2)](ClO_4)_3$	506	148
	360	142
$[CoL(DMF)](ClO_4)_3$	514	273
	362	153
$[CoL(OOCH)](ClO_4)_2H_2O$	530	106
	375	135

[a]Spectra determined using dilute $NaHCO_3$ solutions, all other spectra determined using aqueous solutions.

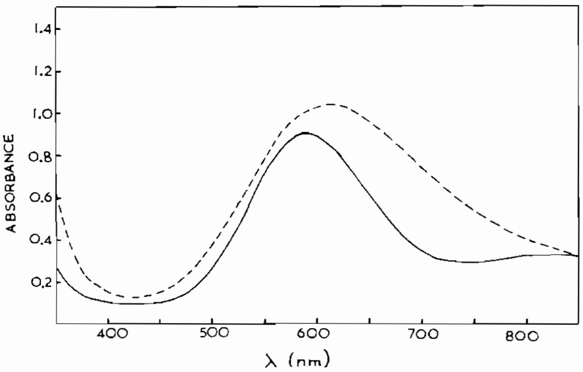


Fig. 1. Absorption spectra of $[Cu([17]aneN_5)](ClO_4)_2$ (——) in acetonitrile and $[Cu(haco)](ClO_4)_2$ in water (------).

The complex $CuL(ClO_4)_2$ is kinetically labile in dilute acid and the kinetics of dissociation were investigated using perchloric acid solutions, Table II. The reaction is first order in the complex and second order in [H$^+$]; rate = $k_H[CuL][H^+]^2$, with k_H = 1.2 × 10^3 M^{-2} s^{-1} at 25 °C and I = 0.1 *M* ($NaClO_4$). The temperature dependence of k_H, Table III, gives $\Delta H^{\ddagger}$ = 29.8 kJ mol^{-1} and $\Delta S_{298}{}^{\ddagger}$ = −86 JK^{-1} mol^{-1} with a correlation coefficient of 0.9835 for the Eyring plot.

TABLE II. The Acid Catalysed Dissociation of $CuL(ClO_4)_2$ at I = 0.1 *M* ($NaClO_4$).

10^2 [$HClO_4$] (*M*)	10^4[H^+]^2 (M^2)	k_{obs} (s^{-1})	$10^{-3}k_{obs}/[H^+]^2$ (M^{-2} s^{-1})
2.05	4.20	0.50	1.19
4.20	17.69	2.35	1.33
6.10	37.21	4.31	1.16
7.90	62.24	6.69	1.07
8.90	79.21	8.98	1.13
	$k_H = 1.2 \times 10^3$ M^{-2} s^{-1}		

TABLE III. Temperature Dependence of the Dissociation of $CuL(ClO_4)_2$ at I = 0.1 *M*.

Temp. (°C)	k_{obs}^{a} (s^{-1})	10^{-3} k_H (M^{-2} s^{-1})
20	1.59	0.90
25	2.35	1.19
29.5	2.63	1.49
35	3.00	1.70

[a] [$HClO_4$] = 2.05 × 10^{-2} *M*. $\Delta H^{\ddagger} = 29.8 \pm 3.9$ kJ mol^{-1}; $\Delta S_{298}^{\ddagger} = -86 \pm 13$ J K^{-1} mol^{-1} (r = 0.9835).

The dissociation of the copper(II) complexes of [15]aneN$_5$, [16]aneN$_5$ and [17]aneN$_5$ all show a second order dependence on [H^+], Table IV. A plot of log k_H *versus* the ring size shows good linearity, Fig. 2. Dissociation of [Cu([17]aneN$_5$)]$^{2+}$ is some 2.4 × 10^3 times faster than that of [Cu([15]-aneN$_5$)]$^{2+}$ at 25 °C [3].

TABLE IV. Acid Dissociation Kinetics of Copper(II) Complexes of [15]aneN$_5$, [16]aneN$_5$ and [17]aneN$_5$ at 25 °C.

Ring Size	k_H (M^{-2} s^{-1})
15	0.049
16	4.85^a
17	1.18 × 10^3

[a] R. W. Hay and R. Bembi, unpublished results.

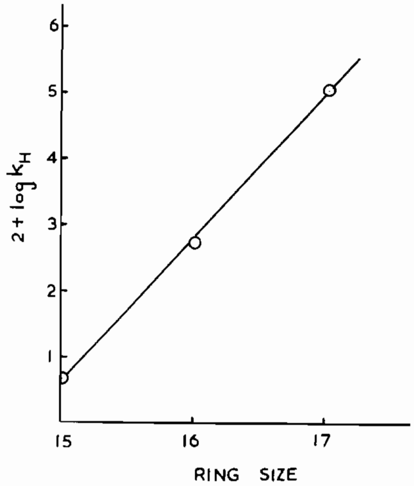


Fig. 2. Dissociation rates of copper(II) complexes of penta-aza macrocycles as a function of ring size.

The second order dependence on the hydrogen ion concentration indicates the participation of two protons in the transition state of the reaction. The kinetic behaviour of [CuL]$^{2+}$ in acidic solution can be described in terms of the eqns. (1) to (3). Monoprotonation of [CuL]$^{2+}$ to [Cu(HL)]$^{3+}$ is expected

$$[CuL]^{2+} + H^+ \underset{}{\overset{K_1}{\rightleftharpoons}} [Cu(HL)]^{3+} \qquad (1)$$

$$[Cu(HL)]^{3+} + H^+ \overset{K_2}{\rightleftharpoons} [Cu(H_2L)]^{4+} \qquad (2)$$

$$[Cu(H_2L)]^{4+} \xrightarrow{k} Cu^{2+}(aq) + H_2L^{2+} \qquad (3)$$

to involve protonation at the apical nitrogen atom, as the axial copper–nitrogen bond is expected to be weaker as a result of Jahn-Teller distortion. Species of the type [Cu(HL)]$^{3+}$ have often been reported in potentiometric studies of copper(II) polyamine complexes [12]. The rate equation (4) can be readily derived from eqns. (1) to (3). Under the conditions of the present experiments ($K_1[H^+] + K_1K_2[H^+]^2$) ⩽ 1 and $k_H = kK_1K_2$. Protonation in the equatorial plane of the macrocycle is a prerequisite for dissociation to occur. Possible mechanisms have been previously outlined [3].

$$\text{Rate} = \frac{k_1K_1K_2[CuL^{2+}][H^+]^2}{(1 + K_1[H^+] + K_1K_2[H^+]^2)} \qquad (4)$$

The nickel(II) complex [NiL(H_2O)](ClO_4)$_2$ was isolated as a violet solid. The complex is a 2:1 electrolyte in water (Λ_M = 235 $ohm^{-1}cm^2$ mol^{-1} at 25 °C) and gives a typical octahedral d–d spectrum, Table I. Fabbrizzi *et al.* [13] have reported that the nickel(II) complexes of [15]aneN$_5$, [16]aneN$_5$ and [17]aneN$_5$ (perchlorate salts) dissolve in acetonitrile as 2:1 electrolytes, and display electronic spectra typical for high spin distorted octahedral chromophores. The pentadentate macrocycle is probably folded to span five coordination sites with the sixth site occupied by a solvent molecule. The energy of the lowest energy absorption band decreases in the series Ni([15]aneN$_5$) > Ni([16]-aneN$_5$) > Ni([17]aneN$_5$) indicating a progressive

TABLE V. Cyclic Voltammetry on $[Ni([15]aneN_5)](ClO_4)_2$ at 25 °C.[a]

ν (mV/s)	Ip(c) (μA)	Ip(a) (μA)	Ip(c)/Ip(a)	ΔEp (mV)	½Ep (V)
50	51	49	1.03	65	+1.03
100	67	59	1.13	80	+1.03
200	93.5	86.5	1.08	80	+1.03
500	135	128.5	1.05	90	+1.03

[a] 1 × 10^{-3} *M* $[Ni([15]aneN_5)](ClO_4)_2$ in acetonitrile with 0.1 *M* $Bu_4\underset{+}{N}\ ClO_4^-$ as the supporting electrolyte. Cyclic voltammetry on Pt with SCE reference.

TABLE VI. Cyclic Voltammetry on $[Ni([17]aneN_5)]$ $ClO_4)_2$ at 25 °C.[a]

ν (mV/s)	Ip(c) μA	Ip(a) μA	Ip(c)/Ip(a)	ΔEp (mV)	½Ep (V)
50	36	40	0.90	70	+1.10
100	50	54	0.92	70	+1.10
200	87.5	80	1.09	70	+1.10
500	117.5	125	0.94	80	+1.10

[a] 1 × 10^{-3} *M* $[Ni(17]aneN_5)](ClO_4)_2$ in acetonitrile with 0.1 *M* $Bu_4\underset{+}{N}ClO_4^-$ as the supporting electrolyte. Cyclic voltammetry on Pt with SCE reference.

TABLE VII. Summary of Electrochemical Data for the Ni(II)/Ni(III) Couples.

Complex	$E_{1/2}$[a] (V)	$E_{1/2}$(lit)[b] (V)
$[Ni([15]aneN_5)]^{2+}$	+1.03(+0.73)	+0.737
$[Ni([16]aneN_5)]^{2+}$	+1.04(+0.74)[c]	+0.772
$[Ni([17]aneN_5)]^{2+}$	+1.10(+0.80)	+0.817

[a] Present data *versus* SCE reference, the values in parenthesis have been converted to the Ag/0.1 *M* $AgNO_3$ reference. [b] Ag/0.1 *M* $AgNO_3$ reference, from ref. 2. [c] R. W. Hay and F. McLaren to be published.

TABLE VIII. The Acid Catalysed Dissociation of $NiL(ClO_4)_2H_2O$ at I = 0.1 *M* ($NaClO_4$) at 25 °C.

$10^3[HClO_4]$ (*M*)	10^3k_{obs} (s^{-1})	$k_{obs}/[H^+]$ ($M^{-1}\ s^{-1}$)
2.1	0.48	0.23
6.0	1.39	0.23
9.9	2.38	0.24
20.7	4.98	0.24
40.6	9.42	0.23

TABLE IX. The Temperature Dependence of the Dissociation of $NiL(ClO_4)_2 \cdot H_2O$ at I = 0.1 *M*.

Temp. (°C)	k_{obs}[a] (s^{-1})	k_H ($M^{-1}\ s^{-1}$)
25	1.39	0.23
29.5	1.78	0.297
33	2.39	0.395
39	3.15	0.525

[a] $HClO_4$ = 6.0 × 10^{-3} *M*. $\Delta H^{\ddagger}$ = 44.0 ± 3.1 kJ mol^{-1}; $\Delta S_{298}^{\ddagger} = -109 \pm 10$ J K^{-1} mol^{-1} (r = 0.9951).

weakening of the Ni–N bonds as the ring size increases.

The oxidation of $[Ni([15]aneN_5)](ClO_4)_2$ and $[Ni([17]aneN_5)](ClO_4)_2$ to the corresponding nickel(III) complexes was studied by cyclic voltammetry using acetonitrile as solvent. Cyclic voltammetry was carried out on Pt with an SCE reference. The data obtained with $[Ni[15]aneN_5]^{2+}$ are summarised in Table V. The Ni(II)/Ni(III) couple is essentially reversible with Ip(c)/ Ip(a) close to unity and ΔEp = 65 mV at $\nu = 50$ mV s^{-1}. A plot of Ip(c) *versus* $\nu^{1/2}$ is linear passing through the origin indicating diffusion control. The value of $E_{1/2}$ = +1.03 V with reference to an SCE. AC measurements on Pt also gave $E_{1/2}$ = +1.03 V while stirred CV measurements gave $E_{1/2}$ = +1.08 V.

Similar measurements were carried out on $[Ni([17]aneN_5)]^{2+}$ giving the data shown in Table VI. The Ni(II)/Ni(III) redox couple is essentially reversible, thus plots of Ip(c) *versus* $\nu^{1/2}$ are linear passing through the origin indicating diffusion control and the ratio Ip(c)/Ip(a) is close to unity. The value ΔEp (*ca.* 70 mV) is somewhat higher than expected for a fully reversible one electron process (60 mV) presumably indicating sluggish electron transfer. The $E_{1/2}$ values obtained are in good general agreement with the results obtained by Bencini, Fabbrizzi and Poggi [2] which relate to a Ag/$AgNO_3$ (0.01 *M*) reference in acetonitrile solvent. Correction of $E_{1/2}$ to the Ag/$AgNO_3$ reference (–0.30 V) [14] gives the data shown in Table VII.

Dissociation of the nickel(II) complex of [17]-aneN_5 occurs quite readily in acidic solutions. In the range (2.1–40.6 × 10^{-3} *M* $HClO_4$, the reaction shows a first order dependence on $[H^+]$, with rate = k_H[complex $[H^+]$, Table VIII, with k_H = 0.23 M^{-1} s^{-1} at 25 °C and I = 0.1 *M* ($NaClO_4$). The tempera-

TABLE X. Mercury(II) Catalysed Aquation of $[CoLCl]^+$ at 25 °C and I = 0.49 *M* ($NaNO_3$).

$10^3[Hg^{2+}]$ (*M*)	10^3k_{obs} (s^{-1})	10^2k_{Hg} (M^{-1} s^{-1})
9.0	0.62	6.9
18.0	1.26	7.0
29.0	2.15	7.4
41.0	3.12	7.6
48.3	3.54	7.3
	$k_{Hg} = 7.2 \pm 0.3\,M^{-1}\,s^{-1}$	

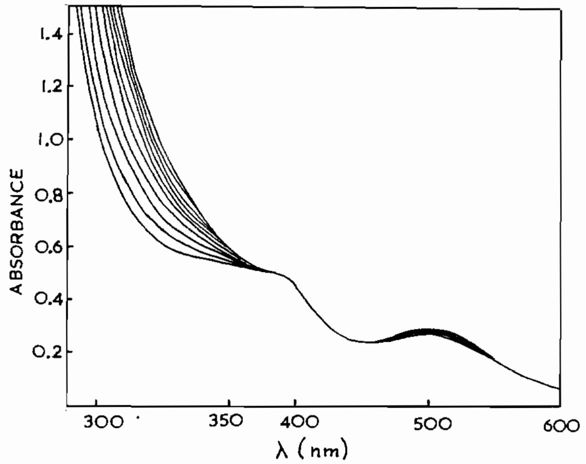


Fig. 3. Uptake of CO_2 by $[Co([17]aneN_5)OH]^{2+}$ in borax buffer at pH 9.66. The time interval between scans is 1 min.

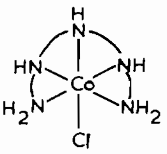
ture dependence of k_H gives $\Delta H^{\ddagger}$ = 44.0 kJ mol^{-1} and $\Delta S_{298}^{\ddagger}$ = −109 JK^{-1} mol^{-1} with a correlation coëfficient of 0.9951, Table IX.

The dissociation of $Ni([17]aneN_5)^{2+}$ differs from that of $Ni([15]aneN_5)^{2+}$ as the dissociation of the latter complex displays a second order dependence on the concentration of the hydrogen ion. It appears that $Ni([17]aneN_5)^{2+}$ is fully protonated as $[NiLH]^{3+}$ throughout the acidity range employed, with only the four equatorial nitrogens coordinated.

Cobalt(III) Complexes

Reaction of the ligand pentahydrochloride with $[Co(CO_3)_3]^{3-}$, followed by addition of $NaClO_4$ gives the pink cobalt(III) complex $[CoLCl](ClO_4)_2$. The ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition occurs at 550 nm (ϵ = 132 M^{-1} cm^{-1}) and the ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transition at 380 nm (ϵ = 174 M^{-1} cm^{-1}), Table I.

The mercury(II) catalysed aquation of the complex was studied at 25 °C and I = 0.49 *M*, Table X. The rate expression is of the form, rate = k_{Hg}[complex] $[Hg^{II}]$ with k_{Hg} = 7.2 M^{-1} s^{-1}. Mercury(II) catalysed aquation of the macrocyclic complex is considerably faster than that of the αα-$[Co(tetren)Cl]^{2+}$ (*X*) where k_{Hg} = 1.42 × 10^{-2} M^{-1} s^{-1} at 25 °C and I = 0.3 *M* [15].



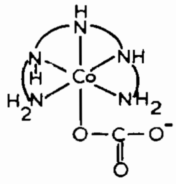
(X)

The aqua-complex $[CoL(OH_2)]^{3+}$ was readily prepared from the chloro-complex by silver(I) catalysed aquation. Potentiometric titration of the aqua-complex gives a pK_a of 6.2 for the aqua ⇌ hydroxo equilibrium at 25 °C and I = 0.1 *M*. The hydroxo-complex reacts rapidly with CO_2 to give the monodentate carbonato complex, Fig. 3. This reaction involves nucleophilic attack by the coordinated hydroxide ion on the CO_2 molecule [16]. The complex $[CoL(CO_3)]ClO_4$ was characterised by the reaction of Li_2CO_3 with the aqua complex. Decarboxylation of the monodentate carbonato complex occurs in acidic solution, and the acid-catalysed decarboxylation was studied kinetically by stopped flow techniques over a range of temperatures, Table XI. Dasgupta and Harris [16] have shown that the acid-catalysed decarboxylation of αβS-$[Co(tetren)CO_3]^+$ (*XI*) involves the equilibria,

$$[Co(tetren)(CO)_3]^{+} + H^{+} \rightleftharpoons [Co(tetren)(CO_3H)]^{2+},\ 1/K_c$$

$$[Co(tetren)CO_3H]^{2+} \xrightarrow[k]{r.d.} [Co(tetren)OH] + CO_2$$

The corresponding rate expression is $k_{obs} = k[H^+]/([H^+] + K_c)$ where pK_c has the value 6.4. Decarboxylation of $[Co([17]aneN_5)CO_3]^+$ and $[Co([15]aneN_5)CO_3]^+$ was studied using 0.05 *M* HCl so that the only process is the direct decarboxylation step of the protonated species. For the $[17]aneN_5$ derivative k = 0.43 s^{-1} at 25 °C ($\Delta H^{\ddagger}$ = 48.4 kJ mol^{-1}, $\Delta S_{298}^{\ddagger}$ = −90 JK^{-1} mol^{-1}) and for the $[15]aneN_5$ complex k = 0.33 s^{-1} at 25 °C, Table XI, with $\Delta H^{\ddagger}$ =



(XI)

TABLE XI. Acid Catalysed Decarboxylation of $[CoLCO_3]^+$ in 0.05 *M* HCl.

	Temp. (°C)	10 k_{obs} (s^{-1})
L = [17]aneN_5[a]		
	25	0.43
	28	0.52
	32	0.65
	37	0.96
L = [15]aneN_5[b]		
	25	0.33
	28.5	0.44
	32	0.59
	37	0.85

[a] For L = [17]aneN_5, $\Delta H^{\ddagger} = 48.4 \pm 3.1$ kJ mol^{-1}; $\Delta S_{298}^{\ddagger} = -109 \pm 10$ JK^{-1} mol^{-1} (r = 0.9959). [b] For L = [15]aneN_5, $\Delta H^{\ddagger} = 58.3 \pm 1.0$ kJ mol^{-1}; $\Delta S_{298}^{\ddagger} = -58 \pm 3$ JK^{-1} mol^{-1} (r = 0.9997).

TABLE XIII. Base Hydrolysis of $[CoL(OOCH)]^{2+}$ in Acetate and Citrate Buffers at 25 °C and I = 0.1 *M*.

pH	$10^{10}[OH^-]$ (*M*)	10^4k_{obs} (s^{-1})	$10^{-4}k_{OH}$ (M^{-1} s^{-1})
4.84	9.02	0.25	2.8
5.31	26.63	0.71	2.7
5.47	38.49	1.16	3.0
5.85	92.34	3.19	3.4
6.15	184.29	6.21	3.3

$k = 3.0 \times 10^4$ M^{-1} s^{-1}

TABLE XIV. Temperature Dependence of the Base Hydrolysis of $[CoL(OOCH)]^{2+}$ at I = 0.1 *M*.

Temp. (°C)	pH	$10^{10}[OH^-]$ (*M*)	10^4k_{obs} (s^{-1})	$10^{-4}k_{OH}$ (M^{-1} s^{-1})
25	5.85	92.3	3.19	3.45
29	5.88	144.7	6.75	4.66
33	5.90	203.8	10.14	4.97
36	5.90	253.5	17.47	6.89

$\Delta H^{\ddagger} = 41.1$ kJ mol^{-1} $\Delta S_{298}^{\ddagger} = -20$ JK^{-1} mol^{-1}

58.3 kJ mol^{-1} and $\Delta S_{298}^{\ddagger} = -58$ JK^{-1} mol^{-1}. For the open chain tetren complex, k = 0.28 s^{-1} at 25 °C with $\Delta H^{\ddagger} = 65.3$ kJ mol^{-1} and $\Delta S_{298}^{\ddagger} = -36$ JK^{-1} mol^{-1} [16]. The kinetic parameters for the acid-catalysed decarboxylation of monodentate carbonato complexes are summarised in Table XII. There is little variation in the values of the rate constants at 25 °C which fall within the range 0.3–1.1 s^{-1} for a wide range of 'inert' ligands ranging from the pentaammine, through the polyamine tetren to the pentadentate macrocycles. The activation parameters indicate that this result arises due to a close interplay of $\Delta H^{\ddagger}$ and $\Delta S_{298}^{\ddagger}$ which exert a compensatory effect. Reaction of $[CoClL]^{2+}$ with formic acid in the presence of $AgClO_4$ gives the pink formato complex $[CoL(OOCH)]^{2+}$ readily isolated as the perchlorate salt. A similar reaction can be used to prepare other derivatives such as $[CoL(DMF)]^{3+}$ in which the DMF ligand is coordinated *via* the carbonyl oxygen. The ^1H NMR spectrum reveals two methyl signals at 2.74 and 2.98, and a formyl singlet at 7.968. The methyl doublet arises due to restricted rotation about the N–CO bond due to delocalisation of the lone pair on nitrogen. The ^1H NMR data is very comparable with that of $[Co(NH_3)_5DMF]^{3+}$ where the $N(CH_3)_2$ doublet occurs at 2.88 and 3.03δ and the formyl singlet at 7.43δ [17]. The infrared spectrum has $\nu C{=}O$ at 1660 cm^{-1} similar to that of $[Co(NH_3)_5DMF]^{3+}$ at 1665 cm^{-1}. The first ligand field band occurs at 514 nm, very similar to that of $[CoL(OH_2)]^{3+}$ (506 nm) so providing additional evidence for the CoN_5O chromophore. The complex

TABLE XII. Kinetic Parameters for the Acid-catalysed Decarboxylation of Monodentate Carbonato Complexes.

Complex	$k_{25°C}$ (s^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (JK^{-1} mol^{-1})
$[Co(NH_3)_5CO_3]^+$ [a]	1.10	66.1	22
αβS-$[Co(tetren)CO_3]^+$ [b]	0.28	65.3	−36
$[Co([15]aneN_5)CO_3]^+$	0.33	58.3	−58
$[Co([17]aneN_5)CO_3]^+$	0.43	48.4	−109

[a] Data for $[Co(NH_3)_5CO_3]^+$ from E. Chaffee, T. P. Dasgupta and G. M. Harris, *J. Am. Chem. Soc., 95,* 4169 (1973) (See footnote 19). [b] Data for αβS-$[Co(tetren)CO_3]^+$ from ref. 17.

TABLE XV. Values of k_{OH} for the Base Hydrolysis of Formato Derivatives of Pentamine cobalt(III) Complexes.

Complex	k_{OH} (25 °C) (M^{-1} s^{-1})	Rel. Rate
$[Co(NH_3)_5OOCH]^{2+}$	5.8×10^{-4} [a]	1
αα-$[Co(tetren)OOCH]^{2+}$	153[b]	2.6×10^5
$[Co([17]aneN_5)OOCH]^{2+}$	3×10^4	5.2×10^7

[a] R. B. Jordan, Ph.D. Thesis, University of Chicago 1964, quoted by D. A. Buckingham, J. MacB. Harrowfield and A. M. Sargeson, *J. Am. Chem. Soc., 96,* 1726 (1974). [b] F. McLaren and R. W. Hay, unpublished results. The αα-nomenclature is that of Snow *et al., J. Chem. Soc. Chem. Comm.,* 891 (1969).

[CoL(OOCH)] undergoes rapid base hydrolysis in the pH range 4.8–6.2, with $k_{OH} = 3.0 \times 10^4$ M^{-1} s^{-1} at 25 °C, Table XIII. The temperature dependence of k_{OH}, Table XIV gives $\Delta H^{\ddagger} = 41.1$ kJ mol^{-1} and $\Delta S_{298}^{\ddagger} = -20$ JK^{-1} mol^{-1}. Current values of k_{OH} for the hydrolysis of formato derivatives of pentaminecobalt(III) complexes are summarised in Table XV. The complex $[Co([17]aneN_5)OOCH]^{2+}$ undergoes base hydrolysis some 5.2×10^7 times faster than $[Co(NH_3)_5OOCH]^{2+}$ at 25 °C.

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References

1 J. E. Richman and T. J. Atkins, *J. Am. Chem. Soc., 96,* 2268 (1974).
2 A. Bencini, L. Fabbrizzi and A. Poggi, *Inorg. Chem., 20,* 2544 (1981).
33 R. W. Hay, R. Bembi, T. Moodie and P. R. Norman, *J. Chem. Soc. Dalton Trans.,* in press.
4 R. W. Hay and P. R. Norman, *J. Chem. Soc. Dalton Trans.,* 1441 (1979).
5 L. Fabbrizzi, *J. Chem. Soc. Chem. Comm.,* 1063 (1979).
6 G. Bombieri, E. Forsellini, A. Del Pra, C. J. Cooksey, M. Humanes and M. L. Tobe, *Inorg. Chim. Acta, 61,* 43 (1982).
7 D. C. Weatherburn, personal communication.
8 B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev., 5,* 143 (1970).
9 T. Sakurai, S. Suzuki and A. Nakahara, *Bull. Chem. Soc. Jpn., 54,* 2313 (1981).
10 K. Miyoshi, H. Tanaka, E. Kimura, S. Tsuboyama, S. Murata, H. Shimizu and K. Ishizu, *Inorg. Chim. Acta, 78,* 23 (1983).
11 R. W. Hay, B. Jeragh, S. F. Lincoln and G. H. Searle, *Inorg. Nucl. Chem. Lett., 14,* 435 (1978).
12 R. Barbucci, L. Fabbrizzi and P. Paoletti, *Inorg. Chim. Acta, 7,* 157 (1973).
13 L. Fabbrizzi, M. Micheloni, P. Paoletti, A. Poggi and A. B. P. Lever, *J. Chem. Soc. Dalton,* 1438 (1981).
14 R. R. Gagne, C. A. Koval and G. C. Lisensky, *Inorg. Chem., 19,* 2854 (1980).
15 R. W. Hay and F. McLaren, unpublished results.
16 T. P. Dasgupta and G. M. Harris, *Inorg. Chem., 17,* 3304 (1978).
17 D. A. Buckingham, J. MacB. Harrowfield and A. M. Sargeson, *J. Am. Chem. Soc., 96,* 1726 (1974).