Tetra-aza Macrocyclic Complexes containing a Pendant Amino Group. Copper(II), Nickel(II), and Cobalt(III) Complexes of 5-Aminomethyl-2,5,10,12-tetramethyl-1,4,8,11-tetra-azacyclotetradecane (L) and *X*-Ray Structural Characterisation of the Cobalt(III) Complex [Co(L)Cl][ClO$_4$]Cl·EtOH†

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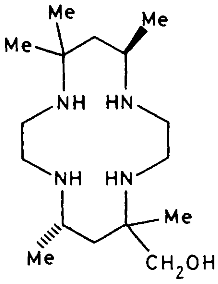
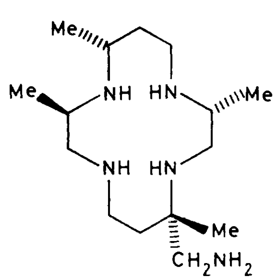
The macrocycle 5-aminomethyl-2,5,10,12-tetramethyl-1,4,8,11-tetra-azacyclotetradecane (L) containing a pendant amino group has been prepared. A variety of copper(II), nickel(II), and cobalt(III) complexes have been characterised. Octahedral $[NiL(H_2O)]^{2+}$ complexes are readily protonated to give yellow or orange planar $[Ni(HL)]^{3+}$ species. Analogous copper(II) complexes have also been prepared. *X*-Ray crystallographic investigation of the complex [Co(L)Cl][ClO$_4$]Cl·EtOH confirms the ligand stereochemistry and establishes a *trans* III (2 N–H bonds up, 2 N–H bonds down) stereochemistry for the chiral NH centres. The pendant amino group acts as a donor in one of the axial sites and lies *trans* to the chloride ligand. Rapid base hydrolysis of the Cl^- ligand occurs with $k_{OH} = 2.2 \times 10^4$ dm^3 mol^{-1} s^{-1} and $k_{aq} = 3.5 \times 10^{-5}$ s^{-1} at 25 °C and $I = 0.1$ mol dm^{-3}.

The preparation of pendant-arm macrocycles has attracted considerable attention in recent years and the topic has been reviewed.[1] House *et al.*[2] have reported the preparation and crystal structure of a quinquedentate N$_4$O ligand (I) prepared by dioxygen oxidation of *trans*-(*RSSR*)-[CoCl$_2$(L′)]ClO$_4$ (L′ = C-*meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-aza-cyclotetradecane). In this reaction oxidation of one of the *gem*-dimethyl substituents to a co-ordinated CH$_2$OH group occurs.

The present paper deals with the synthesis of complexes of a C-functionalised cyclam (cyclam = 1,4,8,11-tetra-azacyclotetradecane) derivative containing a –CH$_2$NH$_2$ side arm which can interact with a metal ion in the central cavity. The synthesis of the ligand, 5-aminomethyl-2,5,10,12-tetramethyl-1,4,8,11-tetra-azacyclotetradecane (L) has been outlined[3] (Scheme 1), and will be discussed in detail in subsequent publications (for further experimental details see ref. 4). The co-ordination chemistry of L with Cu^{II}, Ni^{II}, and Co^{III} is described in the present paper along with the *X*-ray structural characterisation of [Co(L)Cl][ClO$_4$]Cl·EtOH which confirms the ligand stereochemistry defined in (II).


(I)


(II) = L

Experimental

The ligand L was prepared as previously described[3] (Found: C, 63.1; H, 12.3; N, 24.4. Calc. for C$_{15}$H$_{35}$N$_5$: C, 63.1; H, 12.4; N, 24.5%); m.p. 120 °C.

[CoL(H$_2$O)][ClO$_4$]$_3$.—The ligand L (0.36 g) in methanol (10 cm^3) was added to a solution of CoCl$_2$·6H$_2$O (0.18 g) in methanol (10 cm^3). The solution was aerated overnight, and then basified with a few drops of concentrated sodium hydroxide. After standing for 1 h, the solution was acidified with concentrated HClO$_4$ (70%). The solution was then evaporated to dryness and the residue extracted with nitromethane. The red nitromethane extract was evaporated to dryness and the residue dissolved in a small volume of water. The aqueous solution was loaded onto a column of Sephadex C-25, and eluted with 3 mol dm^{-3} pyridinium acetate. Two bands separated on the column, the fastest moving band was rejected and the second more intense band collected. From this second fraction red crystals of the complex (0.2 g) were obtained on evaporation of the solvent (Found: C, 27.5; H, 5.7; N, 10.4. Calc. for C$_{15}$H$_{37}$Cl$_3$CoN$_5$O$_{13}$: C, 27.5; H, 5.7; N, 10.4%).

[Co(L)Cl][ClO$_4$]Cl·EtOH.—The complex [CoL(H$_2$O)]-[ClO$_4$]$_3$ (0.06 g) was dissolved in concentrated hydrochloric acid and the solution refluxed for 10 min. The solution was evaporated to dryness (water bath) and the resultant complex twice recrystallised from ethanol to give violet crystals (0.03 g) (Found: C, 36.3; H, 7.2; N, 12.3. Calc. for C$_{17}$H$_{41}$Cl$_3$CoN$_5$O$_5$: C, 36.4; H, 7.4; N, 12.5%).

[Co(L)Br][ClO$_4$]$_2$.—This was prepared as for the chloro complex, replacing the concentrated HCl with 47% HBr. The

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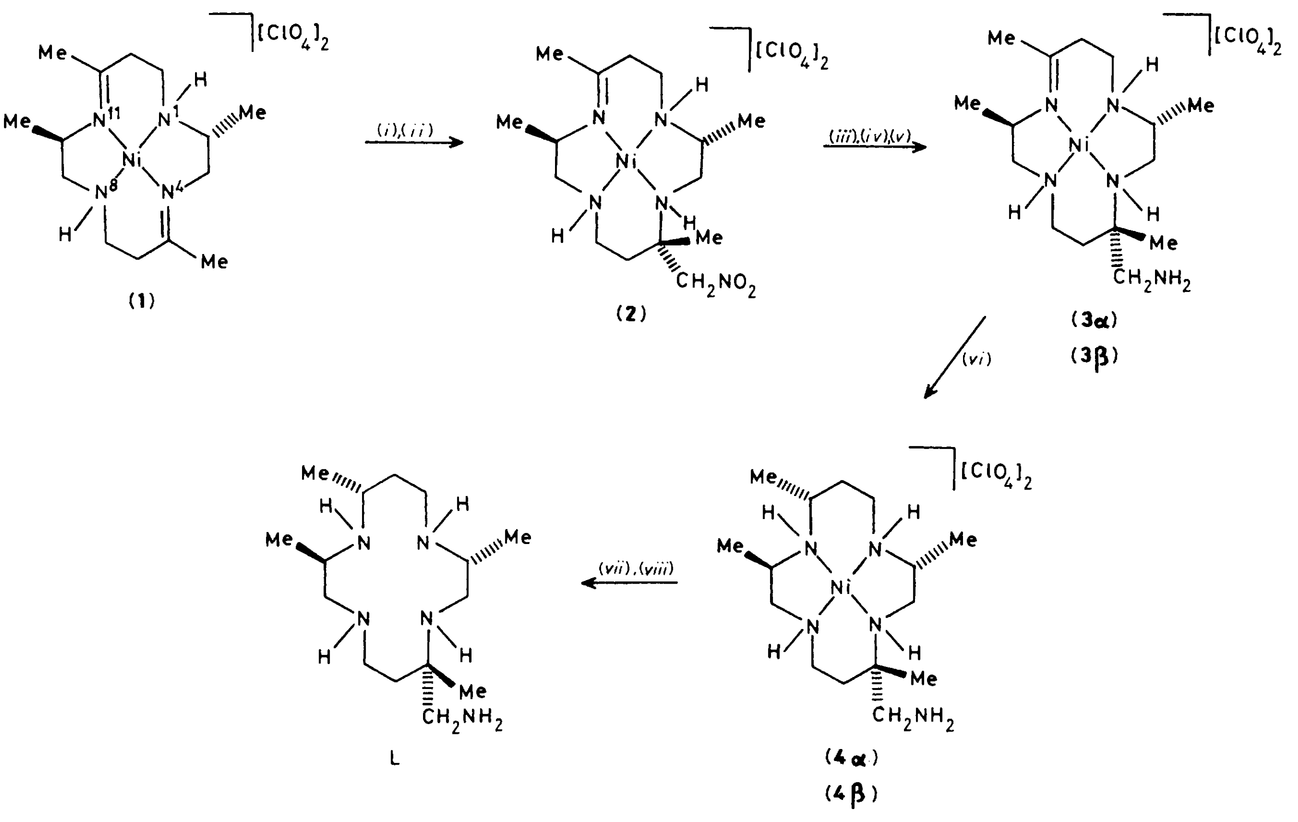
† (5-Aminomethyl-2,5,10,12-tetramethyl-1,4,8,11-tetra-azacyclotetra-decane)chlorocobalt(III) chloride perchlorate–ethanol (1/1).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Positional parameters with estimated standard deviations in parentheses

Atom[a]	x	y	z	Atom[a]	x	y	z
Co	0.770 49(4)	0.287 12(4)	0.712 15(5)	C(15)	0.546 6(3)	0.261 1(3)	0.771 1(4)
Cl(1)	0.986 82(8)	0.398 55(8)	0.807 6(1)	C(17)	0.927 7(4)	0.123 2(4)	1.041 1(5)
N(1)	0.831 9(3)	0.166 3(3)	0.794 4(3)	C(18)	0.649 4(4)	0.404 3(4)	1.036 4(4)
N(4)	0.786 0(3)	0.354 0(2)	0.912 8(3)	C(19)	0.856 3(4)	0.377 4(4)	0.436 7(4)
N(8)	0.710 0(3)	0.407 7(2)	0.628 1(3)	C(20)	0.782 8(5)	0.085 6(5)	0.316 2(5)
N(11)	0.744 3(3)	0.213 8(3)	0.503 1(3)	Cl(2)	0.562 3(1)	−0.038 11(9)	0.709 9(1)
N(16)	0.582 0(3)	0.208 8(2)	0.654 6(3)	Cl(3)	0.210 8(1)	−0.702 88(9)	0.463 5(1)
C(2)	0.906 1(3)	0.215 5(3)	0.964 5(4)	O(31)	0.296 9(3)	−0.749 8(3)	0.423 4(4)
C(3)	0.823 2(4)	0.276 8(3)	1.006 4(4)	O(32)	0.146 6(4)	−0.645 7(3)	0.358 8(4)
C(5)	0.657 2(3)	0.374 8(3)	0.889 0(4)	O(33)	0.292 4(3)	−0.619 6(3)	0.615 5(4)
C(6)	0.654 6(4)	0.479 7(3)	0.833 1(4)	O(34)	0.111 3(3)	−0.793 3(3)	0.455 8(4)
C(7)	0.618 9(4)	0.458 6(3)	0.669 3(4)	O(E1)[b]	0.305 6(8)	0.196 0(8)	−0.000 8(9)
C(9)	0.647 1(4)	0.363 1(3)	0.458 7(4)	O(E2)[c]	0.431 3(9)	0.159 2(8)	0.042 1(10)
C(10)	0.726 6(4)	0.298 1(4)	0.414 4(4)	O(E3)[d]	0.270(1)	0.226(1)	0.106(2)
C(12)	0.832 5(4)	0.146 3(4)	0.483 7(4)	O(E4)[e]	0.393(2)	0.234(2)	0.108(2)
C(13)	0.835 7(4)	0.058 2(4)	0.565 7(5)	O(E5)[f]	0.284(2)	0.244(2)	−0.122(2)
C(14)	0.909 0(4)	0.108 7(4)	0.736 7(5)	O(E6)[g]	0.542(3)	0.092(3)	0.021(3)

[a] Atoms O(E1)—O(E6) are assigned co-ordinates to allow for the highly disordered ethanol of solvation. Occupancy factors: [b] 0.75, [c] 0.57, [d] 0.39, [e] 0.35, [f] 0.30, [g] 0.13.



Scheme 1. (*i*) $MeNO_2$, NEt_3; (*ii*) $HClO_4$; (*iii*) Zn/HCl; (*iv*) NaOH; (*v*) $Ni(ClO_4)_2$; (*vi*) $NaBH_4$; (*vii*) HCl, MeCN; (*viii*) NaOH

blue complex was recrystallised from MeOH–H_2O (Found: C, 29.1; H, 5.7; N, 11.3. Calc. for $C_{15}H_{35}BrCl_2CoN_5O_8$: C, 28.9; N, 5.7; N, 11.2%).

$[CuL][ClO_4]_2$.—A mixture of copper(II) perchlorate hexahydrate (0.2 g) and the ligand L (0.15 g) was heated in methanol (10 cm^3) for *ca.* 0.5 h. On cooling the purple complex crystallised. The complex was twice recrystallised from methanol, yield 0.12 g (Found: C, 32.7; H, 6.3; N, 12.6. Calc. for $C_{15}H_{35}Cl_2CuN_5O_8$: C, 32.9; H, 6.4; N, 12.8%).

$[Cu(HL)][ClO_4]_3{\cdot}H_2O$.—The protonated complex was prepared by dissolving $[CuL][ClO_4]_2$ (0.05 g) in water (2 cm^3). Concentrated $HClO_4$ (0.05 g) was added dropwise. On standing, violet needles of the protonated complex crystallised (Found: C, 27.2; H, 5.65; N, 10.7. Calc. for $C_{15}H_{38}Cl_3CuN_5O_{13}$: C, 27.0; H, 5.75; N, 10.5%). Potentiometric titration of the protonated complex with sodium hydroxide gave $M = 666.6$ (calc. 666.4).

Nickel(II) complexes were characterised as previously described.[3]

Table 2. Molecular dimensions

(*a*) Bond lengths (Å)

Co–Cl(1)	2.264(1)	C(2)–C(3)	1.491(7)	N(4)–C(3)	1.492(5)	C(12)–C(13)	1.508(7)
Co–N(1)	1.983(3)	C(2)–C(17)	1.523(7)	N(4)–C(5)	1.503(5)	C(12)–C(20)	1.511(6)
Co–N(4)	1.965(3)	C(5)–C(6)	1.528(6)	N(8)–C(7)	1.503(6)	C(13)–C(14)	1.496(6)
Co–N(8)	1.984(3)	C(5)–C(15)	1.527(4)	N(8)–C(9)	1.484(5)	Cl(3)–O(31)	1.419(5)
Co–N(11)	2.008(3)	C(5)–C(18)	1.524(6)	N(11)–C(10)	1.512(6)	Cl(3)–O(32)	1.437(4)
Co–N(16)	1.974(3)	C(6)–C(7)	1.494(6)	N(11)–C(12)	1.504(6)	Cl(3)–O(33)	1.437(3)
N(1)–C(2)	1.487(4)	C(9)–C(10)	1.496(7)	N(16)–C(15)	1.492(6)	Cl(3)–O(34)	1.400(4)
N(1)–C(14)	1.489(6)	C(10)–C(19)	1.518(6)				

(*b*) Bond angles (°)

Cl(1)–Co–N(1)	90.17(9)	N(1)–C(2)–C(3)	105.6(3)	N(11)–Co–N(16)	94.1(1)	N(11)–C(10)–C(19)	114.9(3)
Cl(1)–Co–N(4)	88.82(8)	N(1)–C(2)–C(17)	113.2(3)	Co–N(1)–C(2)	108.5(2)	C(9)–C(10)–C(19)	113.3(4)
Cl(1)–Co–N(8)	89.53(8)	C(3)–C(2)–C(17)	110.5(4)	Co–N(1)–C(14)	118.4(3)	N(11)–C(12)–C(13)	109.7(4)
Cl(1)–Co–N(11)	94.24(9)	N(4)–C(3)–C(2)	109.6(4)	C(2)–N(1)–C(14)	111.0(3)	N(11)–C(12)–C(20)	110.9(3)
Cl(1)–Co–N(16)	170.9(1)	N(4)–C(5)–C(6)	106.6(3)	Co–N(4)–C(3)	110.0(2)	C(13)–C(12)–C(20)	110.1(4)
N(1)–Co–N(4)	84.9(1)	N(4)–C(5)–C(15)	104.7(3)	Co–N(4)–C(5)	108.9(2)	C(12)–C(13)–C(14)	115.1(3)
N(1)–Co–N(8)	179.3(2)	N(4)–C(5)–C(18)	112.5(3)	C(3)–N(4)–C(5)	113.5(3)	N(1)–C(14)–C(13)	111.8(3)
N(1)–Co–N(11)	95.1(1)	C(6)–C(5)–C(15)	113.9(3)	Co–N(8)–C(7)	119.7(3)	N(16)–C(15)–C(5)	111.1(3)
N(1)–Co–N(16)	92.8(1)	C(6)–C(5)–C(18)	108.1(4)	Co–N(8)–C(9)	109.3(2)	O(31)–Cl(3)–O(32)	110.2(3)
N(4)–Co–N(8)	95.7(1)	C(15)–C(5)–C(18)	111.1(3)	C(7)–N(8)–C(9)	108.5(3)	O(31)–Cl(3)–O(33)	107.5(2)
N(4)–Co–N(11)	176.9(1)	C(5)–C(6)–C(7)	117.0(3)	Co–N(11)–C(10)	110.5(2)	O(31)–Cl(3)–O(34)	109.3(3)
N(4)–Co–N(16)	82.9(1)	N(8)–C(7)–C(6)	113.0(3)	Co–N(11)–C(12)	120.3(2)	O(32)–Cl(3)–O(33)	109.6(2)
N(8)–Co–N(11)	84.3(1)	N(8)–C(9)–C(10)	109.5(3)	C(10)–N(11)–C(12)	113.4(4)	O(32)–Cl(3)–O(34)	108.6(2)
N(8)–Co–N(16)	87.6(1)	N(11)–C(10)–C(9)	105.3(4)	Co–N(16)–C(15)	112.3(2)	O(33)–Cl(3)–O(34)	111.6(3)

(*c*) Hydrogen-bond dimensions*

X···Y (Å)		H···Y (Å)		X–H···Y (°)	
N(1)···Cl(2)	3.247(3)	H(1)···Cl(2)	2.31	N–H···Cl(2)	168.7
N(4)···Cl(1^{I})	3.347(2)	H(4)···Cl(1^{I})	2.45	N–H···Cl(1^{I})	156.7
N(8)···O(32^{II})	3.026(5)	H(8)···O(32^{II})	2.29	N–H···O(32^{II})	133.5
N(11)···Cl(2^{II})	3.234(3)	H(11)···Cl(2^{II})	2.34	N–H···Cl(2^{II})	157.1
N(16)···Cl(2)	3.213(3)	H(162)···Cl(2)	2.31	N–H···Cl(2)	159.7
N(16)···O(31^{III})	3.380(5)	H(161)···O(31^{III})	2.60	N–H···O(31^{III})	139.8

* Roman numerals refer to the following equivalent positions: I $2 - x, 1 - y, 2 - z$; II $1 - x, -y, 1 - z$; III $x, 1 + y, z$.

Physical Measurements.—Potentiometric titrations were carried out using a Radiometer PHM 26 Research pH meter. Solutions were thermostatted at 25 °C and the ionic strength was adjusted to $I = 0.1$ mol dm^{-3} with potassium chloride. Infrared spectra were determined as KBr discs using a Shimadzu instrument. Visible spectra were obtained using Nujol mulls on filter paper (solid state), or aqueous solutions on a Perkin-Elmer Lambda 5 instrument.

Kinetic Measurements.—Kinetic studies of the base hydrolysis of $[Co(L)Cl]^{2+}$ were carried out using acetate and citrate buffers adjusted to $I = 0.1$ mol dm^{-3} with $NaClO_4$ at 25 °C. Hydroxide ion concentrations were estimated from the pH using $pK_w = 13.997$ (ref. 5) and an activity coefficient of 0.772 at 25 °C.[6] Aquation of the complex was studied using 0.1 mol dm^{-3} solutions of HNO_3. The reaction was monitored at 370 nm (where an absorbance increase occurs) using a Gilford 2400S spectrophotometer interfaced with an Apple II computing system. Excellent first-order or pseudo-first-order rate data were obtained in all cases.

Crystal-structure Determination.—*Crystal data.* $C_{15}H_{35}Cl_3CoN_5O_4 \cdot C_2H_5OH$, $M = 560.8$, triclinic, space group $P\bar{1}$, $a = 11.661(2)$, $b = 12.428(2)$, $c = 10.240(2)$ Å, $\alpha = 101.90(1)$, $\beta = 115.23(1)$, $\gamma = 101.97(1)°$, $U = 1\,238.4$ Å^3, $Z = 2$, $D_c = 1.50$ g cm^{-3}, $F(000) = 592$, Mo-K_α radiation, $\lambda = 0.710\,73$ Å, $\mu = 10.5$ cm^{-1}.

Pale violet diamond-shaped crystals were grown from ethanol. Accurate cell dimensions and the crystal orientation matrix were determined on a CAD-4 diffractometer by a least-squares treatment of the setting angles of 25 general reflections. A crystal of dimensions 0.1 × 0.2 × 0.2 mm was used for data collection with graphite-monochromatised Mo-K_α radiation. Intensities of reflections with $2 < 2\theta < 54°$ were scanned; intensities of three reflections, chosen as standards and measured every 3 h, showed no evidence of crystal decay. A total of 5 847 reflections were measured, of which 5 384 were unique (*R* factor on averaging 0.020). Data were corrected for Lorentz polarisation and absorption effects[7] (max. and min. transmission coefficients 0.877, 0.715) and the 3 013 reflections with $I > 3\sigma(I)$ were labelled observed and used in structure solution and refinement.

Structure solution and refinement. The Co atom co-ordinates were derived from the three-dimensional Patterson function and the remaining non-hydrogen atoms found by application of the heavy atom method. At the outset, the exact composition of the crystals examined was uncertain, but it soon became clear that the counter anions were chloride and perchlorate. There was also an ill defined set of peaks filling what would have been a void in the crystal lattice. The dimensions of this set of peaks did not correspond to a simple ethanol (or any other) molecule and after many attempts we assumed that the electron density corresponded to a scrambled ethanol and simply allowed for these 'atoms' in the calculation by assigning them to be fractionally occupied O atoms. Refinement was by full-matrix least-squares calculations initially with isotropic and then with anisotropic thermal parameters (except for the disordered ethanol molecule). At intermediate stages in the refinement difference maps showed maxima in positions consistent with the expected location of the hydrogen atoms of the cation; in the final rounds of calculations, the hydrogen atoms were positioned on geometrical grounds (C–H, N–H 0.95 Å) and included (as riding atoms) in the structure factor calculations with an overall B_{iso} of 5 Å^2. The final round of calculations converged with $R = 0.040$ and $R' = 0.048$; the maximum shift/error ratio was less than 0.009. Weights in the refinement were derived from the counting statistics and a final difference map had no chemically significant features. Scattering factors and anomalous dispersion corrections were from International Tables.[8] Atomic co-ordinates are given in Table 1 and details of the molecular geometry are in Table 2. Figure 1 is a view of the cation prepared using ORTEP II.[9]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

Results and Discussion

Ligand Synthesis.—The synthesis of the ligand L is summarised in Scheme 1. Addition of NEt_3 to a nitromethane solution of the nickel(II) racemic complex (**1**),[3] which has an N-*meso* chiral nitrogen stereochemistry, leads to addition of $CH_2NO_2^-$ to the less hindered C=N group to give the sparingly soluble monoperchlorate salt of (**2**). The paramagnetic product was then protonated with perchloric acid in $MeOH–CH_3NO_2$ (9:1) solution to give the yellow diamagnetic diperchlorate (**2**).

Reduction of the nitro group with zinc powder and hydrochloric acid gave two paramagnetic N-isomeric 5-aminomethyl derivatives (**3**α)·H_2O and (**3**β)·$2H_2O$. Further reduction with sodium tetrahydroborate in methanol solution reduced the remaining C=N double bond, giving the paramagnetic N-isomeric complexes (**4**α)·H_2O and (**4**β)·$2H_2O$. Demetallation

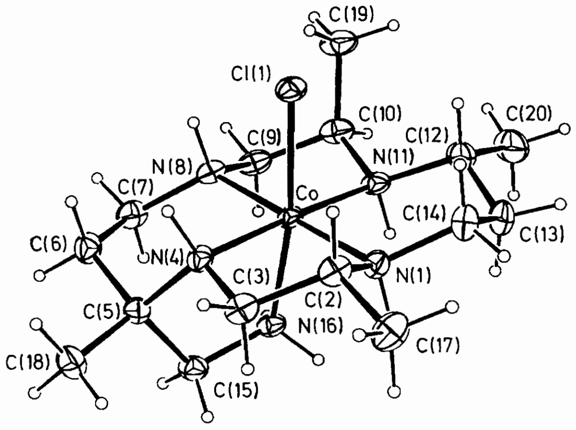
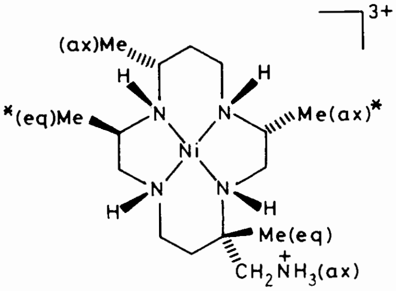
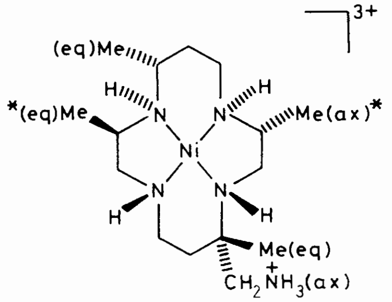


Figure 1. A view of the cation $[Co(L)Cl]^{2+}$ with the crystallographic numbering scheme

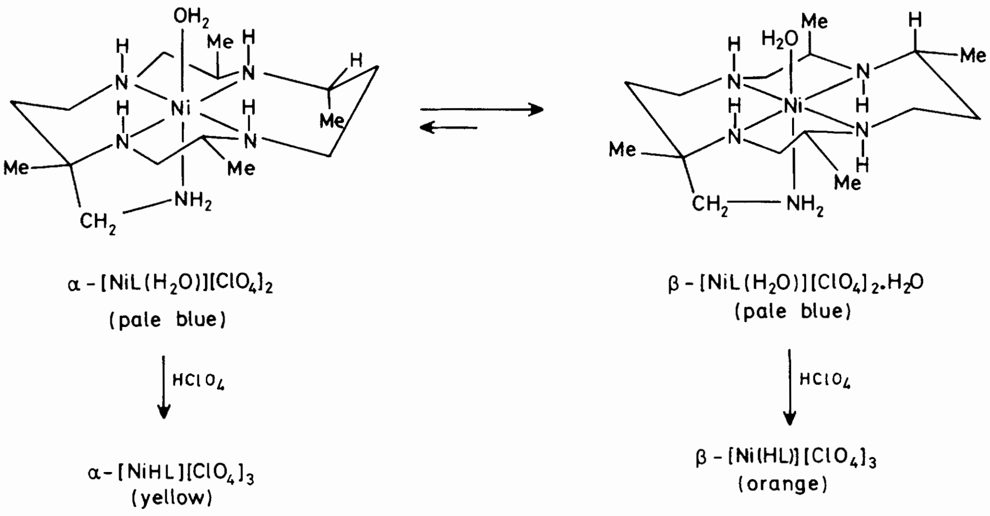


α configuration
(*trans* I)



β configuration
(*trans* III)

Figure 2. Configurations of the diamagnetic square-planar nickel(II) complexes (* pseudo)



Scheme 2. Configurations and reactions of the nickel(II) complexes

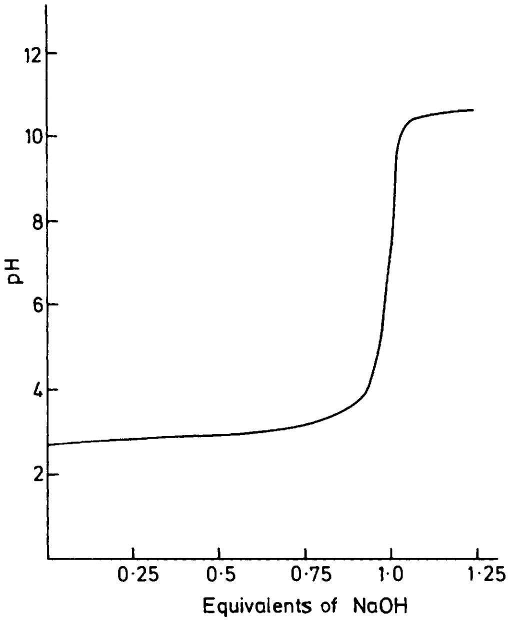


Figure 3. Potentiometric titration of β-$[Ni(HL)][ClO_4]_3$ with sodium hydroxide at 25 °C and I = 0.1 mol dm^{-3} (KCl)

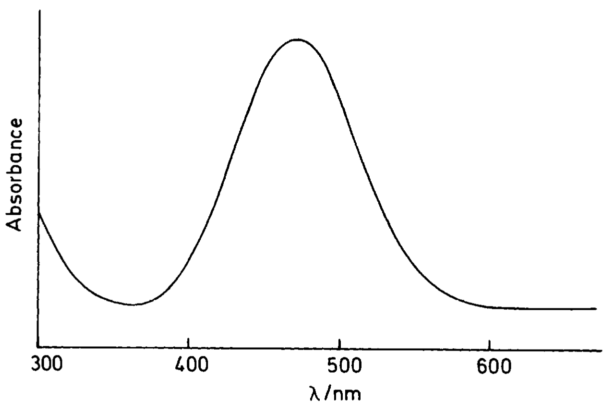


Figure 4. Solid-state spectrum of β-$[Ni(HL)][ClO_4]_3$ showing the $^1B_{1g}\leftarrow{}^1A_{1g}$ transition at 473 nm of singlet ground-state nickel(II)

of (4α) and (4β) in acetonitrile saturated with dry hydrogen chloride gas gave L, m.p. 120 °C.

Nickel(II) *Complexes.*—Two nickel(II) complexes α-$[NiL(H_2O)][ClO_4]_2$ and β-$[NiL(H_2O)][ClO_4]_2 \cdot H_2O$ were characterised. Both complexes are pale blue, but on acidification with $HClO_4$ they give yellow α-$[Ni(HL)][ClO_4]_3$ and orange β-$[Ni(HL)][ClO_4]_3$ due to protonation of the aminomethyl side arm, Scheme 2. The α isomer has the *trans* I configuration of the chiral nitrogen centres (all N–H bonds up) while the β isomer has the *trans* III configuration (two N–H bonds up and two down).* The β isomer is the more thermodynamically stable. The ^{13}C and ^1H n.m.r. spectra of the diamagnetic triperchlorate salts are consistent with the configurations defined in Scheme 2[3] and Figure 2.

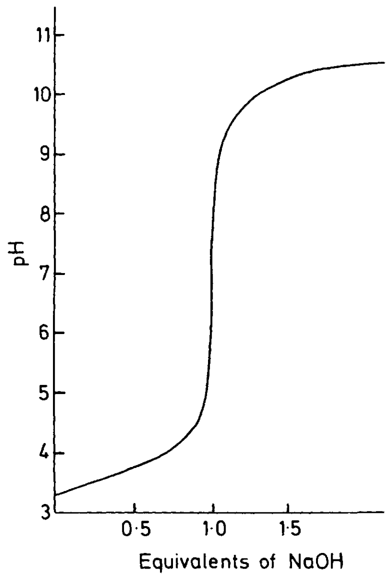


Figure 5. Potentiometric titration of $[Cu(HL)][ClO_4]_3 \cdot H_2O$ at 20 °C

Potentiometric titration of the orange β-$[Ni(HL)][ClO_4]_3$ with sodium hydroxide gave the titration curve shown in Figure 3. The pK_a of the pendant $-CH_2NH_3^+$ group is 2.97 at 25 °C and I = 0.1 mol dm^{-3}. A similar pH titration of α-$[Ni(HL)][ClO_4]_3$ gave a pK_a of 2.86 under the same conditions.

The solid-state spectrum of blue β-$[NiL(H_2O)][ClO_4]_2 \cdot H_2O$ has bands at 324 (30 860) and 492 nm (20 300 cm^{-1}) quite typical of six-co-ordinate tetra-aza macrocyclic complexes of nickel(II). The solid-state spectrum of the orange β-$[Ni(HL)][ClO_4]_3$ has a single strong *d–d* band at 473 nm (21 140 cm^{-1}) due to the $^1B_{1g}\leftarrow{}^1A_{1g}$ transition of singlet ground-state nickel(II), Figure 4.

Copper(II) *Complexes.*—The purple complex $[CuL][ClO_4]_2$ was readily prepared by the reaction of $Cu(ClO_4)_2 \cdot 6H_2O$ with the ligand in methanol. Addition of $HClO_4$ to an aqueous solution of this complex gives violet needles of the protonated complex $[Cu(HL)][ClO_4]_3 \cdot H_2O$. Potentiometric titration of the protonated species with sodium hydroxide in aqueous solution gives the titration curve shown in Figure 5. The molecular weight obtained from these data is 666.6 (calc. 666.4). The approximate pK_a for the equilibrium $[Cu(HL)]^{3+} \rightleftharpoons [CuL]^{2+} + H^+$ is 3.7 at 20 °C.

Cobalt(III) *Complexes.*—The red $[CoL(H_2O)][ClO_4]_3$ and the violet $[Co(L)Cl][ClO_4]Cl \cdot EtOH$ complexes were readily prepared. The visible spectrum of the cation $[Co(L)Cl]^{2+}$ is shown in Figure 6. Bands at 556 and *ca.* 480 nm can be assigned to the transitions $^1A_{1g}\rightarrow{}^1E_g$ and $^1A_{1g}\rightarrow{}^1A_{2g}$ arising from a reduction in symmetry from the $^1T_{1g}$ state.[11] This large splitting arises due to the combination of medium field and weak field ligands in the two axial sites.

Crystal Structure of $[Co(L)Cl][ClO_4]Cl \cdot EtOH$.—The *X*-ray analysis defines the structure and stereochemistry of the cation to be as shown in Figure 1 with a *trans* III configuration of the *sec*-NH centres. The Co atom has octahedral co-ordination distorted by the co-ordination of the pendant $-CH_2NH_2$ group. Principal dimensions (Table 2) include Co–N 1.965—2.008(3), Co–Cl 2.264(1) Å with N–Co–N 82.9—94.1(1)° and Cl(1)–Co–N(16) 170.9(1)°. A preliminary account of the synthesis and stereochemistry of the cobalt(III) complex of the related N_4O donor macrocycle (**I**) has appeared[2] without crystallographic

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* For a discussion of the stereochemistry of metal complexes of cyclam see ref. 10.

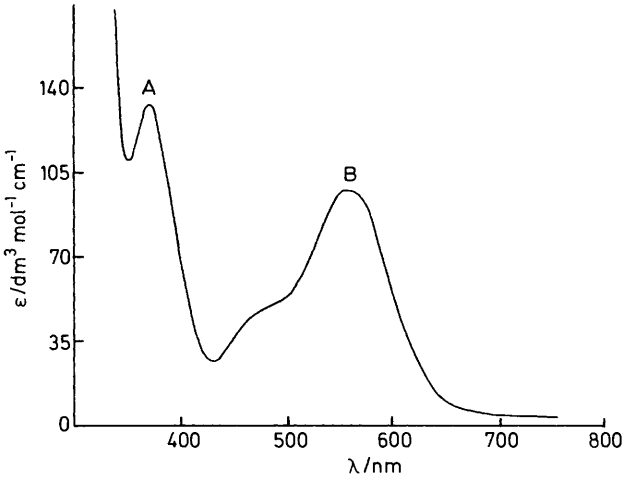


Figure 6. Visible spectrum of the cation $[Co(L)Cl]^{2+}$ in aqueous solution: A, $\lambda_{max.}$ = 372 (ε = 133); B, $\lambda_{max.}$ = 556 nm (ε = 98 dm^3 mol^{-1} cm^{-1})

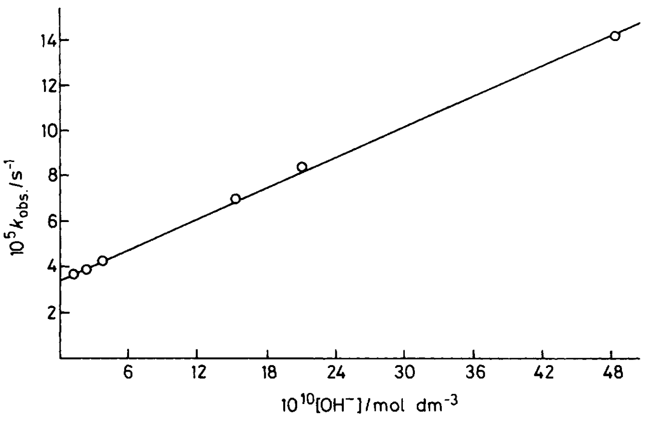


Figure 7. Plot of $k_{obs.}$ *versus* the hydroxide ion concentration for the base hydrolysis of $[Co(L)Cl]^{2+}$ at 25 °C and I = 0.1 mol dm^{-3} ($NaClO_4$)

details, and in [1,9-bis(2-pyridyl)-2,5,8-triazanonane]chlorocobalt(III), the Co–N distances are in the range 1.95—1.97 and Co–Cl 2.242 Å.[12]

The two six-membered rings in the cation adopt chair conformations, with methyl groups at C(2), C(5), and C(12) equatorial, and that at C(10) axial. The two 'equatorial' five-membered CoN_2C_2 rings are in a slightly flattened *gauche* conformation [torsion angles N(1)–C(2)–C(3)–N(4) −48.2, N(8)–C(9)–C(10)–N(11) 50.0°]. The remaining five-membered ring, Co,N(4),C(5),C(15),N(16) has a flattened *gauche* conformation [torsion angle N(4)–C(5)–C(15)–N(16) −37.0°].

The remaining bond lengths in the macrocycle (Table 2) with N–C 1.484(5)—1.512(6) Å [mean 1.496(9) Å], C–C 1.491(7)—1.528(6) Å [mean 1.510(14) Å] are in accord with previously reported values.[13]

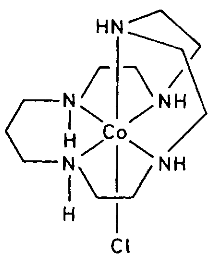
In the crystal structure, all six N–H groups take part in N–H ··· O and N–H ··· Cl hydrogen bonding to the Cl atom of an adjacent cation or to the chloride or perchlorate anions; details are given in Table 2.

Aquation and Base Hydrolysis of $[Co(L)Cl]^{2+}$.—The base hydrolysis of $[Co(L)Cl]^{2+}$ is quite rapid and the reaction was studied using acetate and citrate buffer solutions in the pH range 4—5.6, Table 3. A plot of $k_{obs.}$ (the observed first-order rate constant at constant pH) *versus* the hydroxide ion concentration is linear with a positive intercept, Figure 7.

Table 3. Kinetics of base hydrolysis of $[Co(L)Cl]^{2+}$ in acetate and citrate buffers at I = 0.1 mol dm^{-3} ($NaClO_4$) at 25 °C[a]

pH	$10^{10}[OH^-]$/ mol dm^{-3}	$10^5k_{obs.}/s^{-1}$
4.02	1.33	3.7
4.24	2.27	3.9
4.47	3.85	4.3
5.07	15.34	7.0
5.21[b]	21.12	8.4
5.57[b]	48.51	14.2

[a] Acetate buffer, unless otherwise stated; reaction monitored by the absorbance increase at 370 nm. [b] Using citrate buffer.



(III)

The rate expression takes the form $k_{obs.} = k_{aq} + k_{OH}[OH^-]$, and least-squares analysis of the data gives k_{aq} = 3.5 × 10^{-5} s^{-1} and k_{OH} = 2.23 × 10^4 dm^3 mol^{-1} s^{-1} at 25 °C and I = 0.1 mol dm^{-3}. The aquation rate was determined independently using 0.1 mol dm^{-3} solutions of HNO_3. The reaction displays excellent first-order kinetics over 4.5 half lives giving k_{aq} = 3.4 × 10^{-5} s^{-1} in close agreement with the rate constant previously obtained using buffer solutions.

Base hydrolysis of $[Co(L)Cl]^{2+}$ with k_{OH} = 2.23 × 10^4 dm^3 mol^{-1} s^{-1} is rapid and is comparable with that of chloro-(1,4,7,10,13-penta-azacyclohexadecane)cobalt(III),[14] (**III**) where k_{OH} = 1.1 × 10^5 dm^3 mol^{-1} s^{-1} at 25 °C and I = 0.1 mol dm^{-3}. For the simple chloropenta-ammine complex $[Co(NH_3)_5Cl]^{2+}$, k_{OH} = 0.85 dm^3 mol^{-1} s^{-1} at 25 °C.[15] Henderson and Tobe[16] have considered the factors which influence the reactivity of chloropenta-ammine complexes of cobalt(III) towards base hydrolysis. Deprotonation to form the conjugate base takes place at a nitrogen which is the middle member of a meridional set of three donors (called 'flat' for convenience). The requirements for high lability towards base hydrolysis are (*a*) there should be a flat secondary nitrogen to form the amido group, (*b*) the amido group must be *cis* to the leaving group, (*c*) the plane of the amido group in the intermediate should be able to lie perpendicular to the trigonal plane of cobalt, (*d*) there should be five-membered rings on either side of this group to hold it in position, and (*e*) there should be unidentate amines or a six-membered chelate occupying the remaining equatorial sites in the intermediate, so that there is minimal strain. Many of these criteria are met by macrocyclic complexes of the present type and rapid base hydrolysis is thus expected.

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