Synthesis of a Thirteen-membered Tetra-azamacrocycle employing Formaldehyde and Nitroalkanes directed by Metal Ions. Crystal Structures of (12-Methyl-12-nitro-1,4,7,10-tetra-azacyclotridecane)copper(II) Perchlorate and μ-Chloro-1,1,1-trichloro-2-(12-methyl-12-nitro-1,4,7,10-tetra-azacyclotridecane)dicopper(II)†

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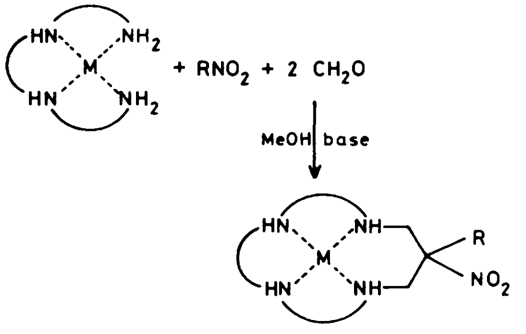
Reaction of formaldehyde and nitroethane or nitropropane with the copper(II) or nickel(II) complexes of 1,8-diamino-3,6-diazaoctane in methanol yields the complexed macrocycle 12-methyl-12-nitro-1,4,7,10-tetra-azacyclotridecane (L^1) or the 12-ethyl analogue (L^2). Both copper(II) and nickel(II) complexes were isolated as perchlorate salts. The latter exists in the singlet ground state, but tetrahydroborato and dithiocyanate nickel(II) compounds with triplet ground states were also isolated. The perchlorate salt of $[Cu(L^1)]^{2+}$, defined by a structure determination, consists of a linear polymer with bridging perchlorate groups occupying axial sites about a square plane of the macrocycle primary amines and the metal ion; Cu–N distances are 1.943(7) and 1.96(1) Å, with Cu–O at 2.62(1) and 2.65(2) Å. Slow crystallization of $[Cu(L^1)]^{2+}$ from chloride ion solution yielded a dark green complex of L^1 which contained an equimolar amount of the $[CuCl_4]^{2-}$ anion. An *X*-ray structure analysis defined the molecule as the binuclear neutral compound $[Cu(L^1)Cl(CuCl_3)]$, with a single bridging chloride ion linking copper(II) ions in either a tetrahedron of chloride ions or a square-based pyramid of four nitrogen donors [Cu–N 2.006(4) and 2.022(3) Å] with an apical chloride ion [Cu–Cl 2.507(2) Å] which bridges to the second copper(II) ion. The Cu ··· Cu distance is 3.928(2) Å, and there are no antiferromagnetic exchange interactions.

Metal-directed syntheses of macrocyclic ligands employing formaldehyde and carbon acids around inert metal ions are well developed,[1–4] and we are currently exploring similar reactions around labile metal ions. At least around copper(II), which has a relative preference for square-planar co-ordination, facile syntheses of macromonocyclic ligands can be achieved.[5–7] We have recently embarked on the task of synthesizing a range of macromonocycles of variable ring size by condensation reactions involving tetra-amine ligands, formaldehyde, and a nitroalkane with either copper(II) or nickel(II) as template. The object is to investigate the facility of the reaction shown by equation (1) for different ring sizes, and to define the structural and physical properties of the major products.



(1)

In this study, we have employed the 1,8-diamino-3,6-diazaoctane (trien) precursor to develop the synthesis of a 13-membered macromonocycle. Synthesis directed by copper(II) follows earlier related studies,[5–7] whereas the macrocyclization reaction employing nickel(II) as template is reported for the first time. The structural characterization of the copper(II) complex as both the perchlorate and tetrachlorocuprate(II) salts, and physical properties of the products, are also reported.

Experimental

Syntheses.—(12-*Methyl*-12-*nitro*-1,4,7,10-*tetra-azacyclotridecane*)*copper*(II) *perchlorate*, $[Cu(L^1)][ClO_4]_2$. The tetra-amine 1,8-diamino-3,6-diazaoctane (trien, 3.18 g, 21.7 mmol) was added to a solution of $Cu(NO_3)_2{\cdot}2.5H_2O$ (5.19 g, 21.9 mmol) in methanol (200 cm^3). The resulting dark blue solution was warmed to *ca.* 50 °C, then nitroethane (1.64 g, 21.9 mmol), triethylamine (2.2 g, 21.7 mmol), and excess formaldehyde (12 cm^3, 36% aqueous, 1.57 mol) were added. After heating for 30 min, the solution was diluted with a large volume of water, sorbed onto a column of SP-Sephadex C-25 (Na^+ form) resin (25 × 4 cm), and eluted with 0.2 mol dm^{-3} $NaClO_4$. Only one major purple band was observed and collected, reduced in volume, and the product crystallized by slow evaporation. The complex was isolated as a dark red solid (1.8 g, 16%); further crystallization was achieved, but with some contamination from

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

the electrolyte (Found: C, 23.6; H, 4.7; N, 13.5. Calc. for $C_{10}H_{23}Cl_2CuN_5O_{10}$: C, 23.65; H, 4.6; N, 13.8%). Electronic spectrum: (in water) $\lambda_{max.}$ 529 (ε 172) and 260 (2 240); [in dimethyl sulphoxide (dmso)] 543 nm (193 $dm^3\ mol^{-1}\ cm^{-1}$). I.r. spectrum: (KBr disc) $\nu_{asym}(NO_2)$ 1 547 and $\nu_{sym}(NO_2)$ 1 349 cm^{-1}.

(12-*Methyl*-12-*nitro*-1,4,7,10-*tetra-azacyclotridecane*)*copper*(II) *tetrachlorozincate*, $[Cu(L^1)][ZnCl_4]$. The perchlorate salt was dissolved in a small volume of water and an excess of zinc chloride was added, followed by acetone until the solution became turbid. The blue product was collected after 24 h, washed with ethanol, and then recrystallized from hot methanol–propan-2-ol (Found: C, 23.9; H, 4.7; N, 13.1. Calc. for $C_{10}H_{23}Cl_4CuN_5O_2Zn$: C, 23.3; H, 4.5; N, 13.6%).

(12-*Methyl*-12-*nitro*-1,4,7,10-*tetra-azacyclotridecane*)*copper*(II) *tetrachlorocuprate*, $[Cu(L^1)][CuCl_4]$. A solution of trien (2.95 g) and $Cu(NO_3)_2{\cdot}3H_2O$ (4.8 g) in methanol (200 cm^3) was treated with nitroethane (3.5 cm^3), formaldehyde (10 cm^3, 36% aqueous), and triethylamine (3 cm^3) and reacted at *ca.* 50 °C for 2 h, then stirred at room temperature for 2 d. On addition of an equal volume of water, some green precipitate was formed and separated. The purple solution was diluted further and sorbed onto a column of SP-Sephadex C-25 resin. Elution with 0.3 mol dm^{-3} NaCl separated the major purple band from a following minor blue band which was readily decomposed by acid and hence not macrocyclic. The purple band was concentrated and set aside to crystallize at room temperature. Over a period of several weeks, large green crystals were deposited, collected, and dried (1.5 g) (Found: C, 23.8; H, 4.7; N, 13.3. Calc. for $C_{10}H_{23}Cl_4Cu_2N_5O_2$: C, 23.35; H, 4.5; N, 13.6%). Electronic spectrum: (reflectance) $\lambda_{max.}$ 565 and 440; (dmso, dissociated mixture) 648 (ε 277) and 415 (sh) nm (*ca.* 300 $dm^3\ mol^{-1}\ cm^{-1}$).

(12-*Methyl*-12-*nitro*-1,4,7,10-*tetra-azacyclotridecane*)*nickel*(II) *perchlorate*, $[Ni(L^1)][ClO_4]_2$. A mixture of $Ni_2(trien)_3(ClO_4)_2{\cdot}2H_2O$[8] (27.5 g) and $[Ni(OH_2)_6][ClO_4]_2$ (11.2 g) was heated in methanol (400 cm^3) until completely dissolved, forming a solution of the $[Ni(trien)]^{2+}$ ion. Nitroethane (20 cm^3) and triethylamine (5 cm^3) were added. The solution was stirred under reflux, and a formaldehyde solution (20 cm^3, 36% aqueous) added over 5 h. Stirring under reflux was continued for a further 20 h. The yellow product (22 g) was filtered from the cold solution, washed with ethanol, and recrystallized from hot water, or by addition of propan-2-ol to a solution in hot acetonitrile–water (10:1) (Found: C, 24.5; H, 5.0; N, 14.0; Ni, 11.8. Calc. for $C_{10}H_{23}Cl_2N_5NiO_{10}$: C, 23.9; H, 4.6; N, 13.9; Ni, 11.7%). Electronic spectrum: (in water) $\lambda_{max.}$ 422 nm (ε 102 $dm^3\ mol^{-1}\ cm^{-1}$). I.r. spectrum: (KBr disc) $\nu_{asym}(NO_2)$ 1 525 cm^{-1}.

An isomeric perchlorate salt was prepared by dissolving the tetrahydroborato compound (see below) in 2 mol dm^{-3} perchloric acid–acetonitrile (1:1), and vacuum evaporating the acetonitrile. The yellow product was filtered off and washed with ethanol. The compound reverts to the original form on recrystallization.

(12-*Methyl*-12-*nitro*-1,4,7,10-*tetra-azacyclotridecane*)*dithiocyanatonickel*(II), $[Ni(L^1)(NCS)_2]$. An excess of sodium thiocyanate was added to a hot aqueous solution of the perchlorate salt. The solution slowly darkened, and deposited the mauve product over a period of hours. This was collected and washed with ethanol. It can be recrystallized from hot water, the product again crystallizing slowly (Found: C, 34.3; H, 5.6; N, 23.3; Ni, 13.9. Calc. for $C_{12}H_{23}N_7NiO_2S_2$: C, 34.3; H, 5.5; N, 23.3; Ni, 14.0%). Electronic spectrum: (in acetone) $\lambda_{max.}$ 936 (ε 28.2) and 553 nm (12.2 $dm^3\ mol^{-1}\ cm^{-1}$). Magnetic susceptibility: χ_m 49.6 × 10^{-9} $m^3\ mol^{-1}$; $\mu_{eff.}$ 3.2 at 298 K.

(12-*Methyl*-12-*nitro*-1,4,7,10-*tetra-azacyclotridecane*)*tetrahydroboratonickel*(II) *perchlorate*, $[Ni(L^1)(BH_4)][ClO_4]$. Sodium tetrahydroborate, in a small excess, was added to a warm aqueous solution of the perchlorate salt. The mauve product was filtered from the cold solution and recrystallized from acetonitrile–water–propan-2-ol (Found: C, 28.7; H, 6.5; N, 17.6; Ni, 14.0. Calc. for $C_{10}H_{27}BClN_5NiO_6$: C, 28.7; H, 6.5; N, 17.8; Ni, 13.8%). Electronic spectrum: (in dmso) $\lambda_{max.}$ 907 (ε 18.3), 552 (24.6), and 355 nm (53.7 $dm^3\ mol^{-1}\ cm^{-1}$). Magnetic susceptibility: χ_m 44.6 × 10^{-9} $m^3\ mol^{-1}$; $\mu_{eff.}$ 3.0 at 298 K.

Table 1. Non-hydrogen atomic co-ordinates for $[Cu(L^1)][ClO_4]_2$

Atom	x	y	z
Cu	0.756 0(1)	0.111 3(1)	$\frac{1}{4}$
C(1)	0.5409(9)	0.163 9(8)	$\frac{1}{4}$
C(11)	0.442(1)	0.140(1)	$\frac{1}{4}$
N(1)	0.543(1)	0.274(1)	$\frac{1}{4}$
O(1)[a]	0.529(1)	0.316(1)	0.357(2)
O(2)[a]	0.609(3)	0.314(2)	$\frac{1}{4}$
C(2)	0.582 1(8)	0.129 9(6)	0.391(1)
N(3)	0.679 3(6)	0.148 8(4)	0.412 4(7)
C(4)	0.717 2(8)	0.094 3(7)	0.539 8(10)
C(5)	0.818 7(10)	0.104 1(8)	0.532 4(11)
N(6)	0.841 9(7)	0.056 6(8)	0.389 4(12)
C(7)	0.926 9(8)	0.055 5(8)	0.329 8(13)
Cl(1)	0.643 5(4)	−0.141 1(2)	$\frac{1}{4}$
O(11)	0.687 7(10)	−0.060 9(9)	$\frac{1}{4}$
O(12)[b]	0.680(2)	−0.217(1)	0.311(3)
O(13)[b]	0.563(2)	−0.125(3)	0.316(7)
O(14)[b]	0.625(2)	−0.167(3)	0.117(2)
Cl(2)	0.169 7(3)	0.161 8(3)	$\frac{1}{4}$
O(21)[b]	0.235(1)	0.210(1)	0.168(3)
O(22)[b]	0.147(1)	0.075(1)	0.202(2)
O(23)[b]	0.178(3)	0.150(1)	0.396(3)
O(24)[b]	0.101(1)	0.225(1)	0.230(5)

[a] Site occupancy: $\frac{2}{3}$. [b] Site occupancy: 0.5.

(12-*Ethyl*-12-*nitro*-1,4,7,10-*tetra-azacyclotridecane*)*nickel*(II) *perchlorate*, $[Ni(L^2)][ClO_4]_2$. This compound was prepared as for the L^1 analogue but by substituting an equimolar amount of 1-nitropropane for the nitroethane (Found: C, 25.6; H, 5.0; N, 13.7; Ni, 11.4. Calc. for $C_{11}H_{25}Cl_2N_5NiO_{10}$: C, 25.6; H, 4.9; N, 13.6; Ni, 11.4%). Electronic spectrum: (in water) $\lambda_{max.}$ 422 nm (ε 89 $dm^3\ mol^{-1}\ cm^{-1}$).

Physical Methods.—Electronic spectra were recorded using Hitachi 220A and 330 spectrophotometers. Diffuse-reflectance spectra were recorded with the latter instrument fitted with an integrating sphere attachment. Infrared spectra were recorded using Nicholet MX-1 FT-IR or Perkin-Elmer 599B spectrophotometers, with the complexes dispersed in KBr discs. Magnetic susceptibility measurements were determined at room temperature by the Faraday method, and at variable temperatures as previously described.[9]

Structure Determinations.—A unique data set was measured for each compound at 295 K within the limit $2\theta_{max.} = 60°$ using Syntex $P2_1$ and CAD-4 four-circle diffractometers fitted with monochromatic Mo-K_α radiation, $\lambda = 0.710\ 69$ Å, and operating in conventional $2\theta/\theta$ scan mode. N Independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement after analytical absorption correction and solution of the structure by vector methods. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included and constrained at estimated values. Residuals on $|F|$ at convergence are conventional R, R' {statistical weights, derived from $\sigma^2(I) = [\sigma^2(I)_{diff} + 0.000\ 37{\cdot}\sigma^4(I)_{diff}]$}. Neutral complex scattering factors were employed;[10] computation

Table 2. Copper environment in $[Cu(L^1)][ClO_4]_2$*

Distances (Å)	
Cu-N(3)	1.943(7)
Cu-N(6)	1.96(1)
Cu-O(11)	2.62(1)
Cu-O(12^i)	2.65(2)
Angles (°)	
N(3)-Cu-N(3′)	99.6(3)
N(3)-Cu-N(6)	89.5(4)
N(6)-Cu-N(6′)	81.1(4)
N(3)-Cu-N(6′)	169.8(4)
O(11)-Cu-N(3)	91.3(3)
O(11)-Cu-N(6)	83.8(4)
O(12^i)-Cu-N(3)	97.2(6)
O(12^i)-Cu-N(6)	105.0(7)
O(11)-Cu-O(12^i)	167.8(5)

* i Atoms are generated by $(1.5 - x, 0.5 + y, 0.5 - z)$; note however, that the atom lies close to the mirror plane through the Cu and is distant from its image $(1.5 - x, 0.5 + y, z)$ by 1.11(3) Å. Angles to the image are similar; the angle at the copper subtended by the two images is 50(1)°.

Table 3. Non-hydrogen atomic co-ordinates for $[Cu(L^1)Cl(CuCl_3)]$

Atom	*x*	*y*	*z*
Cu(1)	0.105 05(4)	0.847 87(7)	$\frac{3}{4}$
C(1)	0.064 9(2)	0.504 4(5)	$\frac{3}{4}$
C(11)	0.088 8(4)	0.350 1(6)	$\frac{3}{4}$
N(1)	−0.019 9(3)	0.500 6(5)	$\frac{3}{4}$
O(1)	−0.051 6(2)	0.497 9(4)	0.655 8(3)
C(2)	0.091 9(2)	0.570 2(4)	0.634 3(3)
N(3)	0.071 9(2)	0.719 8(3)	0.615 9(3)
C(4)	0.106 5(3)	0.777 2(4)	0.504 9(4)
C(5)	0.181 5(3)	0.835 2(5)	0.532 8(4)
N(6)	0.172 0(2)	0.938 1(4)	0.628 9(4)
C(7)	0.238 1(3)	0.983 4(8)	0.691 0(5)
Cu(2)	−0.110 97(4)	0.898 48(8)	$\frac{3}{4}$
Cl(1)	−0.001 80(8)	1.015 7(2)	$\frac{3}{4}$
Cl(2)	−0.106 89(7)	0.811 7(1)	0.562 8(1)
Cl(3)	−0.227 43(9)	0.971 4(2)	$\frac{3}{4}$

used the XTAL program system[11] implemented by S. R. Hall on a Perkin-Elmer 3240 computer. Non-hydrogen atomic co-ordinates are listed in Tables 1 and 3 and important non-hydrogen interatomic distances and angles are collected in Tables 2 and 4. Additional material available from the Cambridge Crystallographic Data Centre comprise H-atom co-ordinates, thermal parameters, and ligand geometries.

Crystal data. $[Cu(L^1)Cl(CuCl_3)]$. $C_{10}H_{23}Cl_4Cu_2N_5O_2$, $M = 514.2$, orthorhombic, space group *Pnam* (variant of $D_{2h}{}^{16}$, no. 62), $a = 18.045(6)$, $b = 9.551(5)$, $c = 11.142(3)$ Å, $U = 1\,920(1)$ Å^3, D_c $(Z = 4) = 1.79$ g cm^{-3}, $F(000) = 1\,040$, $\mu_{Mo} = 27.2$ cm^{-1}. Specimen: 0.54 × 0.20 × 0.24 mm. $A^*_{min.,max.} = 1.66$, 1.87. $N = 2\,661$, $N_o = 1\,616$. $R = 0.040$, $R' = 0.036$.

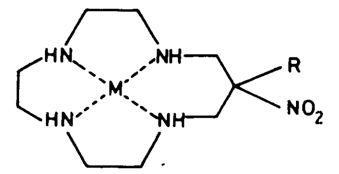
$[Cu(L^1)][ClO_4]_2$. $C_{10}H_{23}Cl_2CuN_5O_{10}$, $M = 507.8$, orthorhombic, space group *Pbnm* (variant of $D_{2h}{}^{16}$, no. 62), $a = 14.848(2)$, $b = 14.012(3)$, $c = 9.139(3)$ Å, $U = 1\,901\,(1)$ Å^3, D_c $(Z = 4) = 1.74$ g cm^{-3}, $F(000) = 1\,044$, $\mu_{Mo} = 11.9$ cm^{-1}. Specimen: 0.26 × 0.40 × 0.16 cm. $A^*_{min.,max.} = 1.20$, 1.32. $N = 2\,740$, $N_o = 1\,302$. $R = 0.10$, $R' = 0.10$.

Abnormal features. Residuals for the perchlorate in the latter structure are high in consequence of disorder/thermal motion in the perchlorate and nitro groups; refinement of the model in the related non-centrosymmetric space group effected no significant improvement, nor for that matter an independent refinement on an independently measured data set.

Table 4. Non-hydrogen interatomic distances (Å) and angles (°) for $[Cu(L^1)Cl(CuCl_3)]$*

Cu(2)–Cl(1)	2.266(2)	N(1)–O(1)	1.195(4)
Cu(2)–Cl(2)	2.246(1)	C(1)–C(2)	1.515(5)
Cu(2)–Cl(3)	2.214(2)	C(2)–N(3)	1.488(5)
Cu(1)–Cl(1)	2.507(2)	N(3)–C(4)	1.490(5)
Cu(1)–N(3)	2.022(3)	C(4)–C(5)	1.496(7)
Cu(1)–N(6)	2.006(4)	C(5)–N(6)	1.463(6)
Cu(1) ··· Cu(2)	3.928(2)	N(6)–C(7)	1.445(7)
C(1)–C(11)	1.536(8)	C(7)–C(7′)	1.315(8)
C(1)–N(1)	1.531(8)		
Cl(1)–Cu(2)–Cl(2)	98.85(4)	C(11)–C(1)–N(1)	104.9(4)
Cl(1)–Cu(2)–Cl(3)	132.06(8)	C(1)–N(1)–O(1)	118.6(3)
Cl(2)–Cu(2)–Cl(3)	98.47(4)	O(1)–N(1)–O(1′)	122.8(5)
Cl(2)–Cu(2)–Cl(2)	136.49(6)	C(1)–C(2)–N(3)	115.9(3)
Cu(2)–Cl(1)–Cu(1)	110.67(9)	C(2)–N(3)–C(4)	111.5(3)
Cl(1)–Cu(1)–N(3)	99.14(9)	C(2)–N(3)–Cu(1)	114.0(2)
Cl(1)–Cu(1)–N(6)	100.87(11)	C(4)–N(3)–Cu(1)	105.4(2)
N(3)–Cu(1)–N(6)	86.63(14)	N(3)–C(4)–C(5)	110.1(3)
N(3)–Cu(1)–N(3′)	95.32(12)	C(4)–C(5)–N(6)	107.1(4)
N(6)–Cu(1)–N(6′)	84.55(15)	C(5)–N(6)–C(7)	117.0(4)
N(3)–Cu(1)–N(6′)	159.33(14)	C(5)–N(6)–Cu(1)	105.9(3)
C(2)–C(1)–C(11)	107.9(3)	C(7)–N(6)–Cu(1)	107.7(3)
C(2)–C(1)–N(1)	109.3(3)	N(6)–C(7)–C(7′)	118.6(5)
C(2)–C(1)–C(2′)	116.7(4)		

* Cu(1) lies 0.348 Å out of the plane of the four co-ordinated nitrogen atoms, toward Cl(1).



L^1 : R = CH_3

L^2 : R = C_2H_5

Results and Discussion

Reaction of $[Cu(trien)]^{2+}$ or $[Ni(trien)]^{2+}$ in basic methanol with aqueous formaldehyde and RNO_2 (R = C_2H_5 or C_3H_7) results in the ready formation of complexes of the macromonocyclic ligands 12-methyl-12-nitro-1,4,7,10-tetra-azacyclotridecane (L^1) and 12-ethyl-12-nitro-1,4,7,10-tetra-azacyclotridecane (L^2) in high yield. Formation of the new six-membered chelate ring to form the macrocycle is apparently favoured entropically, and the reaction probably proceeds by a series of steps previously described for the formation of a related compound around copper(II),[6] and similar to related reactions around an inert metal template.[1]

In this case the product is a saturated macromonocycle, readily distinguished by the observation that complexes of L^1 and L^2 are far less susceptible to dissociation in aqueous acid than the non-cyclic precursors, as well as by spectroscopic properties. Preliminary results of a study of the dissociation reaction of $[Ni(L^1)]^{2+}$ in HCl-NaCl ($I = 2$ mol dm^{-3}) at 25 °C show pseudo-first-order rate constants which follow the expression $k_{obs.} = 2.0 \times 10^{-5}[H^+]$ s^{-1}. The reaction of $[Cu(L^1)]^{2+}$ in HCl-NaCl is more complex with consecutive reactions, the last step being appreciably slower than the reaction of the nickel(II) cation. At least with copper(II) complexes, preliminary investigation has revealed that macrocycle cleavage adjacent to the nitro group can occur in aqueous HCl, complicating the reaction.[12] The hydrolysis reactions are also considerably slower in 2 mol dm^{-3} $HClO_4$, showing pseudo-

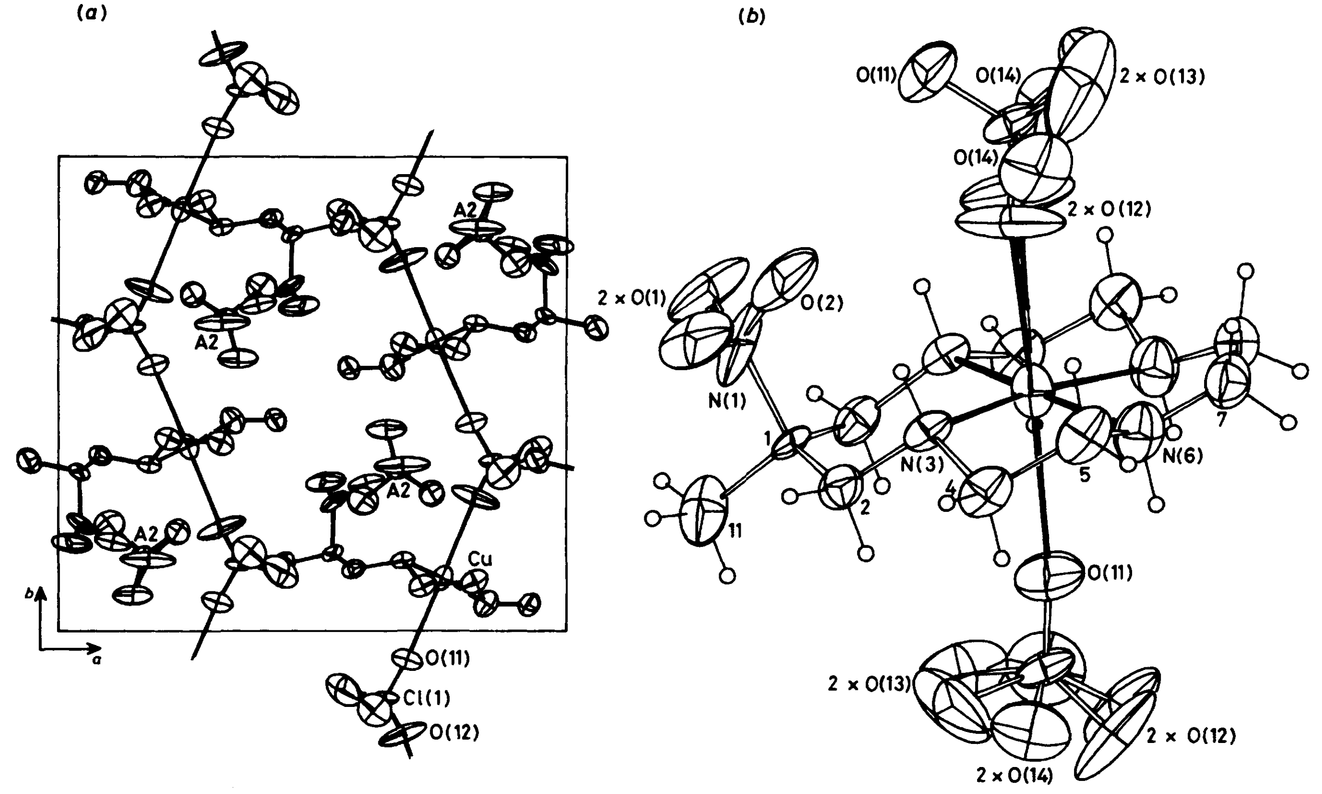


Figure 1. (*a*) Packing diagram of $[Cu(L^1)][ClO_4]_2$, containing both bridging and non-co-ordinated perchlorate ions, with the latter identified as A2. (*b*) A view of the copper ion environment in $[Cu(L^1)][ClO_4]_2$

first-order kinetics for both ions, with $k_{obs.} = 8.4 \times 10^{-7}$ s^{-1} for Cu at 25 °C and 4.1×10^{-5} s^{-1} for Ni at 50 °C, behaviour commonly observed for like systems. Detailed studies of dissociation and hydrolysis reactions will be pursued independently.

Copper(II) *Compounds*.—Chromatography of reaction mixtures on cation-exchange resin indicated that the macrocyclic ligand complex is the only major reaction product, isolated as a number of different salts. The electronic spectrum of the perchlorate salt of $[Cu(L^1)]^{2+}$ in water has a single band in the visible region near 530 nm, similar to a range of analogues where the geometry around the copper ion is known to be essentially square planar.[5] In water, the $[ZnCl_4]^{2-}$ and $[CuCl_4]^{2-}$ compounds dissociate. Even in dmso electronic spectra are simply those of cation–anion mixtures, although the $[CuCl_4]^{2-}$ derivative differs in the solid state, as defined by structural studies. The complex cation exhibits i.r. spectra with $\nu_{asym}(NO_2)$ and $\nu_{sym}(NO_2)$ vibrations near 1 550 and 1 350 cm^{-1} respectively; further, an irreversible multielectron reduction is observed using polarography in water near −0.97 V (*versus* Ag–AgCl). Both observations are characteristic of compounds with a nitro-substituted ligand.[5–7]

Prior to crystallization, the copper(II) complex was purified by chromatography on SP-Sephadex C-25 cation-exchange resin, eluting with aqueous $NaClO_4$. When the elution was performed with aqueous NaCl, the major purple band deposited, over a period of weeks, dark green lustrous crystals which were clearly different in form from the red perchlorate salt. The intense colour of the former compound suggested that some form of binuclear compound had formed, although i.r. spectroscopy indicated the macrocycle was present in both forms of the crystals. Microanalysis was consistent with formulation as a tetrachlorocuprate salt. Free copper to form $[CuCl_4]^{2-}$ presumably arose from slow ring cleavage and dissociation of the complexed copper during the weeks of crystallization, supported by study of an analogue which shows that cleavage adjacent to the nitro group in the ring can occur.[12] The subsequent dissociation of the amine ligand is facilitated by the high concentration of chloride ion. Recrystallization of a sample of the green solid from aqueous $NaClO_4$ led to the isolation of only a purple mixed chloride–perchlorate salt of $[Cu(L^1)]^{2+}$, also consistent with formulation of the former as a $[CuCl_4]^{2-}$ compound. The electronic diffuse-reflectance spectrum of the green solid has two separate transitions which could be associated with the separate tetrahedral and pyramidal copper ions at 440 and 565 nm respectively; for the perchlorate salt, a single maximum at 525 nm is observed in the solid state. The structures of both the perchlorate and tetrachlorocuprate forms of the complex were finally elucidated by *X*-ray crystal structure analyses.

Both complexes crystallize in the orthorhombic space group. The perchlorate salt determination suffered from relatively high thermal motion and disorder, but nevertheless clearly defines the geometry around the metal ion. The copper environment is essentially planar, with the metal ion deviating only slightly from the N_4 mean plane (0.07 Å); there may be some slight disorder since N(6)–C(7) is short, as is apparently C(7)–C(7′). Perchlorate oxygens occupy axial sites around the copper, with O(12) disordered over two sites. The perchlorate ions bridge two copper ions, leading to a linear polymeric structure in the crystal. The cation environment can be seen in Figure 1.

By contrast, the tetrachlorocuprate shows the macrocyclic copper ion adopting a square-based pyramidal co-ordination geometry. In the solid state, the molecule is best described as the neutral binuclear compound $[Cu(L^1)Cl(CuCl_3)]$, since one

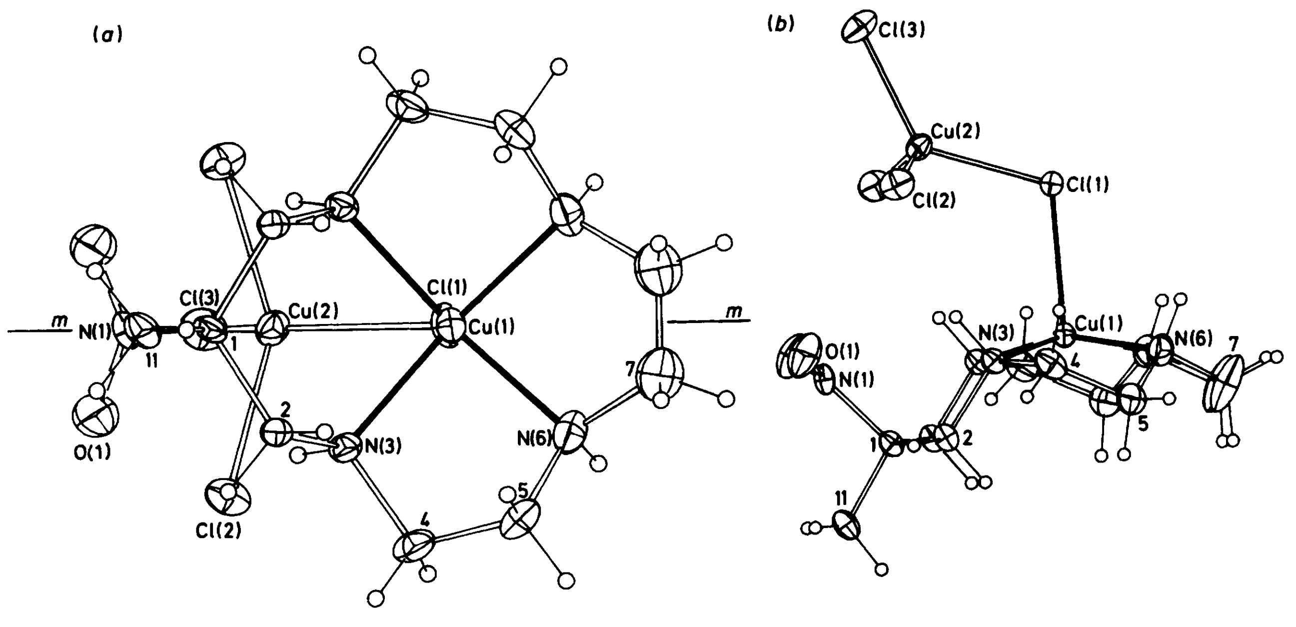
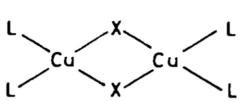


Figure 2. Two views of the neutral binuclear molecule $[Cu(L^1)Cl(CuCl_3)]$. Molecular projections (*a*) down Cl(1)–Cu(1), and (*b*) almost normal to the mirror plane. Hydrogen atoms have arbitrary radii of 0.1 Å

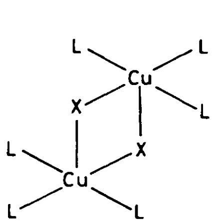
unique chloride of the $[CuCl_4]^{2-}$ entity bridges the two copper ions. This μ-chloro has a Cu–Cl bond perpendicular to the plane of the co-ordinated nitrogen atoms, and the copper ion is displaced 0.348 Å out of the plane of the nitrogen atoms towards the chloride ion. The Cu–N distances in the molecule, at 2.006(4) and 2.022(3) Å, are slightly longer than distances in the perchlorate, 1.943(7) and 1.96(1) Å, perhaps in consequence of Cu displacement from the plane of the macrocycle in the former.

The six-membered chelate ring of the macrocycle adopts a chair conformation with the nitro group on the same side of the macrocycle plane as the two copper ions. All bond lengths and angles in the ligand are normal except for C(7)–C(7′), which is unreasonably short, and may be a consequence of disorder, libration, or possibly a lower symmetry space group. The bridging chloride is not equidistant from both metal ions; the Cu–Cl distance of 2.507(2) Å to the macrocycle-bound copper is longer than the distance of 2.266(2) Å to the other copper. The latter copper lies in a distorted tetrahedron of chloride ions, with other Cu–Cl bonds up to 0.05 Å shorter than the bridging Cu–Cl, and angles far from the ideal tetrahedral angle. The Cu–Cl–Cu angle, at 110.67(9)°, is close to a tetrahedral angle. Despite this, the Cu ··· Cu separation is long at 3.928(2) Å. The shape of the binuclear complex can be seen from the two projections shown in Figure 2. This type of discrete binuclear compound is rare, although recently $[Cu(cyclam)]^{2+}$ (cyclam = 1,4,8,11-tetra-azacyclotetradecane) complexes have been isolated which have linear polymer structures with bridging $[CuCl_4]^{2-}$ anions.[13]

Binuclear copper(II) compounds with bridging chloride ions which have been characterized structurally usually have two bridging atoms with planar (I) or parallel-planar (II) geometries.[14,15] At least in the solid state, there is evidently some virtue in describing the tetrachlorocuprate salt of $[Cu(L^1)]^{2+}$ as a binuclear molecule with a single bridging anion, on the basis of the structural evidence. For species such as (I) and (II), antiferromagnetic exchange interactions have been observed, and it has also been noted that the singlet–triplet splitting ($2J$) varies linearly with φ, the bridging Cu–Cl–Cu angle.[16] A recent example of a molecule with a distorted parallel-planar geometry is the dimer $[Cu_2Cl_2(L^3)_2]\cdot dmf\cdot H_2O$ [L^3 = *N*-(2-hydroxy-2-phenylethyl)salicylideneiminate, dmf = dimethylformamide], where each copper adopts a distorted square-planar geometry and where each chloride forms long bonds [2.824(19) Å] with the other copper ion; the Cu ··· Cu distance is 3.448 Å.[17] Magnetic susceptibility measurements from 5.1 K show a weak antiferromagnetic spin coupling in that case. Likewise, the molecule $[Cu_2(terpy)Cl_4]$ (terpy = 2,2′:6′,2″-terpyridyl) has been studied and found to consist of discrete dimers $[Cu_2(terpy)_2Cl_2]^{2+}$ and $[Cu_2Cl_6]^{2-}$, of types (II) and (I) respectively, and both antiferromagnetically coupled.[18] In the present example, where there is only a single chloride linking two geometrically distinct centres, we have found from magnetic susceptibility and e.s.r. studies of the solid that there is no antiferromagnetic spin coupling. The magnetic susceptibility from 4.25 to 301.6 K follows the Curie law, with a magnetic moment of 1.86 μ_B. The absence of coupling is not unexpected even from the relatively long Cu ··· Cu distance of 3.928(2) Å, since molecules showing antiferromagnetic coupling usually have Cu ··· Cu separations below 3.6 Å, with distances as short as 2.6 Å observed in some carboxylate-bridged molecules.[15] Moreover, in $[Cu(L^1)Cl(CuCl_3)]$ the orbital arrangements of the two copper ions do not have the appropriate symmetry for coupling. The $d_{x^2-y^2}$ orbital of the macrocycle-bound copper ion will not overlap with the bridging chloride of the tetrahedral $[CuCl_4]^{2-}$ moiety.



(I)



(II)

Nickel(II) *Compounds*.—The perchlorate salts of $[Ni(L^1)]^{2+}$ and $[Ni(L^2)]^{2+}$ have singlet ground states, the spectra showing relatively intense single absorption bands typical of species with a square-planar NiN_4 chromophore. The two perchlorate salt forms for $[Ni(L^1)]^{2+}$ have similar but not identical i.r. spectra, with a strong ν(NH) absorption at 3 200 cm^{-1} (original compound) or 3 220 cm^{-1} (compound prepared from tetrahydroborato species), but differ in details of the 'fingerprint' region. The metastable form was obtained by treatment of the tetrahydroborato compound, where the macrocycle is in a folded configuration, with acid. It is probable that the two forms are nitrogen configuration isomers, with the original product having the nitrogen configuration found for the copper(II) cation, while the metastable form has the nitrogen configuration favoured for folded co-ordination of the 13-membered cyclic amine, with NH groups on alternating sides of the macrocycle.

The thiocyanato and tetrahydroborato compounds are mauve, triplet ground-state compounds. They exhibit similar ν(NH) absorptions (3 308, 3 293, 3 223 cm^{-1} and 3 325, 3 287, 3 255 cm^{-1}, respectively); the thiocyanate has a broad ν(C≡N) band, with a distinct shoulder [2 102vs, 2 015(sh) cm^{-1}], while the BH_4^- absorption region of $[Ni(L^1)(BH_4)][ClO_4]$ is complex (2 422m, 2 374m, 2 240w, 2 075m, 2 015 cm^{-1}). The triplet ground-state tetrahydroborato compound crystallized when an attempt was made to reduce the nitro group using sodium tetrahydroborate. The i.r. region assignable to the tetrahydroborato group is similar to that of $[Ni(tetb)(BH_4)][ClO_4]$ (tetb = *rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane),[19] which was assigned a structure with bidentate co-ordinated tetrahydroborate. The electronic spectrum shows a single $^3T_{2g} \longleftarrow {}^3A_{2g}$ absorption, supporting the assignment of a structure with a *cis*-NiN_4H_2 chromophore, and with the macrocycle in a 'folded' co-ordination. The compound is very sparingly soluble in water, yet crystallizes slowly from water, presumably because of slow inversion of the nitrogen centres. The compound is stable indefinitely on exposure to the atmosphere.

The triplet ground-state compound $[Ni(L^1)(NCS)_2]$ is also very sparingly soluble in water, but crystallizes very slowly from a solution of the perchlorate, or on recrystallization, suggesting that this too has the 'fold' isomer of the cation. The i.r. spectrum is structurally ambiguous, with a single broad ν(C≡N) band with a shoulder. The electronic spectrum shows a single $^3T_{2g} \longleftarrow {}^3A_{2g}$ band, but because of the small difference in ligand-field strength between secondary amino and NCS^- groups this is only weak evidence in support of a *cis* configuration.

Folded geometries are found almost exclusively for 12-membered macrocyclic tetra-amines, whereas 14-membered analogues prefer planar geometries, folding usually being enforced by another chelate.[20] The 13-membered macrocyclic tetra-amine, being intermediate between these two, may have some tendency towards folded or distorted geometries.[21] It is notable with copper(II) that co-ordination on one side of the macrocycle plane only leads to a pyramidal geometry with the metal ion displaced out of the N-donor plane. Although we have no structural evidence for the nickel(II) complexes, a folded geometry can be no less likely than that assigned[19] to the 14-membered tetb ligand in $[Ni(tetb)(BH_4)][ClO_4]$. Further structural studies in this series of variable ring size macrocycles are envisaged.

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