Comparisons of Thirteen- to Sixteen-membered Tetra-azacycloalkane Copper(II) Complexes derived from Template Syntheses involving Nitroethane and Formaldehyde. Crystal Structures of (10-Methyl-10-nitro-1,4,8,12-tetra-azacyclopentadecane)copper(II) and (3-Methyl-3-nitro-1,5,9,13-tetra-azacyclohexadecane)copper(II) Perchlorates†

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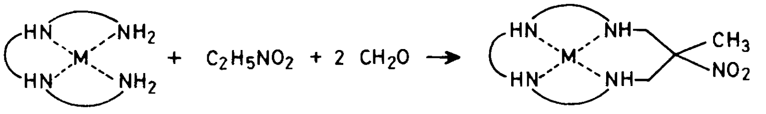
Reaction of the (1,11-diamino-4,8-diazaundecane)copper(II) ion with formaldehyde and nitroethane yields the co-ordinated 16-membered macrocycle 3-methyl-3-nitro-1,5,9,13-tetra-azacyclohexadecane (L^4). The 13- to 15-membered analogues 12-methyl-12-nitro-1,4,7,10-tetra-azacyclotridecane (L^1), 6-methyl-6-nitro-1,4,8,11-tetra-azacyclotetradecane (L^2), and 10-methyl-10-nitro-1,4,8,12-tetra-azacyclopentadecane (L^3) have been described, and structures reported for salts of the 13- and 14-membered complexes. Structures of compounds of the 15- and 16-membered ligands are now reported, and structural parameters for the series of copper(II) cations are compared. The $[Cu(L^3)]^{2+}$ and $[Cu(L^4)]^{2+}$ cations contain the copper in a distorted square plane of the macrocycle amine donors, with the pendant nitro group occupying one axial site (Cu–O 2.443 and 2.703 Å in the L^3 and L^4 compounds, respectively) and a perchlorate oxygen in the other (Cu–O *ca.* 2.58 Å in each case). The Cu–N distances lie in the range 2.005—2.093 Å in $[Cu(L^3)]^{2+}$ and 2.007—2.029 Å in $[Cu(L^4)]^{2+}$. The effect of ring size for the series on solution structures analysed by electronic and e.s.r. spectroscopy, on copper(II) reduction potentials, and on rate constants for acid hydrolysis are reported; the L^2 cavity appears most appropriate for accommodating copper(II).

The copper(II)- or nickel(II)-directed synthesis of macromonocyclic amines employing formaldehyde and the carbon acid nitroethane has been developed recently as a viable and facile route to new ligands.[1-4] Earlier, related studies involving octahedral hexa-amine metal complexes led to the development of new macrobicyclic ligands.[5-7] Previous synthetic routes to multidentate ligands have been extensively reviewed,[8-12] with several types of metal-directed or template reactions identified. Apart from direct organic synthesis, cyclic polyamines have been commonly prepared by template reactions involving reaction of a bifunctional aldehyde or ketone with a multidentate amine complex,[8,9] reaction of a diamine with a complexed dialdehyde,[9] or reaction of acetone or a similar ketone with multidentate amines.[10]

The nitroalkane/formaldehyde approach to the synthesis of macrocyclic tetra-amine ligands has two notable advantages compared with conventional syntheses of comparable ligands: (*i*) the syntheses are virtually one-step reactions and usually lead to high yields of one major product; (*ii*) the resulting nitro-substituted macrocycle is an interesting starting material for various derivatizations. For example, extra amine donor groups may be introduced by nitro group reduction,[1] the carbon side-chain may be varied by altering the nitroalkane,[4,13] the macrocycle may be fixed to biologically and/or medically interesting polymers,[13] and the redox and spectral properties may be 'tuned' through varying substituents by various reactions of the nitro group.[14]

We have been pursuing syntheses and structural characterizations of copper(II) complexes for a series of macrocycles with from 13- to 16-membered rings, based on the reaction in equation (1). In this paper, spectroscopic, voltammetric, and structural properties of the complete series are compared, and *X*-ray crystal structures of the 15- and 16-membered ring complexes are reported in detail.



(1)

Experimental

Syntheses.—(3-*Methyl*-3-*nitro*-1,5,9,13-*tetra-azacyclohexadecane*)*copper*(II) *perchlorate*, $[Cu(L^4)][ClO_4]_2$. To a solution of $Cu(NO_3)_2\cdot3H_2O$ (4.8 g) and 1,11-diamino-4,8-diazaundecane (3.75 g) in methanol (200 cm^3) was added

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.
Non-S.I. unit employed: G = 10^{-4} T.

nitroethane (2 g), aqueous formaldehyde (37% H_2O, 12 cm^3), and triethylamine (2 cm^3). The mixture was stirred and heated at *ca.* 55 °C for 2 h, diluted with water (*ca.* 1 dm^3), filtered, and sorbed onto a column of SP-Sephadex C-25 cation-exchange resin (Na^+ form, 4 × 25 cm). The column was washed and eluted with aqueous 0.2 mol dm^{-3} $NaClO_4$. Only one major blue-purple band was detected and collected. Following concentration by rotary evaporation, crystals of the product deposited on standing, were collected by filtration, washed with ethanol, and dried (Found: C, 34.1; H, 7.0; N, 15.2. $C_{13}H_{29}Cl_2CuN_5O_{10}{\cdot}2H_2O$ requires C, 34.1; H, 7.25; N, 15.3%).

The analogues (12-methyl-12-nitro-1,4,7,10-tetra-azacyclotridecane)copper(II) perchlorate, $[Cu(L^1)][ClO_4]_2$,[4] 6-methyl-6-nitro-1,4,8,11-tetra-azacyclotetradecane)copper(II) perchlorate, $[Cu(L^2)][ClO_4]_2$,[15] and (10-methyl-10-nitro-1,4,8,12-tetra-azacyclopentadecane)copper(II) perchlorate, $[Cu(L^3)][ClO_4]_2$,[3] were prepared as described previously.

Physical Methods.—Electronic spectra were recorded using Hitachi 220A or Hewlett-Packard 8450A spectrophotometers. I.r. spectra were recorded using a Nicolet MX-1 FT-IR spectrometer, with complexes dispersed in KBr discs. E.s.r. spectra were determined at or above 77 K using a Varian E3 spectrometer. For e.s.r., concentrations of the fluid or frozen solutions were in the range 10^{-5}—10^{-3} mol dm^{-3}; diphenylpicrylhydrazyl was employed as reference compound.

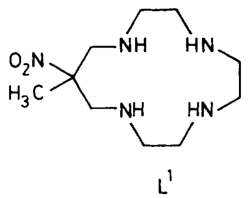
Voltammetry in aqueous solution (0.1 mol dm^{-3} $NaClO_4$) was performed with a conventional three-electrode configuration and argon purge gas using either a BAS model CV27 or an AMEL model 473 electrochemical controller. Working electrodes were an EG & G PAR 303 static mercury drop electrode (s.m.d.e.) and glassy carbon or platinum billet electrodes. An Ag–AgCl reference electrode and platinum wire auxiliary electrode were also employed. All measurements were performed at ambient temperature.

Structure Determinations.—Unique data sets were measured at 298 K to $2\theta_{max.} = 50°$ using an Enraf-Nonius CAD-4 four-circle diffractometer (monochromatic Mo-K_α radiation source, $\lambda = 0.710\,69$ Å; conventional $2\theta/\theta$ scan mode). N Independent reflections were measured, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the 9 × 9 block-diagonal least-squares refinement after Gaussian 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 constrained at estimated values. Residuals at convergence, R, R' on $|F|$ are quoted, with statistical weights derived from $\sigma^2(I) = \sigma^2(I)_{diff.} + 0.000\ n\ \sigma^4(I)_{diff.}$. Neutral atom complex scattering factors were used;[16] computation used the XTAL program system[17] implemented by S. R. Hall on a Perkin-Elmer 3240 computer. Pertinent results and atom numbering are given in Figures 1 and 2 and in Tables 1—4.

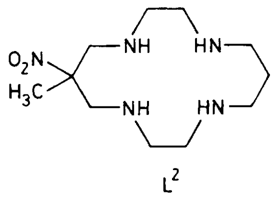
Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond length and angles.

Crystal data. $[Cu(L^3)][ClO_4]_2$. $C_{12}H_{27}Cl_2CuN_5O_{10}$, $M = 535.8$, monoclinic, space group $P2_1/c$ (C^5_{2h}, no. 14), $a = 8.635(8)$, $b = 12.755(3)$, $c = 19.716(8)$ Å, $\beta = 105.08(5)°$, $U = 2\,097$ Å^3, $D_c = 1.70$ g cm^{-3} ($Z = 4$), $F(000) = 1\,108$, $\mu_{Mo} = 13.3$ cm^{-1}. Specimen: 0.30 × 0.08 × 0.36 mm; $A^*_{min.,max.} = 1.11$, 1.51; $N = 3\,681$, $N_o = 2\,866$, $R = 0.061$, $R' = 0.072$, $n = 9$.

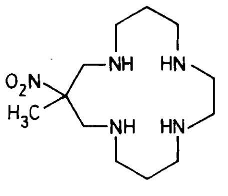
$[Cu(L^4)][ClO_4]_2$. $C_{13}H_{29}Cl_2CuN_5O_{10}$, $M = 549.9$, monoclinic, space group $P2_1$ (C^2_2, no. 4), $a = 8.718(3)$, $b = 13.977(2)$, $c = 9.102(9)$ Å, $\beta = 105.93(6)°$, $U = 1\,066$ Å^3, $D_c = 1.71$ g cm^{-3} ($Z = 2$), $F(000) = 570$, $\mu_{Mo} = 13.0$ cm^{-1}. Specimen: 0.22 × 0.12 × 0.38 mm; $A^*_{min.,max.} = 1.12$, 1.26; $N = 3\,043$, $N_o = 2\,447$, $R = 0.061$, $R' = 0.074$ (preferred chirality), $n = 7$.



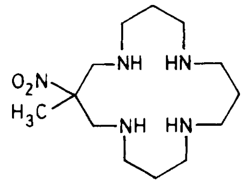
L^1



L^2



L^3



L^4

Abnormal features. In both structures perchlorate groups exhibited abnormalities; in the L^4 structure simply very high thermal motion but in the L^3 structure resolvable disorder for both species with oxygen atoms distributed over two sets of sites and refined as such with anisotropic thermal parameters in a stable fashion (but of limited credibility; see Figure 1). No evidence was found for a larger cell or lower symmetry space group.

Results and Discussion

Condensation of the copper(II) complexes of linear aliphatic tetra-amines with formaldehyde and nitroethane in basic methanol proceeds readily to produce macromonocycles with 13- to 16-membered rings in good yield. A new six-membered ring forms from condensation of two formaldehyde molecules and one nitroethane molecule with the two *cis* primary amines in each precursor complex. Reaction proceeds by initial formation of a monoimine, attack by the carbon acid to produce a new ligand arm with a nitro substituent, then ring closure by attack of this carbon acid arm at the second *cis* monoimine, as described previously.[3] The copper(II) ion acts to direct the reaction, the small chelate ring resulting being a favourable outcome compared with alternatives which would not form a ring. Macrocyclization occurs using other metal ions as templates also, such as nickel(II)[1] and palladium(II),[13] and with other carbon acids such as diethyl malonate.[3] However, the strong nitroalkane carbon acids, where the pK_a is below 10, are the most successful.

All ligands synthesized form complexes with combinations of five- and six-membered chelate rings, since each nitrogen donor is separated by only two or three carbons. The arrangements in terms of numbers of separating methylenes are for L^1, [3222], for L^2, [3232], for L^3, [3332], and for L^4 [3333], as defined in structures shown. In the series of complexes prepared the efficacy of the reaction to form the macrocycle is not affected much by the variable ring sizes. Yields of crystallized product are as high as 75%, with cation-exchange chromatography indicating that the macrocyclic compound may represent over 95% of complexed species. Depending on reaction conditions, copper hydroxide and/or precursor complex may also be recovered, although the solubility of the cyclic product usually determines the yield of pure crystalline material isolable. No significant amounts of other complexes are detected, with competing reactions being apparently simply organic in nature.

Identification of products is relatively straightforward, since macrocyclization is readily identified by the very slow dissociation of the products in aqueous acid compared with the non-cyclic precursors. Rates of hydrolysis of the complexes in 1

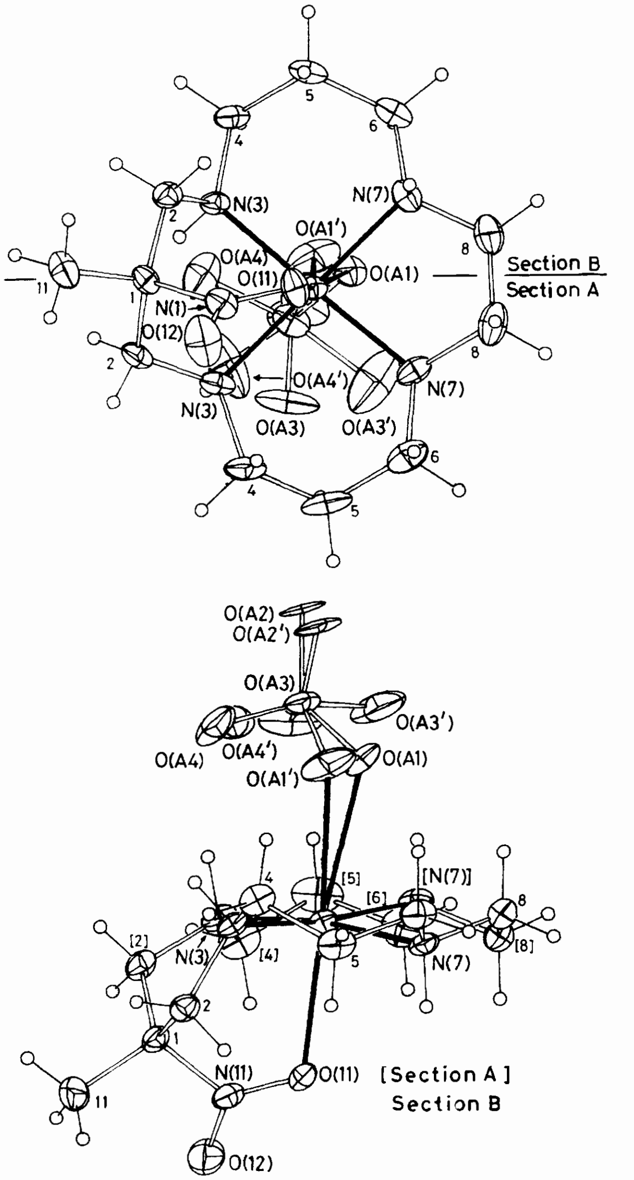


Figure 1. Projections of the cation [Cu(L^3)]$^{2+}$ with skeletal atom numbering. For the non-hydrogen atoms, 20% thermal ellipsoids are shown; hydrogen atoms have arbitrary radii of 0.1 Å. Two views are shown to clarify the presentation of the co-ordinated perchlorate disorder

mol dm^{-3} HCl at 50 °C are 2.8 × 10^{-5} s^{-1} (L^1), < 10^{-7} s^{-1} (L^2), 7.7 × 10^{-4} (L^3), and 0.3 s^{-1} (L^4), with kinetic stability paralleling perceived thermodynamic stability. Substitution on the ring by the nitro group also slows dissociation, since the unsubstituted copper(II) 15-membered macrocycle complex aquates under the same conditions at 3.9 × 10^{-2} s^{-1}, approximately 50 times faster. This may arise from electronic effects of the nitro group. Hydrolysis may not be a simple process of metal ion dissociation however, since at least for L^3, reaction in aqueous HCl leads to hydrolysis of a C–C bond in the six-membered ring adjacent to the nitro group.[13] When the nitro group is reduced to an amine, this cleavage reaction is not observed. Detailed analysis of these reactions is in progress. Also characteristic of product formation are the nitro group i.r. resonances at 1 550 and 1 350 cm^{-1}, and the multi-electron, irreversible nitro reduction process observed in voltammetry experiments near −0.95 V (*vs.* Ag–AgCl).[1]

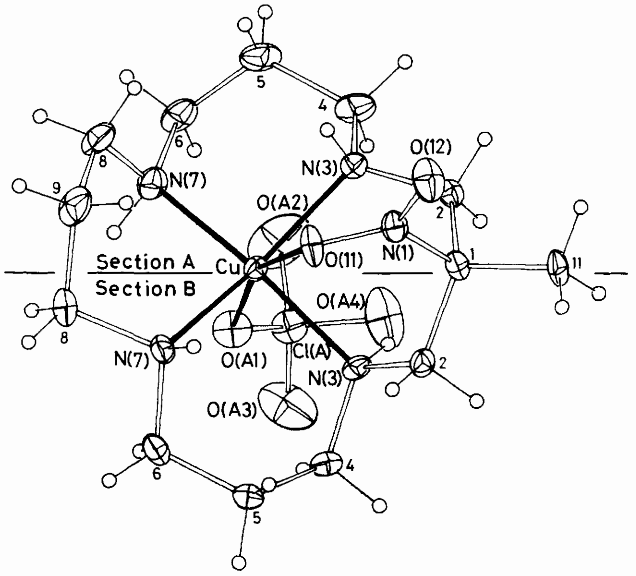
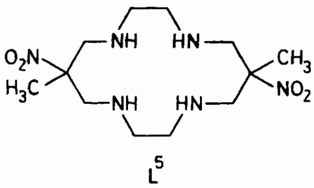
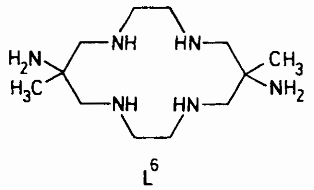


Figure 2. Projection of the cation [Cu(L^4)]$^{2+}$; 20% thermal ellipsoids are shown for the non-hydrogen atoms, whereas hydrogen atoms have arbitrary radii of 0.1 Å



L^5



L^6

Reaction based on [Cu(en)$_2$]$^{2+}$ (en = NH$_2$CH$_2$CH$_2$NH$_2$) reported earlier gave a 14-membered macrocycle L^5, where two six-membered rings form at opposite ends of the molecule.[1] In principle, this reaction should yield two isomers, depending on whether the nitro substituents are *syn* or *anti* to the ring. Two products, presumed to be the expected C-based isomers, were isolated, although there is some possibility that the species are isomers based on nitrogen which interconvert slowly. Structural studies should elucidate this problem, although it is apparent from large-scale isolation of the free hexa-amine macrocycle L^6 that the condensation favours the *anti* isomer L^5.[18] Certainly in the present cases, where a single new ring is formed, such problems with C-based isomers do not exist, the single ring closure occurring essentially to the exclusion of other complexed reaction products.

The *X*-ray crystal structure analyses of the copper(II) complexes of L^3 and L^4 determined as perchlorate salts both contain the copper ion co-ordinated in a distorted square plane of secondary nitrogen donors, with axial sites occupied in each case by one oxygen of the pendant nitro group (at 2.443 Å for L^3 and 2.703 Å for L^4) and by a perchlorate oxygen (at 2.58 Å). Non-hydrogen atomic co-ordinates for the two structures appear in Tables 1 and 2, with details of the copper atom environments collected in Table 3, and macrocycle torsion angles in Table 4. Projections of the two complex cations are shown in Figures 1 and 2.

The bonding of the nitro substituent is notable, and was not observed in the structures of L^1 [14] and L^2,[15] although it is known that amine analogues such as L^6 can co-ordinate with the pendant amines as axial ligands.[19] The configuration at the secondary nitrogens of the six-membered substituted ring

Table 1. Non-hydrogen atom co-ordinates for $[Cu(L^3)][ClO_4]_2$

	Section A			Section B		
Atom*	*x*	*y*	*z*	*x*	*y*	*z*
Anions						
Cl(m)	−0.144 6(2)	0.037 2(2)	0.100 4(1)	0.223 7(2)	0.684 7(2)	0.153 8(1)
O(m1)	−0.015(3)	0.039(2)	0.161(1)	0.369(3)	0.723(2)	0.185(2)
O(m2)	−0.273(3)	−0.044(3)	0.089(2)	0.117(2)	0.759(2)	0.124(2)
O(m3)	−0.202(2)	0.135(1)	0.083(1)	0.276(3)	0.590(2)	0.128(2)
O(m4)	−0.064(1)	−0.001(2)	0.042(1)	0.175(5)	0.626(4)	0.196(3)
O(m1′)	0.007(3)	0.024(2)	0.137(1)	0.375(1)	0.689(3)	0.157(1)
O(m2′)	−0.237(4)	−0.038(4)	0.105(2)	0.180(2)	0.742(1)	0.084(1)
O(m3′)	−0.204(2)	0.113(2)	0.152(1)	0.099(3)	0.612(1)	0.145(1)
O(m4′)	−0.161(3)	0.089(3)	0.043(1)	0.203(2)	0.746(2)	0.214(1)
Cation						
Cu	0.197 34(7)	0.182 97(5)	0.148 44(3)			
C(1)	0.376 4(7)	0.249 0(5)	0.034 5(3)			
C(11)	0.465 5(9)	0.272 7(7)	−0.020 8(4)			
N(1)	0.430 5(6)	0.328 2(4)	0.095 1(3)			
O(11)	0.417 2(5)	0.305 4(4)	0.152 6(2)			
O(12)	0.478 4(9)	0.412 9(5)	0.080 9(3)			
C(m2)	0.194 5(7)	0.265 8(5)	0.004 6(3)	0.418 4(6)	0.140 0(5)	0.063 7(3)
N(m3)	0.096 7(6)	0.265 8(4)	0.055 8(3)	0.292 1(5)	0.087 0(4)	0.089 4(2)
C(m4)	0.040 2(9)	0.374 7(5)	0.063 9(4)	0.346 0(7)	−0.019 5(5)	0.116 2(4)
C(m5)	−0.062 5(9)	0.382 7(6)	0.114 8(6)	0.452 3(8)	−0.020 9(5)	0.188 6(4)
C(m6)	0.030 0(11)	0.371 6(6)	0.190 0(5)	0.365 6(8)	0.007 2(6)	0.243 1(4)
N(m7)	0.081 3(6)	0.263 7(4)	0.208 2(3)	0.321 9(5)	0.118 5(4)	0.240 9(3)
C(m8)	0.177 1(9)	0.253 7(7)	0.282 3(3)	0.236 6(8)	0.143 8(7)	0.293 4(3)

* Anion oxygen site occupancies are 0.5; m = A or B.

Table 2. Non-hydrogen atom co-ordinates for $[Cu(L^4)][ClO_4]_2$

	Section A			Section B		
Atom*	*x*	*y*	*z*	*x*	*y*	*z*
Anions						
Cl(m)	0.054 2(3)	0.177 5(2)	0.345 8(3)	0.378 9(3)	0.591 5(2)	0.193 9(3)
O(m1)	0.151 1(8)	0.093 4(5)	0.361 9(8)	0.394 9(10)	0.528 6(6)	0.079 5(9)
O(m2)	0.147 1(15)	0.259 4(7)	0.364 6(20)	0.233 6(12)	0.632 8(10)	0.168 6(14)
O(m3)	−0.062 1(13)	0.170 2(9)	0.414 5(15)	0.388 4(15)	0.538 1(11)	0.326 0(12)
O(m4)	−0.024 9(16)	0.181 5(10)	0.184 2(13)	0.494 4(14)	0.661 1(11)	0.205 4(15)
Cation						
Cu	0.274 83(9)	0	0.177 78(9)			
C(1)	0.102 7(9)	−0.022 3(5)	−0.182 9(8)			
C(11)	0.004 1(11)	−0.022 3(6)	−0.348 2(8)			
N(1)	0.253 7(8)	−0.080 4(5)	−0.170 2(7)			
O(11)	0.320 3(7)	−0.113 3(5)	−0.047 3(6)			
O(12)	0.300 4(9)	−0.093 3(6)	−0.280 6(7)			
C(m2)	0.160 7(9)	0.080 2(6)	−0.138 1(8)	0.011 6(9)	−0.067 4(6)	−0.079 5(9)
N(m3)	0.290 8(7)	0.087 5(5)	0.004 6(7)	0.043 1(7)	−0.026 5(4)	0.073 4(7)
C(m4)	0.319 8(11)	0.190 3(6)	0.048 9(13)	−0.046 4(9)	−0.077 9(6)	0.162 4(9)
C(m5)	0.481 4(13)	0.200 0(8)	0.170 3(12)	0.030 8(10)	−0.171 8(7)	0.231 5(10)
C(m6)	0.490 9(11)	0.159 9(7)	0.319 3(12)	0.184 5(11)	−0.163 1(7)	0.350 0(9)
N(m7)	0.472 5(9)	0.053 2(6)	0.323 6(8)	0.312 0(8)	−0.128 7(5)	0.280 7(7)
C(m8)	0.619 9(9)	0.002 9(11)	0.323 6(11)	0.475 6(12)	−0.141 5(8)	0.392 8(10)
C(9)	0.599 6(11)	−0.105 3(8)	0.318 7(14)			

* m = A or B.

determines whether the nitro group is able to co-ordinate [structure (**I**)] or not [structure (**II**)]. Arrangement (**I**) occurs in the copper(II) complexes of L^3 and L^4, while the configuration (**II**) applies for L^1 and L^2. We have found no evidence for both isomers with one particular ligand. Possibly the favoured ligand is defined by constraints of the macrocycle at large, with a co-ordinated nitro group only favoured for the larger, more flexible rings where distortions from planarity of the CuN_4 donors are observed.

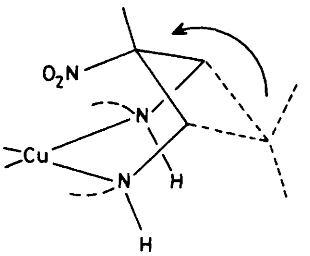
Since structures of the complete series are now available, it is appropriate to make some comparisons of the copper ion environments. Some comparative data are collected in Figure 3.

Table 3. Copper atom environments[a]

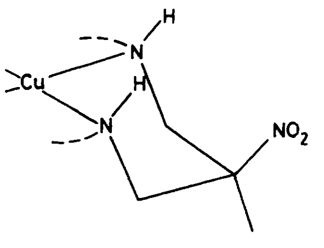
	$[Cu(L^3)][ClO_4]_2$[b]						
	r	O(A1′)	O(11)	N(A3)	N(A7)	N(B3)	N(B7)
O(A1)	2.65(2)	12.8(8)	171.7(4)	106.9(4)	80.7(5)	91.6(5)	81.6(4)
O(A1′)	2.58(3)		167.4(7)	102.1(5)	92.9(7)	79.4(7)	86.4(5)
O(11)	2.443(5)			81.4(2)	98.8(2)	88.8(2)	90.2(2)
N(A3)	2.093(5)				95.5(2)	86.6(2)	171.5(2)
N(A7)	2.016(6)					172.3(2)	84.8(2)
N(B3)	2.005(5)						94.2(2)
N(B7)	2.033(5)						

	$[Cu(L^4)][ClO_4]_2$[c]					
	r	O(11)	N(A3)	N(A7)	N(B3)	N(B7)
O(A1)	2.582(8)	164.2(2)	109.2(2)	79.6(3)	81.7(2)	101.1(3)
O(11)	2.703(6)		73.1(2)	116.1(3)	82.6(2)	77.9(2)
N(A3)	2.029(7)			93.5(3)	91.4(3)	149.7(3)
N(A7)	2.007(7)				161.2(3)	91.0(2)
N(B3)	2.017(6)					93.9(3)
N(B7)	2.012(7)					

[a] *r* Is the copper–ligand distance (Å). Other entries in the matrix are the angles (°) between the relevant atoms at the head of the row and column. [b] Cu–O(A1)–Cl(A) 110(1), 118(2); Cu–O(11)–N(1) 112.7(3). [c] Cu–O(A1)–Cl(A) 133.6(4); Cu–O(11)–N(1) 110.3(5)°.



(I)



(II)

Notably, the Cu–N bond length increases from L^1 to L^2 to L^3, with no marked difference from L^3 to L^4. Deviations from the mean CuN_4 plane are at a maximum with L^4, where a tetrahedral distortion limits Cu–N bond extension. The smallest chelate ring shows a square-based pyramidal co-ordination in the $[Cu(L^1)ClCuCl_3]$ molecule; the copper lies 0.35 Å out of the N_4 plane with a N–Cu–N angle of 159.3°.[4] The perchlorate salt, with axial Cu–O bonds on both sides of the macrocycle plane, apparently contains the copper in the L^1 donor plane. Nevertheless, the short Cu–N bonds and rather high residuals could imply disordering of the metal ion on both sides of the plane in an effective square-based pyramidal arrangement, a geometry most consistent with solution spectroscopy. We are extending our study of 13-membered cyclic systems to elucidate the problem. The structural results for the series are fairly consistent with thermodynamic solution data for unsubstituted ring analogues, where the stability constants for the 13- and 14-membered rings are highest in the series, supporting our view that the 14-membered ring is the optimum size.[12,20]

Table 4. Macrocycle torsion angles (°)*

	$[Cu(L^3)][ClO_4]_2$		$[Cu(L^4)][ClO_4]_2$	
Section	A	B	A	B
2–1–2–*3*	67.7	−27.2	70.2	−22.6
1–2–*3*–4	108.5	179.5	−171.4	−177.9
2–*3*–4–5	179.4	80.9	−164.9	80.6
3–4–5–6	73.0	69.8	−68.9	66.2
4–5–6–7	−73.1	−71.1	65.0	−68.6
5–6–7–8	178.3	179.3	79.5	−166.9
6–7–8–8′,9	−174.5	−172.6	−176.7	−179.6
7–8–8′,9–7′,8′	54.3		−29.6	80.1

* Carbon atoms are denoted by number only; those for nitrogen are italized.

The co-ordinated macrocycles adopt a range of conformations, depending upon the ring size, and the individual chelate rings present. For $[Cu(L^1)]^{2+}$, with mirror symmetry, the nitro-substituted six-membered chelate ring adopts a normal chair conformation, and the adjacent five-membered chelate rings adopt symmetrical *gauche* conformations, with the 'central' five-membered ring in an eclipsed conformation, very similar to that found for nickel(II) in another 13-membered macrocyclic amine.[21] The 14-membered macrocycle adopts a conformation very similar to that observed for $[Cu(L^6)]^{2+}$,[1] and for many complexes of the unsubstituted parent macrocycle (1,4,8,11-tetra-azacyclotetradecane),[12] with the six-membered chelate rings in chair, and the five-membered chelate rings in *gauche* conformations.

The 15- and 16-membered macrocycles have the nitro-substituted six-membered chelate ring in a boat conformation, which places the nitro oxygen in the axial co-ordination site. The configuration of the chiral nitrogen centres differs from that for the two smaller ring compounds, with the NH groups of the substituted chelate ring and one other on the same side of the macrocycle. For the 15-membered macrocycle the two adjacent chelate rings adopt flattened chair conformations, and the 'central' five-membered ring a *gauche* conformation. For the 16-membered macrocycle the 'adjacent' six-membered chelate rings adopt somewhat twisted chair conformations, and the 'central' chelate ring a boat conformation. Unusual chelate ring conformations are commonly observed for co-ordination compounds of cyclic amines with more than 14 members when co-ordinated to copper(II) or smaller cations, and can be attributed to the strain inherent in distorting the macrocycle from its 'normal' *endo* conformation to match the relatively inflexible metal–nitrogen distance.[22] The strain is also shown in the 'tetrahedral' distortions from square-planar co-ordination of *ca.* ±0.14 and *ca.* ±0.43 Å respectively for 15- and 16-membered macrocyclic cations. Strained chelate ring

Table 5. Electronic transitions and spin-Hamiltonian parameters, and redox potentials, for the copper(II) tetra-amine macrocycles

Complex	Electronic transition[a] $\tilde{\nu}$/cm^{-1} (ε/dm^3 mol^{-1} cm^{-1})	Spin-Hamiltonian parameters[b]						Voltammetry[c]	
		g_{iso}	$g_{\perp}$	$g_{\parallel}$	A_{iso}	$A_{\perp}$	$A_{\parallel}$	$E_{\frac{1}{2}}(Cu^{II/I})$	$E_p(NO_2)$
$[Cu(L^1)]^{2+}$	18 870 (166)	2.09	2.05	2.18	87	33	193	−0.56 (130)	−0.94 (irr.)
$[Cu(L^2)]^{2+}$	19 570 (77)	2.10	2.05	2.19	90	35	199	−0.76 (irr.)	−0.96 (irr.)
$[Cu(L^3)]^{2+}$	17 480 (124)	2.11	2.06	2.21	81	26	193	−0.64 (*ca.* 200)	−0.90 (irr.)
$[Cu(L^4)]^{2+}$	16 560 (230)	2.11	2.06	2.21	77	23	184	−0.40 (128)	−0.87 (irr.)

[a] Aqueous solution. [b] A values in 10^{-4} cm^{-1}. [c] Cyclic voltammetry, hanging mercury drop electrode, scan rate 50 mV s^{-1}, ambient temperature, 0.1 mol dm^{-3} aqueous $NaClO_4$; value in parentheses is peak separation, irr. = irreversible or complex pattern; measured *vs.* Ag–AgCl. Peak maxima for differential pulse polarograms and behaviour at a glassy carbon electrode are qualitatively similar.

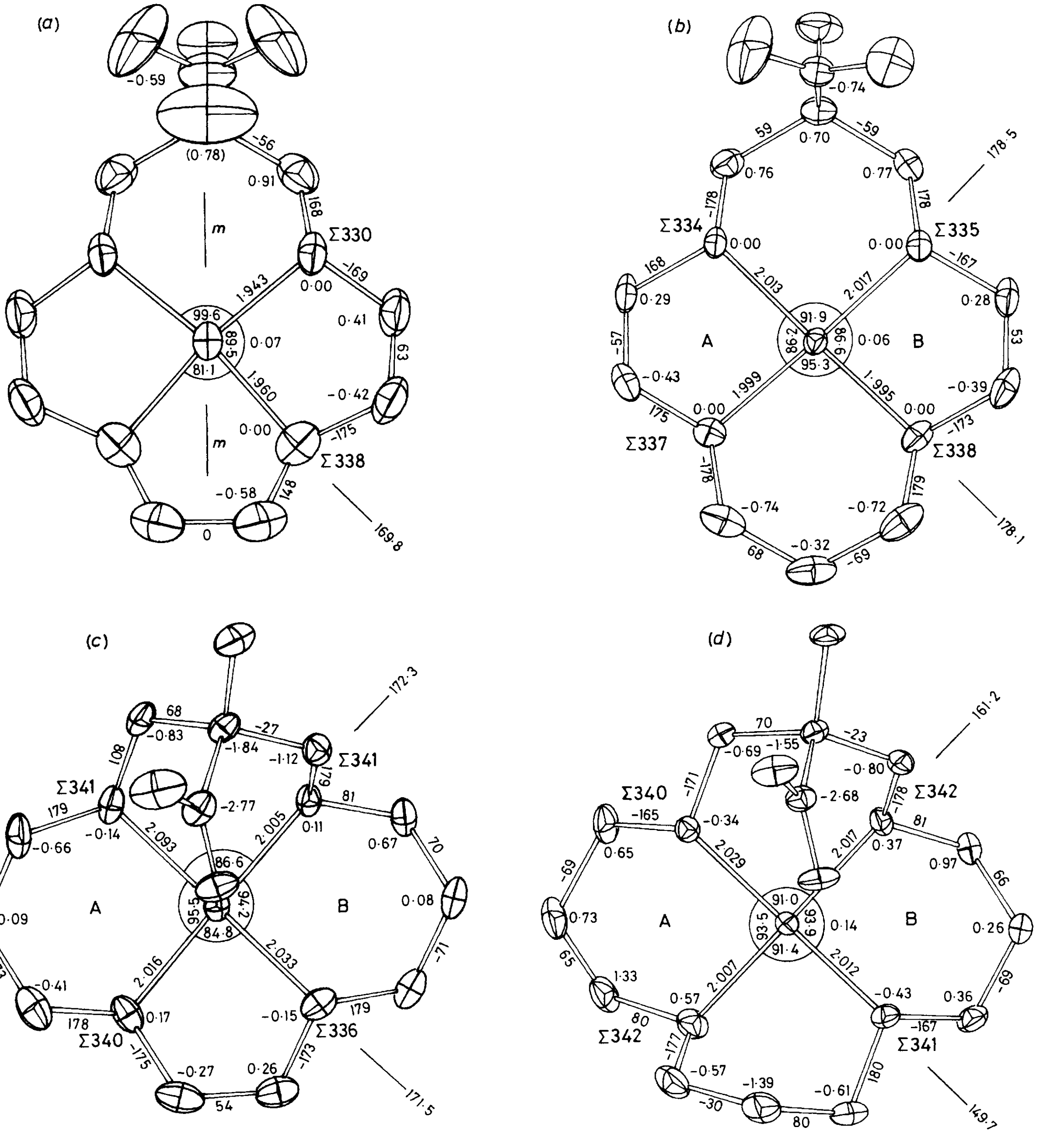


Figure 3. Comparisons of (tetra-azacycloalkane)copper(II) cations $[Cu(L^n)]^{2+}$ based on *X*-ray structural data for perchlorate salts: L = L^1 (*a*), L^2 (*b*), L^3 (*c*), L^4 (*d*). Data entered on the separate projections, drawn with the nitro group above the plane of the paper in each case, are: Cu–N bond lengths (along bonds from Cu); N–Cu–N angles (around the Cu, and external to the ring); angle sums at co-ordinating atoms (Σ); deviations of atoms from the plane (adjacent to each atom, with positive deviations lying beneath the plane of the paper); macrocycle torsions (along bonds)

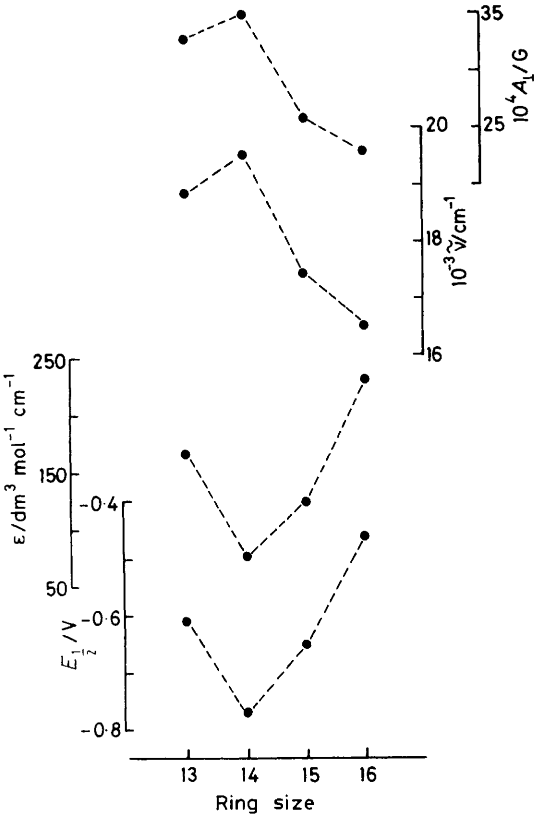


Figure 4. Variation of physical properties with ring size for the series of $[Cu(L^n)]^{2+}$ complexes. Data are from e.s.r. ($A_{\perp}$), electronic spectroscopy ($\tilde{\nu}$,ε), and voltammetry ($E_{\frac{1}{2}}$); see Table 5

conformations and tetrahedral distortions have been reported for compounds of other cyclic tetra-amines with these ring sizes; for example, compounds of the unsubstituted 15- and 16-membered cyclic amines with the larger nickel(II) ion (triplet ground state) in the *trans*-dichloro and *trans*-dithiocyanato compounds,[23] the 'tropocoronand' compounds with copper(II)[24] and nickel(II),[25] and other tetra-azamacrocycles.[26]

Physical properties of the series reflect differences in ring size. Both the maximum in the electronic spectrum and the absorption coefficient vary with ring size, as does the Cu^{II} reduction potential (Table 5). Reversibility of the $Cu^{II/I}$ couple varies, and is actually very limited for the L^2 complex, perhaps as a result of the inability of the ring to accommodate the larger Cu^I or adopt its preferred tetrahedral geometry. Larger and tetrahedrally distorted rings may accommodate both the size and geometry constraints arising upon reduction, whereas smaller rings could possibly accommodate the metal ion above the macrocycle plane effectively.

Spin-Hamiltonian parameters deduced from the e.s.r. spectra of the copper(II) complexes are collected in Table 5. The g values are indicative of a $d_{x^2-y^2}$ ground state,[27] and both $g_{\parallel}$ and $g_{\perp}$ values lie in the typical range for CuN_4 chromophores of 2.17—2.23 and *ca.* 2.05 respectively.[27,28] Variations in g values with ring size are small, but then variations in g from such different effects as distortions from square-planarity and changes in covalency make g values generally of limited value for structural analyses.[29] The hyperfine parameters reflect the local geometry much more clearly. Observed $A_{\parallel}$ and $A_{\perp}$ of 175—195 and 27—36 G respectively are consistent with a basically square-planar geometry. There is no definitive evidence for nitro group co-ordination in solution; however, small changes in the nitro–copper charge-transfer region in electronic spectra suggest that nitro–copper ion interaction may increase with ring size, although the assignment is tenuous. Distortions from square-planarity are obvious from decreasing $A_{\parallel}$ and from decreasing $\tilde{\nu}_{max.}$ and increasing $\varepsilon_{max.}$ with ring size. There is a rough correlation of $g_{\parallel}$ and $A_{\parallel}$, indicating an increasing tetrahedral distortion from L^2 to L^4.[30] Notably $\tilde{\nu}_{max.}$ and $\varepsilon_{max.}$ and $g_{\parallel}/A_{\parallel}$ are at minima whereas $A_{\parallel}$ is at a maximum for the L^2 complex. This is entirely consistent with earlier observations that a 14-membered macrocycle has the most favourable cavity size in the series to accommodate copper(II), leading to square-planar CuN_4 co-ordination.[12] It is notable that a range of physical parameters show a similar trend with ring size, as illustrated in Figure 4; all point to L^2 as the most favourable cavity for copper(II). These observations are in good agreement with the structural studies.

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