Electron Spin Resonance Studies and Crystal Structures of Copper(II) Complexes of some 12-, 13- and 14-Membered Oxatriaza Macrocycles†

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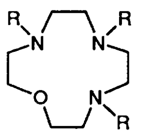
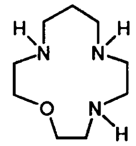
Electronic and ESR spectroscopic studies in aqueous solution and single-crystal X-ray diffraction analyses of copper(II) complexes of the following oxatriaza macrocycles have been undertaken: 1-oxa-4,7,10-triazacyclododecane (L^1), 4,7,10-trimethyl-1-oxa-4,7,10-triazacyclododecane (L^2), 1-oxa-4,7,11-triazacyclotridecane (L^3), 1-oxa-4,8,12-triazacyclotetradecane (L^4), and 4,8,12-trimethyl-1-oxa-4,8,12-triazacyclotetradecane (L^5). The complexes for solution studies were prepared in an excess of $NaClO_4$, but the bulky counter ion PF_6^- was added to induce crystallization. The crystal structures of $[CuL^1(Br)][PF_6]$, $[CuL^2(Cl)][PF_6]$, $[CuL^4(H_2O)][PF_6]_2 \cdot H_2O$ and $[CuL^5(Cl)][PF_6]$ were determined. The co-ordination geometry around the copper atom in the four complexes can be described as a distorted square pyramid, but whereas the basal planes comprise the three nitrogens and the oxygen from the macrocycle in the last two complexes, in the first two complexes they comprise the three macrocyclic nitrogens and a halogen atom, bromine and chlorine respectively. The apical co-ordination in the latter is by the macrocyclic oxygen, but in $[CuL^4(H_2O)][PF_6]_2 \cdot H_2O$ it is the oxygen of a water molecule and in $[CuL^5(Cl)][PF_6]$ it is a chlorine atom. The main conclusions on the structures of these complexes from spectroscopic measurements and X-ray studies are in good agreement. However, for the complex of the 13-membered macrocycle (L^3) published X-ray results point to a structure similar to those found in this work for the 14-membered macrocyclic complexes, while the spectroscopic studies now reported indicate a structure with a pronounced tetrahedral distortion similar to that observed in the 12-membered macrocyclic complexes. The replacement of hydrogen atoms by methyl groups on the nitrogen atoms does not affect the overall final geometry of these complexes. For this series of macrocyclic complexes, the smaller the ligand the more pronounced is the folding necessary to accommodate the metal at its centre. The structure of a complex of a 12-membered macrocycle having four donor atoms one of which approaches the metal from the apical position is reported for the first time.

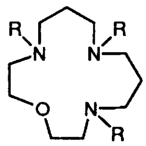
The stability constants of copper(II) and other divalent metal-ion complexes of some 12- to 14-membered oxatriaza macrocycles have been determined previously.[1] The specific compounds were 1-oxa-4,7,10-triazacyclododecane ([12]ane-N_3O) L^1, 4,7,10-trimethyl-1-oxa-4,7,10-triazacyclododecane (Me_3[12]aneN_3O) L^2, 1-oxa-4,7,11-triazacyclotridecane ([13]-aneN_3O) L^3, 1-oxa-4,8,12-triazacyclotetradecane ([14]ane-N_3O) L^4, and 4,8,12-trimethyl-1-oxa-4,8,12-triazacyclotetradecane (Me_3[14]aneN_3O) L^5. It was found that the stability of the complexes formed with this series of macrocycles is lower than that of the tetraaza macrocyclic series with comparable ring sizes (L^6–L^{10}), the differences being more pronounced for the 14-membered cases. The stability of the copper(II) complexes increases with the size of the macrocycle in the tetraaza series, from L^6 to L^9, while in the oxatriaza series it has a maximum at the 13-membered macrocycle. The introduction of *N*-methyl substituents leads to macrocycles which form complexes with stability constants lower than those of the unsubstituted amines, the differences being more pronounced for the tetraaza than for the oxatriaza macrocycles. These differences are smaller for the complexes of the 12-membered macrocycles.



L^1 R = H
L^2 R = Me



L^3



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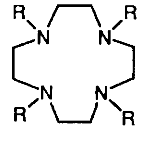
L^5 R = Me



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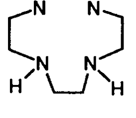
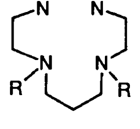
L^7 R = Me



L^8



L^9 R = H
L^{10} R = Me

In order to understand the different behaviours of the complexes formed with the two series of macrocycles (oxatriaza and tetraaza) we decided to undertake electronic and ESR

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

spectroscopic studies in aqueous solution and single-crystal X-ray diffraction studies of the copper(II) complexes of the oxatriaza macrocycles. Our results together with the crystal structure of $[CuL^3(Br)]Br$ previously reported by Hancock and co-workers[2] are compared to provide an overview of the structural changes caused by stepwise increase of the ring size of the macrocycle, from one too small to accommodate the metal ion to another which is probably large enough to provide optimum co-ordination. The effect of the introduction of methyl substituents at the nitrogen atoms on the structures of the copper(II) complexes is also analysed.

Experimental

Reagents.—The macrocycles were synthesized and purified in our laboratories.[1] The salt $CuSO_4 \cdot 5H_2O$ (99.5%) was obtained from AnalaR, $Ba(OH)_2 \cdot 8H_2O$ (98%) and $BaCl_2 \cdot 2H_2O$ (99%, p.a.) from Merck. The chemicals were used without further purification.

Synthesis of the Copper Complexes and Preparation of Crystals for X-Ray Analysis.—The copper(II) complexes of L^1–L^5 were synthesized in a minimum of solvent (10–20 cm^3) as follows, giving yields of 70–75%. (*a*) $[CuL^1(Br)][PF_6]$ **1**. The salt $TlPF_6$ (0.3 mmol, 0.105 g) was added to an aqueous solution of L^1 in the trihydrobromide form (0.1 mmol, 0.042 g). The TlBr formed was filtered off and $CuSO_4$ (0.1 mmol, 0.025 g) was added to the solution. On addition of $Ba(OH)_2$, $BaSO_4$ was precipitated and filtered off. The pH was adjusted to 7 with sodium hydroxide and a concentrated solution was allowed to stand at room temperature. Blue crystals were formed in a few days.

(*b*) $[CuL^2(Cl)][PF_6]$ **2**. A mixture of L^2 (0.1 mmol, 30.3 cm^3 of a 3.3×10^{-3} mol dm^{-3} solution) and $CuSO_4$ (0.1 mmol, 0.025 g) in water was refluxed for 2 h. Barium chloride (0.1 mmol, 0.025 g) and $TlPF_6$ (0.1 mmol, 0.035 g) were successively added and the $BaSO_4$ and TlCl then formed were filtered off. The solution was concentrated and blue crystals were formed by slow evaporation at room temperature, after a few days.

(*c*) $[CuL^3(H_2O)][PF_6]_2$ **3** *and* $[CuL^4(H_2O)][PF_6]_2 \cdot H_2O$ **4**. A water solution of $CuSO_4 \cdot 5H_2O$ (0.22 mmol, 0.056 g) was added to a stirred aqueous solution of L^3 (or L^4) in the trihydrobromide form (0.22 mmol) and the mixture was refluxed for 45 min after addition of $Ba(OH)_2$ (0.22 mmol, 0.071 g). The $BaSO_4$ formed was filtered off. The salt $TlPF_6$ (0.75 mmol, 0.26 g) was then added to the filtrate and the precipitate formed filtered off. The pH of the filtrate was adjusted to 9 with NaOH. Blue crystals were formed when the solution was allowed to stand at room temperature for about 3 weeks.

(*d*) $[CuL^5(Cl)][PF_6]$ **5**. A mixture of $CuCl_2$ (0.26 mmol, 0.035 g) and L^5 (0.26 mmol, 0.065 g) in water was refluxed for 2 h, then $TlPF_6$ (0.26 mmol, 0.091 g) was added and filtered off. The filtrate was adjusted to about pH 8 and left to stand at room temperature. Blue crystals were formed in 2 months.

The blue crystals of complex **3** obtained in this work were not good enough for X-ray crystallography but, as stated above, this complex had already been studied.[2] In all the other cases the irregular crystals obtained were of good X-ray quality.

Spectroscopic Studies.—Electronic (UV/VIS–near IR) spectra were recorded with a Perkin-Elmer Lambda 9 spectrophotometer using aqueous solutions of the complexes prepared by the addition of the metal ion to the trihydrobromide form of the macrocycle at the appropriate pH value (corresponding to total formation of the metal complex). The total concentrations of the metal complexes were about 0.75–1.66 mmol dm^{-3}.

The ESR spectra were obtained using a Bruker ER 200-SRC spectrometer equipped with an Oxford Instruments continuous-flow cryostat. The complexes were prepared as described for the measurements of the electronic spectra but in dilute solution in 1.0 mol dm^{-3} $NaClO_4$ (about 1.2×10^{-3} mol dm^{-3}). Spectra were recorded both at room temperature and at 77 K (in liquid nitrogen), in the X-band frequency range of approximately 9.42 GHz. The concentration of the copper complexes used was well below the range where ion–ion dipolar broadening can be detected. At higher concentrations and lower ionic strength only one broad resonance was observed. The spectra were simulated with a program for a microcomputer.[3] The accuracy of the g values estimated by the mean-squares deviation between experimental and simulated spectra is ± 0.001 for g_3 and ± 0.002 for g_1 and g_2.

Crystallographic Measurements and Processing.—The pertinent crystal data for complexes **1**, **2**, **4** and **5** are given in Table 5. Single-crystal data for **2** and **4** were collected with an Enraf–Nonius CAD-4 diffractometer, using graphite-monochromated Mo-Kα ($\lambda = 0.710\,69$ Å) radiation. The unit-cell parameters and orientation matrix were calculated by least-squares refinement of 25 well centred reflections in ranges $14 < \theta < 17$ and $13 < \theta < 17°$ for **2** and **4**, respectively. The intensity data were collected by ω–2θ scans. Three strong reflections were measured after every 3600 s, and their intensities did not show appreciable decay. The data were corrected for absorption, Lorentz and polarization effects with the CAD-4 software and merged with SHELX 76.[4]

Data for complexes **1** and **5** were collected with an Enraf–Nonius FAST diffractometer, equipped with a rotating molybdenum anode and graphite monochromator. The detector was kept at 40 mm from the crystal and at a θ swing angle of 25°. An exposure time of 10 s for complex **1** and 25 s for **5** were used per 0.20° frame of data collected. The data were evaluated on-line using SADNES, a modified version of the MADNES software for small molecules.[5] The unit-cell dimensions together with the orientation matrix were obtained in each case by autoindexing of 50 strong reflections collected by ω scan in two narrow ($\approx$ 5°C) orthogonal zones of reciprocal space. These parameters were refined every 10° of data measured. Data reduction, including Lorentz and polarization corrections, was carried out by the Kabsch method of profile fitting, using PROCOR.[6] Intensities were not corrected for absorption effects. The data were then scaled and merged with SHELX 76.[4]

Structure analysis and refinement. The positions of the heavy atoms were obtained from three-dimensional Patterson maps and the remaining non-hydrogen atoms were found by successive Fourier-difference syntheses. The structures were refined by least squares until convergence was achieved using anisotropic thermal parameters for all non-hydrogen atoms.

The hydrogen atoms for complex **1** were included in the refinement in calculated positions for an idealized tetrahedral geometry. The methylenic hydrogens were refined with a global isotropic thermal parameter $U_{iso} = 0.056(6)$ Å^2 and the hydrogens bonded to nitrogen atoms were refined with a fixed U_{iso} of 0.06 Å^2. The C–H and N–H distances were constrained to 1.08 Å. The hydrogen atoms for complex **2** were refined isotropically at a fixed distance of 1.08 Å from the parent carbon atom. Those in compounds **4** and **5** were located from Fourier-difference maps. The methylenic hydrogens were refined with global isotropic thermal parameters, $U_{iso} = 0.059(6)$ and 0.054(4) Å^2 for **4** and **5** respectively. The methyl hydrogens of complex **5** were refined in three groups with U_{iso} 0.092(15), 0.057(9) and 0.061(10) Å^2 according to the nitrogen to which the group is bound, while the hydrogens bonded to nitrogen atoms in **4** were refined with a fixed isotropic thermal parameter, $U_{iso} = 0.05$ Å^2. The C–H and N–H distances were constrained to 0.95 Å in both cases. The hydrogen atoms of the water molecules in complex **4** were not found in final Fourier maps and were not introduced in the refinement. The last ΔF map done for each compound showed a residual electron density less than 1.0 e Å^{-3}.

In the final structure-factor calculation for complex **2** the Flack absolute structure parameter was calculated with

Table 1 Electronic spectroscopic data for the copper(II) complexes of the oxatriaza macrocycles

Complex	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})
$[CuL^1]^{2+}$	690.6 (161), 840 (sh)
$[CuL^2]^{2+}$	675.0 (340), 920 (sh)
$[CuL^3]^{2+}$	626.4 (160), 780 (sh)
$[CuL^4]^{2+}$	622.0 (147), 780 (sh)
$[CuL^5]^{2+}$	610 (sh), 680.0 (262), 810 (sh)

SHELXL 93[7] ($x = -0.005 \pm 0.03$) to assign the correct absolute configuration. All calculations required to solve and refine the structures were carried out with SHELX 76[4] and SHELXS 86.[8] The atomic scattering factors were taken from ref. 9. The puckering parameters were calculated with the PARST program[10] and the molecular diagrams drawn with ORTEP II.[11]

Final atomic coordinates of non-hydrogen atoms are given in Table 6.

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

Results and Discussion

Spectroscopic Measurements.—The electronic spectra of all the copper complexes of L^1–L^5, in aqueous solution, exhibit an intense absorption in the near-UV region which may be assigned to a charge-transfer transition and a single broad band in the visible region (622–691 nm) due to the copper d–d transition. The absorption in the visible presents an ill defined shoulder at lower energy, and the complex of L^5 also exhibits a shoulder at higher energy, as can be seen in Table 1.

Frozen-solution ESR spectra of all the complexes are similar in appearance (see Fig. 1), exhibiting three well resolved lines of the four expected at low field, arising from interaction of the unpaired electron spin with the copper nucleus, and no superhyperfine splitting due to coupling with the three nitrogen atoms of the macrocycle. This part of the spectra can be used for fairly accurate measurements of g_3 and A_3. The fourth copper line is completely overlapped by the much stronger and not resolved bands of the high-field part of the spectrum, which renders accurate determinations of g_1, g_2 and A_1, A_2 only possible by computational simulation. Simulation of the spectra[3] has shown rhombic symmetry for the four copper(II) complexes studied in this work, as expected from the non-axial character of the molecules. However, the differences between the values of g_1 and g_2 for the complexes of the 14-membered ligands L^4 and L^5 are very small. The hyperfine coupling constants and g values obtained are presented in Table 2.

Room-temperature ESR spectra of the solutions of the copper complexes are more symmetrical than those obtained from the frozen solutions, as is usual for small copper complexes. The g_0 and A_0 values are also given in Table 2. There are small differences between the experimental values and those calculated by $g_0 = (g_1 + g_2 + g_3)/3$ and $A_0 = (A_1 + A_2 + A_3)/3$. In general the g_0^{calc} values are smaller and A_0^{calc} larger than the values obtained experimentally at room temperature. This can be explained by small modifications in the co-ordination at low temperature, causing changes in bonding parameters.[12]

For all the complexes studied in this work $g_3 > (g_1 + g_2)/2$, which is typical of tetragonal Cu^{II}, where the tetragonal distortion takes the form of elongation of the axial bonds. Hence it appears that it is possible to exclude a trigonal-bipyramidal geometry or a tetragonal structure involving compression of axial bonds.[12–14]

The ESR parameters for copper complexes are determined by the chemical composition and the physical constraints on the atoms nearest to the metal ion. Using diagrams of $g_{\parallel}$ and $A_{\parallel}$ values, compiled by Peisach and Blumberg[15] for a series of model compounds with three nitrogen and one oxygen donor atoms and known as having square-planar structures, it was found that the copper complexes of the 14-membered macrocycles L^4 and L^5 fall inside the model area (Fig. 2), whereas those of the 12- and 13-membered L^1–L^3 lay outside that area (considering $g_{\parallel}$ and $A_{\parallel}$ as g_3 and A_3, respectively). This indicates a square-planar arrangement of the donor atoms in the copper complexes of L^4 and L^5.

Similar diagrams applied to a series of copper complexes of tetraaza macrocycles where one of the nitrogen donor atoms is of a pyridine[16] show identical behaviour. However, in this

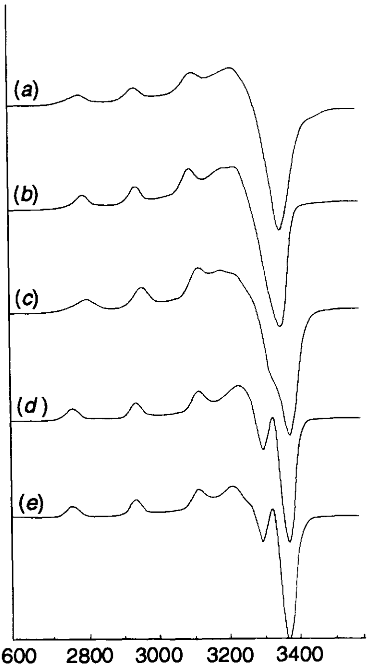

Fig. 1 The ESR spectra of the complexes $[CuL^1]^{2+}$ (*a*), $[CuL^2]^{2+}$ (*b*), $[CuL^3]^{2+}$ (*c*), $[CuL^4]^{2+}$ (*d*) and $[CuL^5]^{2+}$ (*e*)

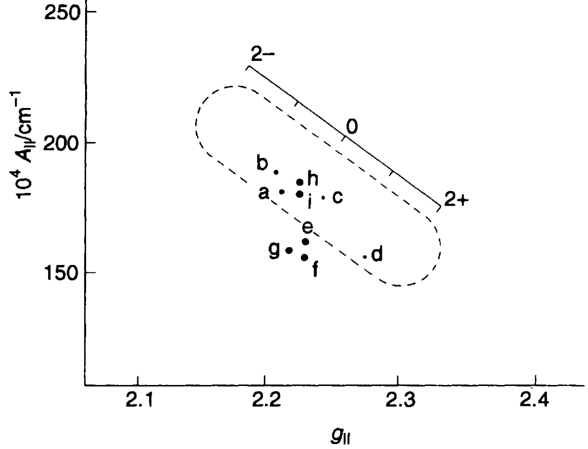

Fig. 2 Relation between the ESR parameters, $A_{\parallel}$ *versus* $g_{\parallel}$, for a series of model copper(II) complexes where the atoms lying close to the metal are three nitrogen and one oxygen atoms: a, Gly-Gly-Gly-Gly, pH 8; b, Gly-Gly-Gly, pH 8; c, Gly-Gly-Gly, pH 7; and d, Gly-Gly-Gly, pH 6. The diagonal scale shows the total charge for the copper atom and its four close-lying ligand atoms.[15] The ESR parameters of our complexes are also included: e, $[CuL^1]^{2+}$; f, $[CuL^2]^{2+}$; g, $[CuL^3]^{2+}$; h, $[CuL^4]^{2+}$ and i, $[CuL^5]^{2+}$

Table 2 The ESR spectroscopic data for the copper(II) complexes

	$[CuL^1]^{2+}$	$[CuL^2]^{2+}$	$[CuL^3]^{2+}$	$[CuL^4]^{2+}$	$[CuL^5]^{2+}$
g_1	2.037	2.051	2.027	2.050	2.053
g_2	2.077	2.081	2.082	2.059	2.058
g_3	2.226	2.228	2.216	2.224	2.224
$10^4\ A_1/cm^{-1}$	23.8	27.5	26.9	10.9	10.5
$10^4\ A_2/cm^{-1}$	21.6	10.4	15.1	20.5	24.3
$10^4\ A_3/cm^{-1}$	162.8	157.2	160.2	183.1	183.4
g_0^{exptl}	2.124	2.122	2.115	2.116	2.116
g_0^{calc}	2.113	2.120	2.108	2.111	2.112
$10^4\ A_0^{exptl}/cm^{-1}$	65.5	61.4	67.1	69.3	73.3
$10^4\ A_0^{calc}/cm^{-1}$	69.4	65.0	67.4	71.5	72.7

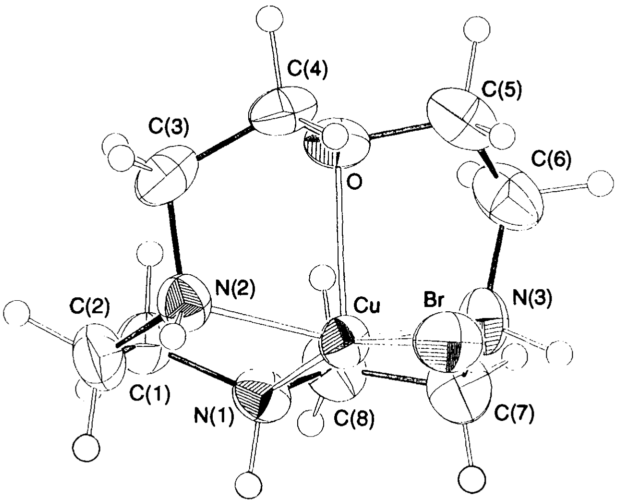

Fig. 3 Molecular diagram of the $[CuL^1(Br)]^+$ complex cation showing the atomic labelling scheme. Thermal ellipsoids are drawn at the 30% probability level and the hydrogen atoms are represented with a U_{iso} of 0.01 Å^2

series, the complex with the macrocycle of smaller cavity size has also smaller A_3 but larger g_3 parameters and exhibits an electronic spectrum with a red shift when compared with that of the 14-membered macrocycle of the same series. Based on these spectroscopic data a square-pyramidal structure was predicted for the complex of the 12-membered macrocycle.[16] Analogous behaviour was found for the copper(II) complexes of L^6 (1,4,7,10-tetraazacyclododecane, cyclen) and L^9 (1,4,8,11-tetraazacyclotetradecane, cyclam): the former complex exhibits, in aqueous solution, an electronic spectrum with a band at λ_{max} 599 nm (ε = 250 dm^3 mol^{-1} cm^{-1}) and an ESR spectrum with $g_{\parallel} = 2.198$ ($A_{\parallel} = 184.2 \times 10^{-4}$ cm^{-1}) and $g_{\perp} = 2.057$ ($A_{\perp} = 24.1 \times 10^{-4}$ cm^{-1}); for that of cyclam a band at λ_{max} 513 nm (ε = 100 dm^3 mol^{-1} cm^{-1}) and an ESR spectrum with $g_{\parallel} = 2.186$ ($A_{\parallel} = 205 \times 10^{-4}$ cm^{-1}) and $g_{\perp} = 2.049$ ($A_{\perp} = 38.7 \times 10^{-4}$ cm^{-1}) were reported.[13,17] A square-pyramidal structure was suggested for the copper(II) complex of cyclen, in solution and in the solid state,[13,18] and it is well known that the copper complex of cyclam adopts a square-planar arrangement in the crystal and in solution.[19,20]

The electronic properties of the copper(II) complexes mentioned in the last paragraph are easily explained by the usual factors taken from the equations for the ESR parameters derived from ligand-field theory,[21-23] the strength of the axial donor and the displacement of the copper from the donor-atom plane. The addition of a fifth ligand has the effect of decreasing $A_{\parallel}$ while increasing $g_{\parallel}$.[24,25]

The copper complexes of the oxatriaza series studied in the present work exhibit a different behaviour that cannot be explained in similar terms. Indeed the complexes of the 12-membered macrocycles have a slightly higher g_3 value and show a drastic decrease in A_3 when compared with the corresponding values for the complex of the 14-membered macrocycles, for which a square-planar arrangement of the donor atoms can be postulated based on the spectroscopic data (see Table 2). The complex of the 13-membered macrocycle has a more peculiar set of ESR parameters with a large decrease both in g_3 and A_3 compared to the values of the 14-membered macrocyclic complexes. In particular this series of complexes does not show any regularity or sequence of ESR parameters with decrease in the ring size, which could be interpreted in terms of the introduction of an axial donor atom or a displacement of the copper from the plane of the donor atoms. On the other hand, the introduction of *N*-methyl substituents on the 12- and the 14-membered macrocycles does not modify the structural arrangement of the copper complexes formed. In fact, there are only minor differences in the ESR parameters for the copper(II) complexes of the *N*-methylated and the parent macrocycles, although the electronic spectra of the former have larger absorption coefficients suggesting more distorted structures.

However, the drastic decrease in A_3 for the copper(II) complexes of L^1–L^3 can be interpreted by the existence of geometrical distortions between the limiting planar and the tetrahedral geometries. Indeed, it was demonstrated that the ESR parameters are quite sensitive to the introduction of a distortion towards a tetrahedron, leading to a significant decrease in A_3 values while small effects are found in A_1 and A_2.[26-28]

Although care must be taken in making stereochemical assignments based on ESR and electronic spectra which are not especially good indicators of geometry,[14] our results suggest more planar geometries around the copper ion for complexes of the 14-membered oxatriaza macrocycles and a degree of tetrahedral distortion from the planar geometries for the complexes of 12- and 13-membered macrocycles. The deviation of the maximum in the visible absorption of all these complexes to lower energies than expected for a set of N_3O donor atoms possibly indicates co-ordination of an apical ligand.[14,29]

X-Ray Analyses.—The cations in the four compounds studied are five-co-ordinated, of the [3 + 2] type with the 12-membered macrocycles, **1** and **2**, and of the [4 + 1] type with the 14-membered macrocycles, **4** and **5**. Molecular diagrams with the corresponding atom-labelling schemes are shown in Figs. 3, 4, 5 and 6 for complexes **1**, **2**, **4** and **5**, respectively. The bond lengths and angles around the central copper atom are listed in Table 3, indicating distorted square-pyramidal co-ordination geometries. The basal planes are formed by the three nitrogens and the oxygen from the macrocycle in complexes **4** and **5**, while in **1** and **2** they are formed by the three macrocyclic nitrogens and the halogen atom, bromine and chlorine respectively. The apical co-ordination is accomplished *via* the oxygen macrocyclic donor atom in **1** and **2** and *via* a water molecule in **4** and a chlorine atom in **5**. To achieve the co-ordination described, macrocycles L^1 and L^2 fold considerably through the N(2)–N(3) line, leading to dihedral angles between the planes N(2),Cu,N(3),O and N(2),Cu,N(3),N(1) of 109.2(2) and 101.2(2)° in complexes **1** and **2** respectively. There is also a slight tendency from square-

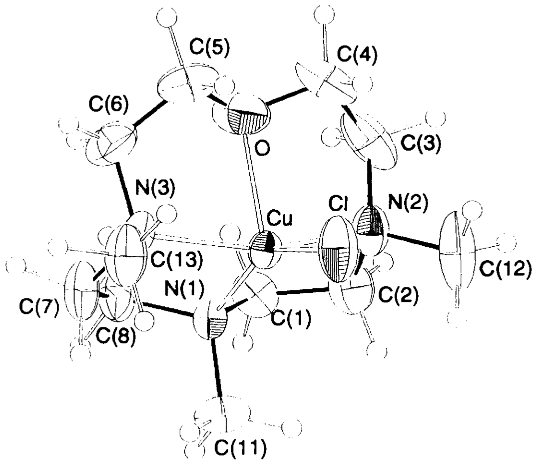

Fig. 4 Molecular diagram of the [CuL^2(Cl)]$^+$ complex cation showing the atomic labelling scheme. Details as in Fig. 3

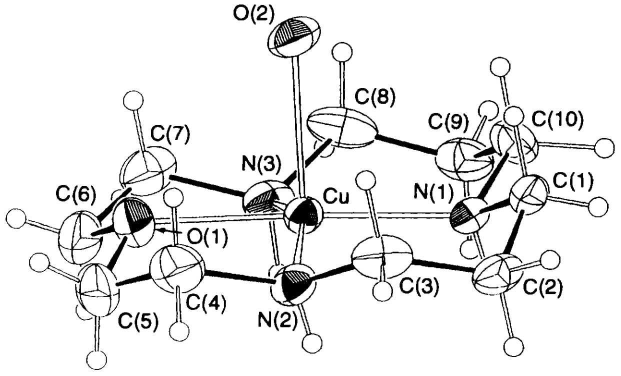

Fig. 5 Molecular diagram of the [CuL^4(H$_2$O)]$^{2+}$ complex cation showing the atomic labelling scheme. Details as in Fig. 3

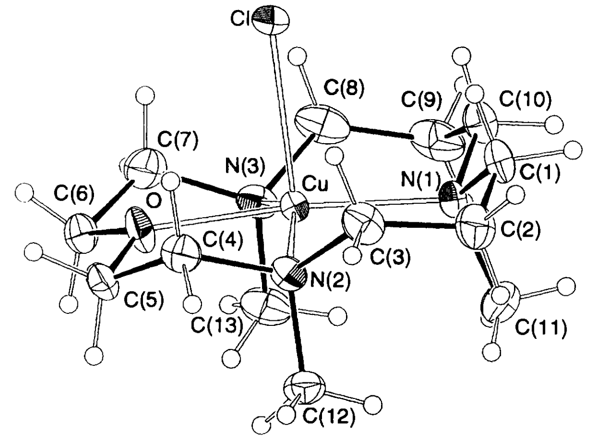

Fig. 6 Molecular diagram of the [CuL^5(Cl)]$^+$ complex cation showing the atomic labelling scheme. Details as in Fig. 3

Table 3 Bond lengths (Å) and angles (°) in the co-ordination sphere of complexes **1**, **2**, **4** and **5**

	1	**2**	**4**	**5**
	(X = Br)	(Cl)	[O(1)]	(O)
Equatorial				
Cu–N(1)	2.000(7)	1.987(6)	1.990(8)	2.031(6)
Cu–X	2.397(3)	2.226(3)	2.031(8)	1.998(5)
Cu–N(2)	2.042(8)	2.090(6)	2.005(9)	2.047(6)
Cu–N(3)	2.030(8)	2.078(5)	1.999(9)	2.059(6)
N(1)–Cu–X	162.1(2)	147.1(1)	177.2(3)	173.6(1)
N(2)–Cu–N(3)	155.1(3)	156.2(2)	154.8(3)	152.1(2)
N(1)–Cu–N(2)	85.8(3)	86.5(3)	97.6(4)	97.9(3)
N(2)–Cu–X	98.5(3)	99.2(2)	101.5(4)	81.1(2)
N(3)–Cu–X	96.9(3)	99.2(2)	97.6(4)	80.6(3)
N(1)–Cu–N(3)	85.5(3)	86.2(3)	97.0(4)	97.9(3)
Axial	(Y = O)	(O)	[O(2)]	(Cl)
Cu–Y	2.347(7)	2.216(6)	2.248(8)	2.474(3)
N(1)–Cu–Y	98.6(3)	104.6(3)	94.7(4)	96.2(2)
X–Cu–Y	99.3(2)	108.3(2)	88.1(3)	90.2(2)
N(2)–Cu–Y	78.2(3)	79.9(3)	101.5(4)	101.3(2)
N(3)–Cu–Y	80.1(3)	80.1(3)	97.6(4)	99.6(2)

Table 4 Tetrahedral distortion in the equatorial plane of the copper complexes

	Deviations (Å) of donor atoms from least-squares basal plane				
Atom	L^1	L^2	L^3*	L^4	L^5
N(1)	−0.426	−0.560	0.171	0.130	0.114
O(1)			0.143	0.167	0.158
Br	−0.280				
Cl		−0.370			
N(2)	0.349	0.462	−0.164	−0.149	−0.136
N(3)	0.356	0.467	−0.152	−0.149	−0.136

* Ref. 2; + = above the plane; − = below the plane.

pyramidal towards trigonal-bipyramidal co-ordination as can be observed from the values of the angles involving the *trans* donor atoms [N(2)–Cu–N(3) and N(1)–Cu–X] in Table 3.

Table 4 lists the deviations from the best least-square planes defined through the basal atoms of the square pyramids, showing that a quite pronounced tetrahedral distortion is present in complexes **1** and **2** where the macrocycle is more folded. The Cu atom deviates from that plane by only 0.017 Å in **1**, while it is out of that plane in the apical direction by 0.124, 0.198 and 0.249 Å in **2**, **4** and **5**, respectively.

The four complexes described show very clearly that when the macrocyclic ring has a small cavity size, as in the 12-membered ones, the incorporation of a Cu atom in that cavity is only achieved because the macrocycle has the required flexibility to fold and distort so as to be able to insert the metal at its centre. This new arrangement was unexpected since no similar situation in complexes with macrocycles of comparable size was previously suggested by spectroscopic techniques or determined by X-ray crystallography.[30] On the other hand, complexes of 14-membered macrocycles have larger cavities and thus the Cu atom fits these comfortably well, only barely out of the respective co-ordination planes.

An intermediate situation is naturally expected in complexes with oxatriaza 13-membered macrocycles. There is only one example in the literature of such a copper complex, [CuL^3(Br)]$^+$, with a structural determination.[2] In this complex the co-ordination geometry around the central metal atom is a square pyramid with the atoms from the macrocycle defining the basal plane, as in **4** and **5**. The Cu atom deviates more from the N$_3$O plane, by 0.47 Å, in the direction of the apical position occupied by the bromine ligand. The basal plane has a tetrahedral distortion comparable to that observed in complexes **4** and **5** (see Table 4). A similar type of co-ordination is also observed in the complex [CuL^6(NO$_3$)]$^+$ where the metal ion deviates even more from the basal N$_4$ plane, by 0.51 Å, towards the apical NO$_3$$^-$ ligand.[18]

Table 5 Crystal data and details of refinement of complexes **1**, **2**, **4** and **5**

	1	**2**	**4**	**5**
Formula	$C_8H_{19}BrCuF_6N_3OP$	$C_{11}H_{25}ClCuF_6N_3OP$	$C_{10}H_{25}CuF_{12}N_3O_2P_2\cdot H_2O$	$C_{13}H_{29}ClCuF_6N_3OP$
M	461.4	459.3	590.8	487.1
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Triclinic
Space group	$P2_1/c$	$P2_12_12_1$	*Pbca*	$P\bar{1}$
a/Å	8.034(5)	9.383(2)	15.996(1)	6.802(4)
b/Å	9.103(2)	13.445(2)	14.502(2)	11.491(5)
c/Å	20.918(1)	14.217(3)	19.504(2)	13.034(6)
α/°				83.65(2)
β/°	96.01(4)			85.20(3)
γ/°				83.48(2)
U/Å^3	1520	1794	4420	1003
Z	4	4	8	2
F(000)	808	940	2392	502
D_c/g cm^{-3}	2.01	1.70	1.78	1.67
μ(Mo-Kα)/cm^{-1}		15.08	12.46	13.64
Diffractometer	FAST	CAD-4	CAD-4	FAST
$2\theta_{max}$/°	60	60	56	60
Scan type	ω	ω-2θ	ω-2θ	ω
Absorption correction	No			No
Minimum, maximum transmission		0.93, 0.98	0.92, 0.99	
Measured reflections	17 993	6680	11 440	10 991
Unique reflections	4229	4011	4750	4875
R_{merge}	0.070	0.037	0.034	0.071
Reflections used	2789 ($\lvert F_o\rvert > 3\sigma\lvert F_o\rvert$)	3740 ($\lvert F_o\rvert > 1\sigma\lvert F_o\rvert$)	3035 ($\lvert F_o\rvert > 3\sigma\lvert F_o\rvert$)	4087 ($\lvert F_o\rvert > 1\sigma\lvert F_o\rvert$)
Data-to-parameters ratio	15:1	14:1	9:1	13:1
R^a	0.085	0.067	0.090	0.075
R'^b	0.093	0.046	0.085	0.084
k and g in $w = k/[\sigma^2(F_o) + g(F_o)^2]$	1.0364, 0.005 68	0.8631, 0.0001^c	3.4562, 0.001 067	2.7827, 0.002 023

^{a} $R = \Sigma(|F_o| - |F_c|)/|F_o|$. ^{b} $R' = \Sigma[w^{\frac{1}{2}}(|F_o| - |F_c|)]/|F_o|w^{\frac{1}{2}}$. ^{c} g was fixed for complex **2**.

The equatorial Cu–N distances in the four complexes (see Table 3) as well as the Cu–O distances in **4** and **5** are similar and within the expected values.[31]

The conformation of the chelate rings can be described using the puckering parameters defined by Cremer and Pople.[32] In complex **1** the chelate ring Cu,O,C(4),C(3),N(2) is in an envelope conformation, while the remaining five-membered rings adopt twisted conformations. In **2** the five-membered rings Cu,O,C(4),C(3),N(2) and Cu,N(3),C(6),C(5),O show twisted conformations, while the five-membered rings Cu,N(1),C(8),C(7),N(3) and Cu,N(2),C(2),C(1),N(1) are in envelope conformations. In **4** the six-membered rings show a half-boat conformation, while the five-membered rings have twisted conformations. In **5** the five-membered rings have envelope conformations, while the six-membered rings Cu,N(1),C(10),C(9),C(8),N(3)andCu,N(2),C(3),C(2),C(1),N(1) adopt a boat and a chair conformation respectively.

Analysis of the intermolecular distances indicates, for complex **2**, hydrogen bonds between the hydrogen of one NMe group and one fluorine atom F(5)···H(111) ($\frac{1}{2} + x$, $\frac{1}{2} - y$, $-z$) 2.288 Å and between another hydrogen of the same NMe group and one chlorine atom Cl···H(113) ($-\frac{1}{2} + x$, $\frac{1}{2} - y$, $-z$) 2.829 Å. The intermolecular distances in **4** also suggest the occurrence of hydrogen bonding between a co-ordinated water and a water molecule of crystallization [O(3)···O(2) ($-\frac{1}{2} + x, y, \frac{1}{2} - z$) 2.677 Å].

Conclusion

The conditions used to prepare the complexes described in this paper for the solution studies did not yield suitable crystals for X-ray analysis. Thus, inclusion of bulky counter ions, such as PF_6^-, was necessary to induce crystallization. However, there is close agreement between the main conclusions concerning the structures observed in solution and in the crystal state.

The ESR and electronic spectroscopic measurements in solution as well as single-crystal X-ray diffraction studies reveal a square-pyramidal geometry for the copper complexes of the 14-membered oxatriaza macrocyclic ligands with the donor atoms of the macrocycles in a square-planar arrangement having a small tetrahedral distortion and the metal atom barely out of the basal plane. Additionally, the ESR and X-ray analysis agree on the type of distortion found for the complexes of the 12-membered macrocycles.

In contrast to what has been described for tetraza macrocyclic complexes,[30] the present study also shows that the replacement of hydrogen atoms by methyl groups on the nitrogen atoms, going from **1** to **2** and from **4** to **5**, does not affect the overall final geometry of these complexes.

Different results have, however, been found for the complex of the 13-membered macrocycle. While the published X-ray results[2] show that a structure similar to those found in this work for the 14-membered macrocyclic complexes exists in the solid state, the present spectroscopic studies in solution point to a structure with a significant tetrahedral distortion similar to that observed in the 12-membered macrocyclic complexes. The reason for this difference is not obvious.

The structural results described show the flexibility of this series of macrocycles when co-ordinating to copper. The smaller the ligand, the more pronounced is the folding necessary to accommodate the metal at its centre. For the first time the structure is reported of a complex of a 12-membered macrocycle with four donor atoms, one of the latter approaching the metal from an apical position.

Acknowledgements

We thank B. Barata for help in the ESR experiments. The authors also acknowledge financial support from the Junta Nacional de Investigação Científica e Tecnológica (Projects STRDA/C/CEN 520/92 and PMCT/C/CEN 367/90) and for a grant (to V. F.).

Table 6 Fractional atomic co-ordinates (× 10^4) with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
[CuL^1(Br)][PF$_6$]							
Br	11 341(1)	1 689(1)	−3.8(4)	C(6)	7 958(11)	4 326(9)	683(5)
Cu	9 323(1)	1 334(1)	748.9(4)	C(7)	5 954(9)	2 276(10)	458(5)
N(1)	7 427(7)	525(6)	1 188(3)	C(8)	6 026(10)	1 602(9)	1 123(4)
N(2)	10 846(8)	348(7)	1 466(3)	P	5 675(3)	3 032(2)	8 481(1)
N(3)	7 643(8)	2 849(7)	372(3)	F(11)	6 250(12)	1 645(7)	8 908(4)
O	10 041(7)	3 317(6)	1 440(3)	F(12)	6 016(9)	4 093(7)	9 069(3)
C(1)	8 100(10)	143(10)	1 851(4)	F(13)	7 529(8)	3 221(9)	8 301(5)
C(2)	9 712(11)	−628(9)	1 815(4)	F(14)	5 117(10)	4 422(8)	8 063(4)
C(3)	11 759(12)	1 446(10)	1 915(4)	F(15)	5 318(10)	1 974(9)	7 890(4)
C(4)	11 769(10)	2 972(9)	1 601(4)	F(16)	3 845(9)	2 819(8)	8 650(5)
C(5)	9 709(12)	4 526(9)	974(5)				
[CuL^2(Cl)][PF$_6$]							
Cu	128.2(6)	−1 440.4(3)	−1 239.6(4)	C(7)	1 168(8)	−789(5)	−3 027(4)
Cl	−366(2)	−3 038(1)	−986(1)	C(8)	1 445(7)	13(4)	−2 333(4)
N(1)	1 622(4)	−404(3)	−1 383(3)	C(11)	3 081(6)	−838(5)	−1 264(5)
N(2)	−147(6)	−899(3)	126(3)	C(12)	−64(11)	−1 643(5)	875(3)
N(3)	−14(6)	−1 422(3)	−2 698(2)	C(13)	108(9)	−2 388(4)	−3 155(3)
O	−1 909(4)	−627(3)	−1 412(4)	P	−255(2)	−2 085(1)	−6 206(1)
C(1)	1 357(7)	350(4)	−640(4)	F(1)	10(6)	−1 279(2)	−5 423(2)
C(2)	1 027(7)	−174(5)	253(4)	F(2)	712(6)	−2 831(3)	−5 653(4)
C(3)	−1 524(8)	−355(7)	174(6)	F(3)	−1 201(7)	−1 352(5)	−6 745(3)
C(4)	−2 559(7)	−763(6)	−533(5)	F(4)	1 082(5)	−1 753(4)	−6 774(3)
C(5)	−2 490(7)	−1 086(6)	−2 226(5)	F(5)	−510(5)	−2 876(3)	−6 988(3)
C(6)	−1 394(7)	−959(6)	−2 963(5)	F(6)	−1 510(6)	−2 480(5)	−5 643(4)
[CuL^4(H$_2$O)][PF$_6$]$_2$·H$_2$O							
Cu	4 042(1)	7 318(1)	924(1)	O(3)	1 714(5)	7 020(5)	3 477(4)
N(1)	4 046(4)	6 213(5)	1 544(3)	P(1)	7 328(2)	−400(2)	1 981(1)
N(2)	4 048(5)	8 278(5)	1 681(4)	F(11)	7 004(5)	625(4)	1 946(5)
N(3)	3 600(4)	6 693(6)	66(4)	F(12)	6 420(4)	−756(5)	2 083(4)
O(1)	3 978(4)	8 453(4)	303(3)	F(13)	7 408(5)	−269(5)	2 794(4)
O(2)	5 409(4)	7 224(5)	658(3)	F(14)	7 687(5)	−1 410(4)	2 061(4)
C(1)	4 559(6)	6 331(7)	2 191(5)	F(15)	8 270(4)	−58(5)	1 901(4)
C(2)	4 296(6)	7 145(7)	2 622(4)	F(16)	7 277(5)	−524(7)	1 179(4)
C(3)	4 531(6)	8 075(8)	2 316(5)	P(2)	1 500(1)	7 100(2)	1 159(1)
C(4)	4 262(8)	9 185(7)	1 350(7)	F(21)	2 075(4)	6 240(5)	1 049(5)
C(5)	3 795(8)	9 265(7)	687(7)	F(22)	926(5)	7 935(5)	1 232(8)
C(6)	3 514(7)	8 295(9)	−324(6)	F(23)	2 277(5)	7 610(8)	1 312(10)
C(7)	3 729(7)	7 322(9)	−545(5)	F(24)	729(5)	6 602(8)	924(7)
C(8)	3 929(7)	5 771(8)	−67(6)	F(25)	1 246(7)	6 803(12)	1 853(5)
C(9)	3 789(6)	5 137(7)	557(6)	F(26)	1 714(7)	7 291(12)	410(6)
C(10)	4 284(6)	5 344(6)	1 187(6)				
[CuL^5(Cl)][PF$_6$]							
Cu	−934(1)	7 137.5(4)	7 910.2(3)	C(8)	−807(9)	9 280(6)	8 964(5)
Cl	2 431(2)	6 616(1)	8 522(1)	C(9)	−464(10)	9 961(5)	7 936(6)
N(1)	−147(6)	8 336(3)	6 725(3)	C(10)	772(9)	9 278(5)	7 144(5)
N(2)	−1 165(6)	5 775(3)	7 056(3)	C(11)	−1 864(10)	8 896(6)	6 126(5)
N(3)	−2 071(6)	8 302(4)	8 957(3)	C(12)	−3 081(7)	5 891(5)	6 555(4)
O	−2 021(5)	6 007(3)	9 033(2)	C(13)	−4 144(8)	8 780(5)	8 760(5)
C(1)	1 396(9)	7 749(6)	5 997(4)	P	4 331(2)	2 342(1)	6 804(1)
C(2)	788(10)	6 713(6)	5 534(4)	F(11)	4 095(12)	3 308(6)	7 538(5)
C(3)	542(8)	5 626(5)	6 279(4)	F(12)	2 044(7)	2 422(6)	6 833(8)
C(4)	−1 088(8)	4 710(4)	7 811(4)	F(13)	4 508(16)	1 415(8)	6 028(7)
C(5)	−2 508(8)	4 929(5)	8 738(4)	F(14)	6 648(7)	2 253(6)	6 682(5)
C(6)	−2 992(8)	6 462(6)	9 934(4)	F(15)	4 324(9)	1 302(5)	7 678(5)
C(7)	−2 057(9)	7 571(6)	9 980(4)	F(16)	4 307(9)	3 370(6)	5 891(4)

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Received 9th *May* 1994; *Paper* 4/02732I