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Synthetic, Structural and Molecular Mechanics Investigation of some Mono- and Dinuclear Copper(I) and Copper(II) Complexes of Macrocyclic and Related Acyclic Ligands

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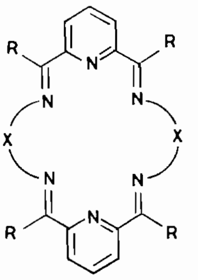
Abstract

A number of di-Cu(II) complexes of the new tetraimine macrocyclic ligand derived from the Schiff base [2 + 2] condensation of 2,5-diformylfuran with 3-oxa-pentane-1,5-diamine have been prepared by methods which employ the heavier alkaline earth metal ions as templates followed by transmetallation. The complexes have been characterised by spectroscopic and other physical methods. Several of the di-Cu(I) complexes react reversibly with CO in solution and irreversibly with O_2 in a 4:1 Cu:O_2 stoicheiometry. Depending on conditions the oxidation product may be a dinuclear Cu(II) complex of the macrocycle or a mononuclear Cu(II) complex of a new ring-opened ligand. The single crystal X-ray structure of the latter complex has been determined.

[CuL]$(BPh_4)_2$ is monoclinic, space group $C2/c$ with $a = 20.12(1)$, $b = 14.48(1)$, $c = 22.37(2)$ Å, $\beta = 110.1(1)°$, $Z = 4$. 1389 Independent reflections above background were measured on a diffractometer and the structure refined to $R = 0.108$. The cation has imposed C_2 symmetry. The copper atom is bonded to four nitrogen atoms in the 'outer' compartment of the ligand with unique Cu–N distances of 2.050(17) and 1.977(17) Å. The geometry of the copper atom is intermediate between square planar and tetrahedral with an angle of 39.7° between two CuN_2 planes. Molecular mechanics calculations show that this distortion is due to steric effects.

Introduction

We have previously reported the metal ion-controlled synthesis of an extensive series of macrocyclic Schiff base ligands (**1**) derived from the cyclic [2 + 2] condensation of 2,6-diformylpyridine (or derivative) with a range of diprimary amines [1–4]. Also described have been several analogous systems (**2** and **3**) containing furan or thiophen moieties in place of pyridine [5–7].



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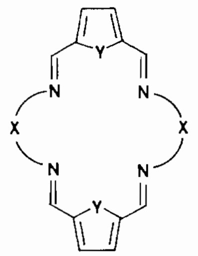

2, Y = O; **3**, Y = S

These ligands display a number of features of chemical interest which include: (i) the formation of both mononuclear and dinuclear metal complexes many of which have unusual structures; (ii) the occurrence of metal exchange (transmetallation) reactions useful for the preparation of new metal complexes not accessible by direct synthetic procedures; (iii) the occurrence of new reactions at the imino centres promoted by a mis-match in the requirements (geometric and electronic) of the metal ion on the one hand and the macrocycle on the other [3, 4, 8]; (iv) the binding of small substrate molecules and ions as bridging ligands between the metal centres in the dinuclear complexes [2]; (v) the use of some of the dinuclear complexes, in the case of copper, as oxidation catalysts for organic substrates [9].

As part of a continuing study of these interesting systems we now report on the co-ordination chemistry of the Schiff base ligands, both acyclic and

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TABLE I. Analytical, Infrared and Electrical Conductance for the Complexes

Complex	Colour	Analysis (%)						IR bands[a] (cm^{-1})			Λ_M[b] ($S\ cm^2\ mol^{-1}$)
		Found			Calculated			ν(C=N)	$\nu(NH_2)$	$\delta(NH_2)$	
		C	H	N	C	H	N				
$[L^1H][BPh_4]$	white	74.9	6.7	7.8	75.0	6.4	8.0	1638(s)			114
$CaL^1(ClO_4)_2 \cdot EtOH \cdot H_2O$	beige	38.1	4.1	7.5	38.4	4.7	8.1	1640(s)			300
$BaL^1(ClO_4)_2 \cdot EtOH \cdot H_2O$	pale pink	33.2	4.1	7.0	33.7	4.1	7.1	1640(s)			290
$CaL^2(ClO_4)_2 \cdot H_2O$	white	30.5	4.3	10.0	30.4	4.7	10.1	1643(m)	3355(m) 3300(m)	1600(m)	320
$SrL^2(ClO_4)_2 \cdot H_2O$	white	28.1	4.0	9.2	28.0	4.4	9.3	1625(m)	3355(m) 3298(m)	1600(m)	293
$[Ag_2L^1(H_2O)_2][ClO_4]_2$	white	28.6	3.1	6.5	28.8	3.4	6.7	1636(s)			227
$Cu_2L^1(ClO_4)_2 \cdot xH_2O$[c]	yellow	32.5	4.0	7.2	32.8	4.1	7.6	1633(s)			
$[Cu_2L^1(MeCN)_2][BPh_4]_2$	orange	69.9	5.9	6.9	69.9	5.8	7.0	1628(s)			
$[Cu_2L^1(pdz)_2][BPh_4]_2$	red	69.4	5.5	8.6	69.7	5.4	8.6	1628(s)			
$[Cu_2L^1(OMe)_2(py)_2][ClO_4]_2 \cdot 2H_2O$	green	39.9	4.6	8.4	39.8	4.6	8.7	1628(s)			294
$[CuL^4][BPh_4]_2$	aqua-marine	72.5	6.5	7.1	72.6	6.4	7.1	1618(s)			220

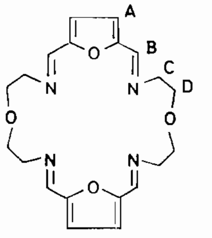
[a] s = strong, m = medium. [b] For 10^{-3} M solutions in MeCN at 20 °C. [c] Calculated for $x = 3$; actual value may be 2, 3 or 4.

macrocyclic, derived from metal-controlled condensation reactions between 2,5-diformylfuran and 3-oxapentane-1,5-diamine. The study may be compared to that of complexes of the [2 + 2] macrocycle formed from 2,5-diformylthiophen and 3-oxa-pentane-1,8-diamine, the crystal structure of which has recently been reported [10].

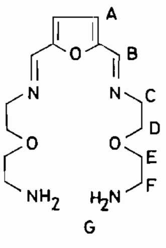
Results and Discussion

The Alkaline Earth Metal Complexes

Reaction of 2,5-diformylfuran with 3-oxapentane-1,8-diamine in the presence of the perchlorate salts of Ca(II), Sr(II) or Ba(II) led to the isolation of complexes of either the [2 + 2] macrocycle (L^1) or of the acyclic [1 + 2] condensation product (L^2) obtained by reaction of one molecule of dialdehyde with two molecules of diamine, depending on the metal ion and choice of solvent. No pure macrocyclic or other products were obtained in the absence of metal salt which is therefore considered to act as a template for product formation as found in related systems [1, 3, 4]. For the case of Ba^{2+} the sole product was the macrocyclic complex $BaL^1(ClO_4)_2 \cdot EtOH \cdot H_2O$ whatever the reaction conditions (see Experimental section). For Sr^{2+} on the other hand, the sole product was $SrL^2(ClO_4)_2 \cdot H_2O$, again irrespective of reaction conditions. However, for the case of Ca^{2+} both $CaL^1(ClO_4)_2 \cdot EtOH \cdot H_2O$ and $CaL^2(ClO_4)_2 \cdot H_2O$ could be obtained. The latter complex was isolated from room temperature reactions conducted in EtOH in which it is poorly soluble. However, if the solvent mixture contained 10% or more of MeCN to prevent precipitation and the reaction mixture was gently refluxed the product was the macrocylic complex. It is a reasonable assumption that co-ordinated L^2 is an intermediate in the formation of L^1 as demonstrated in other cases [4].



L^1



L^2

The identity of L^1 and L^2 in the complexes was readily established as follows: (i) elemental analysis (Table I); (ii) the occurrence in all cases of ν(C=N) vibrations between 1620 and 1650 cm^{-1} in the IR spectra (Table I), together with other features characteristic of the furan ring and aliphatic ether groups; (iii) the absence of ν(C=O) vibrations at *ca.* 1700 cm^{-1} and, in the case of L^1 complexes, of $\nu(NH_2)$ and $\delta(NH_2)$ vibrations at 3300–3450 cm^{-1} and *ca.* 1600 cm^{-1}, respectively; (iv) the presence of $\nu(NH_2)$ and $\delta(NH_2)$ in the spectra of the L^2 complexes (Table I).

^1H NMR data for the complexes in CD_3CN confirm the conclusions relating to the nature of the ligands L^1 and L^2; assignments are in Table II. All the Ca^{2+}, Sr^{2+} and Ba^{2+} complexes show furan ring and imine group proton resonance as sharp singlets at

TABLE II. Proton NMR Spectral Data (δ in ppm) for the Complexes in CD_3CN (relative intensities in square brackets)[a]

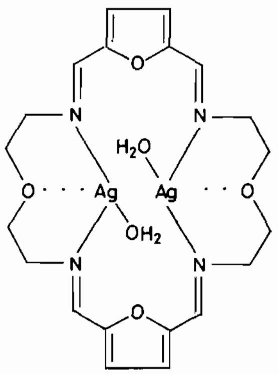
Complex	H^A	H^B	H^C	H^D	H^E	H^F	H^{G+H_2O}
$[L^1H][BPh_4]$	6.70(s)[4]	7.97(s)[4]		3.67(s)[16]			
$CaL^1(ClO_4)_2 \cdot EtOH \cdot H_2O$	7.13(s)[4]	8.24(s)[4]		3.82(s)[16]			
$BaL^1(ClO_4)_2 \cdot EtOH \cdot H_2O$	7.03(s)[4]	8.22(s)[4]		3.82(m)[16]			
$CaL^2(ClO_4)_2 \cdot H_2O$	7.04(s)[2]	8.27(s)[2]	3.87(t)[4]	3.55–3.69(m)[8]		2.92(t)[4]	2.46(s)
$SrL^2(ClO_4)_2 \cdot H_2O$	7.02(s)[2]	8.25(s)[2]	3.86(t)[4]	3.65–3.73(m)[8]		2.93(t)[4]	2.40(s)
$[Ag_2L^1(H_2O)_2][ClO_4]_2$	7.03(s)[4]	8.16(s)[4]		3.75(s)[16]			
$[Cu_2L^1(H_2O)_x][ClO_4]_2$	6.79(s)[4]	7.84(s)[4]		3.62(s)[16]			
$[Cu_2L^1(MeCN)_2][BPh_4]_2$	6.79(s)[4]	7.90(s)[4]		3.66(s)[16]			
$(Cu_2L^1(pdz)_2][BPh_4]2$	6.72(s)[4]	7.91(s)[4]		3.66(s)[16]			

[a] s = singlet, t = triplet, m = multiplet.

ca. δ 7.0 and δ 8.2, respectively. Four sets of triplets each corresponding to 4H are seen in the spectra of the acyclic ligand complexes and assigned to the four non-equivalent methylene groups. In the spectra of L^1 complexes, on the other hand, the chemical shifts of the two non-equivalent CH_2 protons are apparently very similar and only one broadened resonance singlet (16 H) is seen. Detailed structures of the alkaline earth metal complexes are unknown. However, by analogy with the crystallographically determined structures of related complexes containing the furandiimine moiety [6, 11] it is likely that most, if not all, of the potential donor atoms of L^1 and L^2 interact with the metal ion. In all the complexes except $CaL^1(ClO_4)_2 \cdot EtOH \cdot H_2O$ the ν_3 and ν_4 vibrations of the ClO_4^- ions occurring at 1095 and 625 cm^{-1} are broadened and/or split indicating co-ordination to the metal ion. The presence of $\nu(OH)$ vibrations at or near 3420 cm^{-1} also suggests additional co-ordination of EtOH and/or H_2O. Co-ordination numbers of 10–12 are common in complexes of the larger alkaline earth cations [12]. Electrical conductances in MeCN are in the range (Table I) associated with uni-bivalent electrolytes so, presumably, the co-ordinated anions are displaced by solvent molecules in solution.

The Di-copper(I) and Di-silver(I) Complexes

Treatment of $BaL^1(ClO_4)_2 \cdot EtOH \cdot H_2O$ with $AgClO_4$ in MeCN afforded the complex $[Ag_2L^1(H_2O)_2][ClO_4]_2$. IR spectra confirmed the ionic nature of the ClO_4^- ions (no splitting of ν_3 or ν_4) while the occurrence of $\nu(OH)$ as a fairly sharp band at 3520 cm^{-1} suggested that the H_2O molecules are co-ordinated. We therefore propose that this complex has the structure **4** in which each Ag(I) ion is either 3-co-ordinate being bonded to two imino nitrogens and one H_2O molecule, or 4-co-ordinate if the ether oxygen atoms are also co-ordinated. It will be noted that the furanyl oxygen atom is assumed not to be co-ordinated in structure **4** despite its use in several alkaline earth metal complexes of ligands containing the furandiimine group [6, 11]. This is because the furanyl oxygen has a very low basicity and is therefore likely to interact appreciably only with 'hard' or 'class a' metal ions in a predominantly electrostatic (ion–dipole) manner. Significantly, the furanyl oxygen appears not to be part of the co-ordination sphere in any of the several complexes of di-Cu(I), di-Cu(II) and di-Co(II) with the [2 + 2] macrocycle prepared from 2,5-diformylfuran and 1,3-diaminopropane [5, 7, 9, 13].



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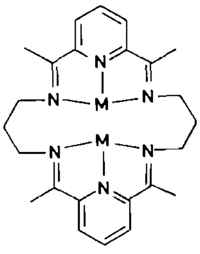
The non-co-ordination of the furan oxygen in transition metal complexes of furandiimine macrocycles contrasts with the situation in corresponding pyridyldiimine macrocycles and leads to a significantly different structural chemistry. The good donor properties of the pyridine nitrogen ensures that the 'N_3' trimethine group will act as a powerful tridentate chelating centre to a single metal ion whereas in the furandiimine rings chelation is via pairs of imine nitrogens of different furandiimine segments. The differences are nicely illustrated for the case of dimetallic complexes of the two 20-membered rings **5** and **6**. Thus, if the macrocycles are drawn with the two pyridine or furan rings on a vertical axis, the disposition of the metal ions is such that they have a 'north–south' (NS) polarity in the former and an 'east–west' (EW) polarity in the latter. There are obvious consequences for the nature of derivative complexes containing exogenous bridging groups.



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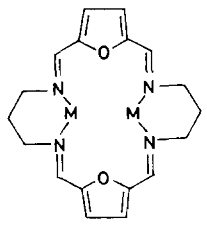

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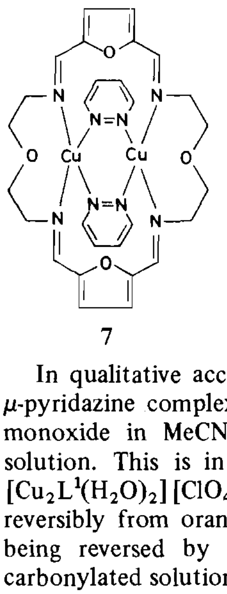
Returning to the complex $[Ag_2L^1(H_2O)_2][ClO_4]_2$, it is difficult to decide whether the aliphatic ether oxygen atoms are co-ordinated to the metal ions. ^1H NMR spectra (Table II) while confirming the macrocyclic nature of the ligand do not aid the resolution of this question. In a related di-Ag(I) complex of the [2 + 2] macrocycle formed from 2,5-diformylthiophen and 3,5-dioxa-octane-1,8-diamine one of the two ether oxygen atoms is weakly bound at a distance of 2.92 Å while the other is remote from the nearest Ag(I) ion at 3.55 Å [10]. While we have no positive evidence on this question it seems probable that the single ether oxygen in the present complex is co-ordinated, at least weakly, since the nature of the aliphatic chain is such that two five-membered chelate rings would be formed. IR spectra of $[Ag_2L^1(H_2O)_2][ClO_4]_2$ are unhelpful in locating the position of the ν(C–O) vibrations between 1050 and 1150 cm^{-1} which might be sensitive to C–O–C group co-ordination because of the overlapping ν_3 mode of ClO_4^-. In an attempt to locate the ν(C–O) bands in a salt of another counter ion an attempt to prepare the di-tetraphenylborate was made. However, the products of the attempted metathesis were $AgBPh_4$ and a white crystalline material of stoicheiometry $[L^1H][BPh_4]$. The parent ion peak of this compound appeared at $m/e = 384$ corresponding to the free macrocycle. The ^1H NMR spectrum in CD_3CN (Table II) was similar to those of the L^1 complexes as was the IR spectrum which showed the additional feature of a sharp medium intensity band at 3530 cm^{-1}. The compound is a 1:1 electrolyte in MeCN.

Treatment of $BaL^1(ClO_4)_2 \cdot EtOH \cdot H_2O$ with $[Cu(MeCN)_4][ClO_4]$ in MeOH afforded the yellow complex $[Cu_2L^1(H_2O)]_2[ClO_4]_2 \cdot H_2O$ in good yield. IR spectra of the solid and ^1H NMR spectra of MeCN solutions (Tables I and II) are closely similar to those of the di-Ag(I) complex discussed above, and a similar structure is envisaged. Conversion of this complex to the di-tetraphenylborate salt via reaction with $NaBPh_4$ in MeCN also led to replacement of the H_2O molecules by MeCN. The colour change (see electronic spectra data in Table III) of yellow to orange is evidence that the replacement of H_2O by MeCN involves the co-ordination sphere. Reaction with pyridazine (pdz) gave the red crystalline complex $[Cu_2L^1(pdz)]_2[BPh_4]_2$. In this complex the two pyridazine molecules are presumed to act as exogenous bridging ligands between the Cu(I) ions (structure 7). In this case it is unlikely that the ether oxygen atoms of L^1 are co-ordinated whatever the situation in $[Cu_2L^1(H_2O)_2][ClO_4]_2 \cdot H_2O$ and $[Cu_2L^1(MeCN)_2][BPh_4]_2$ since the co-ordination requirements of the Cu(I) ions should be satisfied (in a tetrahedral environment) without them.



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In qualitative accord with this conclusion the di-μ-pyridazine complex showed no affinity for carbon monoxide in MeCN or dimethylacetamide (DMA) solution. This is in contrast to DMA solutions of $[Cu_2L^1(H_2O)_2][ClO_4]_2 \cdot H_2O$ which changed colour reversibly from orange to yellow, the colour change being reversed by passage of argon through the carbonylated solutions or by evacuation.

TABLE III. Electronic Spectral and Magnetic Data for the Copper Complexes

Complex	Band positions ($cm^{-1} \times 10^3$), ϵ ($dm^3\ mol^{-1}\ cm^{-1}$) in parenthesis[a]			μ_{eff} (μ_B)[b]	
	Colour	Solid	MeCN	293 K	93 K
$[Cu_2L^1(H_2O)_2][ClO_4]_2 \cdot H_2O$	yellow	29.0(sh), 15.0(sh)			
$[Cu_2L^1(MeCN)_2][BPh_4]_2$	orange	31.6–17.0(br)			
$[Cu_2L^1(pdz)_2][BPh_4]_2$	red	31.0–17.0(br)			
$[Cu_2L^1(OMe)_2(py)_2][ClO_2]_2 \cdot 2H_2O$	green	17.0(sh), 15.0	16.4(240)	0.84	0.40
$[CuL^4][BPh_4]_2$	aquamarine	14.7	14.7(250)	1.94	1.83

[a] Sh = shoulder; br = broad. [b] Per metal atom.

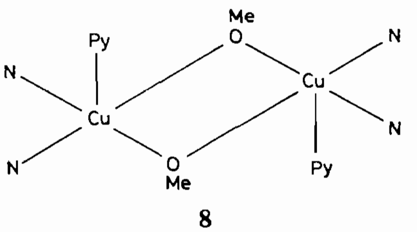
Of the three di-Cu(I) complexes $[Cu_2L^1(H_2O)_2]$-$[ClO_4]_2 \cdot H_2O$ was the most sensitive to O_2, becoming green within hours in the solid state and much more rapidly in solution. $[Cu_2L^1(MeCN)_2][BPh_4]_2$ was considerably more stable as the solid while the pyridazine complex was indefinitely stable to O_2 even in solution. Indeed, this complex can be prepared in air from Cu(II) (*vide infra*).

O_2-uptake measurements performed on DMA solutions of $[Cu_2L^1(H_2O)_2][ClO_4]_2 \cdot H_2O$ showed that 0.5 ± 0.03 mol O_2 is consumed irreversibly per mol di-Cu complex. The O_2:Cu stoicheiometry of 1:4 indicates a complete four-electron reduction of O_2. No clean oxidation products were isolated from the DMA solutions but by use of methanol as solvent in the presence of pyridine air oxidation of $[Cu_2L^1$-$(H_2O)_2][ClO_4]_2 \cdot H_2O$ gave the dinuclear Cu(II) complex described below.

The Di-μ-methoxo-di-copper(II) Complex

The complex $[Cu_2L^1(OMe)_2py_2][ClO_4]_2 \cdot 2H_2O$ was obtained by the slow aerobic oxidation of $[Cu_2L^1(H_2O)_2][ClO_4]_2$ in methanol solution containing added pyridine. The complex separated slowly at room temperature as bright green nuggets over a period of hours. The complex is formulated as in structure **8** on the basis of the analytical data and the following properties. IR spectra confirm the retention of the L^1 macrocycle as well as the presence of co-ordinated pyridine (e.g. as exemplified by the occurrence of a band at 1605 cm^{-1} attributable to the highest energy pyridine ring vibration mode [14]). A medium intensity band at 2800 cm^{-1} not present in the spectra of any other complex of this macrocycle is assigned to the ν_{sym}(C–H) of the bridging OMe group [15]. Confirmation of this assignment was provided by the results obtained when the preparation was carried out in CD_3OD. The spectrum of this product showed a medium intensity band at 2045 cm^{-1} instead of 2800 cm^{-1}, corresponding to a ν(C–H)/ν(C–D) ratio of ~1.37 close to the expected value of $\sqrt{2}$.

The magnetic moment per Cu atom is, at 0.84 μ_B at 293 K, much depressed below the normal spin-only value. This fact, and the further reduction in moment to ~0.4 μ_B on cooling to 93 K, points to strong antiferromagnetic coupling between the paramagnetic centres. We therefore propose the 5-co-ordinate di-μ-methoxo-di-Cu(II) (structure **8**) for this complex similar to that found [9] for closely related complexes such as $[Cu_2L^3(OEt)_2(NCS)_2]$ where L^3 is the macrocycle shown in structure **6**.



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The X-band ESR spectrum of $[Cu_2L^1(OMe)_2$-$(py)_2][ClO_4]_2$ was measured both in the solid state and in dimethylformamide (DMF) and in DMF/MeOH frozen solutions at ~80 K. Little or no signal was apparent in the spectrum of the solid, in agreement with expectations based on the magnetic susceptibility measurements. However, a fairly intense axial type spectrum was found for the DMF frozen solution. The intensity and profile of the spectrum (Fig. 1) indicates that there is extensive dissociation, via rupture of the methoxo-bridges, into mainly mononuclear species. Note that the first two lines of the four-line $g_\parallel$ signal gives $A_\parallel = 170$ G, a value typical of tetragonal mononuclear Cu(II) [16]. Support for the idea of rupture of the methoxo bridges in DMF solution was gained from the effects obtained on progressively enriching the solvent with MeOH at the expense of DMF (Fig. 1). It can be seen that the signal intensity is dramatically reduced as the mole ratio of MeOH in the solvent is increased. We attribute this to a reinstatement of the methoxide bridges to produce a strongly coupled di-Cu(II) system. The dissociation of the methoxide bridges in solvents not containing MeOH is apparent also in the discrepancy between the electronic spectra in the solid state and in MeCN solution (Table III). Noticeable also in the ESR spectra are the presence of at least nine superhyperfine lines superimposed on the $g_\perp$ signal for which $A_\perp \simeq 15$ G. Possibly this arises from coupling of the unpaired spin on a magnetically independent Cu(II) to the nitrogen donors

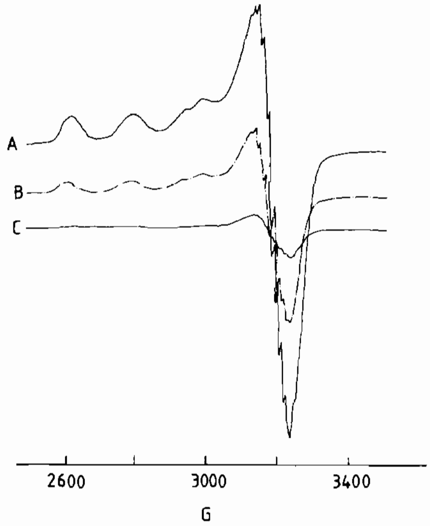
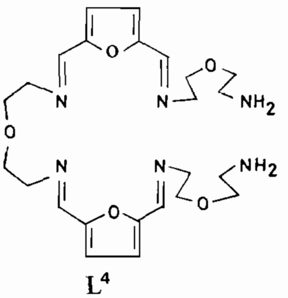


Fig. 1. Frozen solution ESR spectra of $[Cu_2L^1(OMe)_2py_2]$-$[ClO_4]_2 \cdot 2H_2O$ in (A) DMF; (B) 3:1 v/v DMF/MeOH; (C) 2:3 v/v DMF/MeOH.

($I = 1$) in the complex. However, the nature of the solution species remains unknown at the present stage.

A Mononuclear Cu(II) Complex of a Ring-opened Macrocycle

It was mentioned above that the single alkaline earth metal ion, Ca^{2+} or Ba^{2+}, in the complexes of the macrocycle L^1 can readily be replaced by two Cu(I) ions on treatment with $[Cu(MeCN)_4][ClO_4]$ to afford a series of di-Cu(I) complexes of the L^1 macrocycle. When the transmetallation was attempted using hydrated Cu(II) perchlorate in MeCN in the presence of $Na[BPh_4]$ the major product (~50%) was a mononuclear complex of the ring-opened ligand L^4 instead of the expected dinuclear Cu(II) complex of the macrocycle. The same complex was subsequently prepared by reaction of the precursor dialdehyde and diamine in MeCN in the presence of $Cu(ClO_4)_2{\cdot}6H_2O$ and $Na[BPh_4]$ and also by transmetallation of $ML^2(ClO_4)_2{\cdot}H_2O$ (M = Ca or Sr) with $Cu(ClO_4)_2{\cdot}6H_2O$, again in the presence of $NaBPh_4$.



L^4

As will be shown below this aquamarine complex contains the new acyclic ligand L^4 comprising two diformylfuran moieties and three moieties of 3-oxapentane-1,8-diamine. Such a molecule could be formed by the covalent addition of one molecule of diamine across one (co-ordinated) azomethine (C=N) bond of the macrocycle L^1. However, in practice, a more likely route to the formation of L^4 is an initial partial hydrolysis of co-ordinated L^1 followed by re-assembly, via Schiff base condensation, of the appropriate hydrolysis products.

The crystalline aquamarine complex $[CuL^4][BPh_4]_2$ displays two ν(C=N) bands at 1628 and 1618 cm^{-1} suggesting the presence of both co-ordinated and unco-ordinated azomethine bonds. The occurrence of $\nu(NH_2)$ and $\delta(NH_2)$ at 3280, 3182 cm^{-1} and 1605(sh) cm^{-1} indicates the presence of primary amine *i.e.* that the ligand is acyclic rather than macrocyclic. The electrical conductance (Table I) in MeCN is within the range expected for a uni-bivalent electrolyte.

The magnetic moment (Table III) of $[CuL^4][BPh_4]_2$ is normal for non-interacting Cu(II), as is the ESR spectrum in DMF frozen solution. This consists of an axial-type signal with a 4-line hyperfine splitting pattern in the $g_\parallel$ component consistent with mononuclear square or tetragonal Cu(II): $g_\perp = 2.07$, $g_\parallel = 2.29$, $A_\parallel = 160$ G. Essentially the same spectrum was obtained in the solid state at room temperature, indicating that the complex dissolves in DMF without significant structural rearrangement. The same conclusion is reached by a comparison of the electronic spectra of the complex in the solid state and in solution in MeCN (Table III).

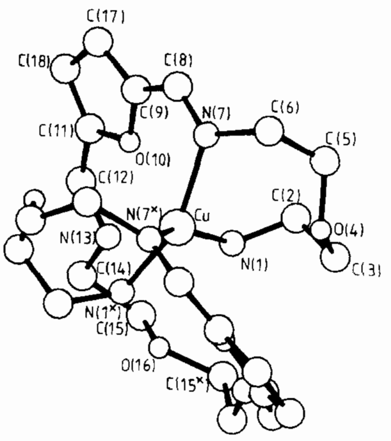


Fig. 2. The structure of $[CuL^4]^{2+}$.

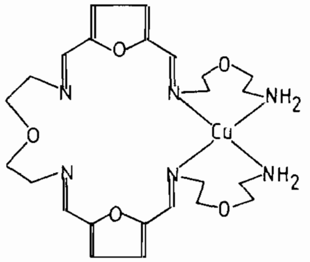


Fig. 3. Representation of the co-ordination of Cu(II) to the acyclic ligand L^4.

The Structure of [CuL^4][BPh$_4$]$_2$

The structure consists of discrete cations and anions. The cation, which has crystallographically imposed C_2 symmetry is shown in Fig. 2 together with the atomic numbering scheme. The structure of the cation is also depicted schematically in Fig. 3 in order to illustrate more clearly how the L^4 ligand is co-ordinated to the Cu(II) ion. Molecular dimensions for the co-ordination sphere are in Table IV. The copper atom is four-co-ordinate being bonded to four nitrogen atoms in the 'outer comparment' of the ligand, that is, to N(7) (2.050(17) Å) and N(1) (1.977(17) Å), and remains unbonded to the 'inner compartment' of the ligand as represented by the nitrogen atom N(13) and the oxygen atoms O(16) and O(10). The copper atom is 2.76(1) Å from

TABLE IV. Molecular Dimensions in the Coordination Sphere. Distances (Å). Angle (°)[a]

Cu–N(1)	1.977(17)
Cu–N(7)	2.050(17)
N(1)–Cu–N(7)	98.8(6)
N(1)–Cu–N(1*)	83.6(7)
N(1)–Cu–N(7*)	154.4(5)
N(7)–Cu–N(7*)	89.9(7)

[a] Note: * denotes the atom in equivalent position $-x$, y, $1.5 - z$ with respect to that at x, y, z (Table VII).

the furan oxygen atoms O(10) and 2.66(1) Å from the ether oxygen atoms O(4A) but these can only represent weak interactions.

The geometry of the copper atom is intermediate between square planar and tetrahedral with an angle of 39.7° between two CuN_2 planes. We have shown by molecular mechanics (*vide supra*) that this distortion is due to steric effects. Clearly, the ligand is under considerable strain as the molecule contains two 8-membered chelate rings based on Cu, N(1) and N(7) and also a 20-membered chelate ring from Cu to N(7)–C(8)...O(16)–C(8*)–N(7*). This accounts for the rather unusual shape of the ligand as it wraps its way around the copper atom and also for the distortion from square planar geometry.

It is interesting to consider whether this ligand could provide any other coordination site for the copper atom. In the present conformation, a copper atom placed in the centroid of N(13), N(7), N(7*), N(13*) would be 2.71 Å from each nitrogen. Clearly, the conformation of the N(13)...O(10)...N(13*) link could change but it seems unlikely that in any coordination site Cu–N distances of *ca.* 2.0 Å could be achieved. No other type of coordination site such as one involving a mixture of N and O donors could be found and it seems clear that the present structure with Cu bonded to N(1), N(7), N(1*), N(7*) is the only one possible.

Force-Field Calculations

The crystal structure of $[CuL^4][BPh_4]_2$ shows that the Cu(II) coordination sphere has a geometry intermediate between that of a tetrahedron and a square plane. A distortion from square planar has been observed previously in a large number of copper(II) complexes [17–22] and is almost invariably ascribed to steric effects. Thus Wei [17] surveyed 16 bis-bidentate copper(II) complexes, calculated the dihedral angle between the two CuX_2 planes, (X = donor ligand) and found values between 0 and 68°. He concluded that the distortion could be related to the ligand stereochemistry and that in particular the introduction of bulky substituents on the ligand markedly disrupted the planar conformation. A more recent study of copper(II) structures of macrocyclic ligands similarly shows that distortions from square planar geometry can be correlated to the size and shape of the macrocycle [18].

TABLE V. Parameters Involving Cu(II) Used in the MM2 Program (nomenclature from ref. 23)

	r_o (Å)	k_s (mdyn Å^{-1})
Bond stretching		
Cu–N_{sp^2}	2.01	2.00
Cu–N_{sp^3}	1.96	2.00
	θ_o (°)	k_b (mdyn Å rad^{-2})
Angle bending		
N–Cu–N	90.0, 180.0 or 109.47	0.030
	r^* (Å)	ϵ (kcal mol^{-1})
van der Waals constants		
Cu(II)	2.35	0.165

However it is easy to ascribe a distortion in the coordination sphere to steric effect but more difficult to provide quantitative evidence. The method of molecular mechanics has been used to calculate strain energies for organic molecules for many years [23] and recently we have begun to apply the method to inorganic molecules [24]. This present cation offers a good opportunity to test the method because models do not show why an ideal square planar copper geometry is not observed.

Allinger's MM2 molecular mechanics program [25] was used throughout the calculations. Force-field parameters for the organic part of the cation were taken or estimated from values in the program. Values for parameters involving copper are given in Table V. Bending force constants were taken from ref. 26 and van der Waals constants estimated from ref. 27. A value of 2.00 mdyn Å^{-1} was assumed for the Cu–N bond stretching force constant. This value is rather higher than that used by other workers [26, 28, 29], who have applied force-field methods to inorganic complexes but in previous work [24] we have found this value to work well for metal atoms in the MM2 program. The two Cu–N ideal bond lengths were varied until distances found in the crystal structure were reproduced. These ideal values, as is often found in molecular mechanics, needed to be slightly smaller (by *ca.* 0.03 Å) than the observed values (see Table V).

In the initial calculations we attempted to fit both square planar and tetrahedral copper co-ordination spheres into the ligand. We derived a complete set of coordinates for an ordered molecule from the disordered molecule in the crystal structure. These coordinates were then refined using two different sets of ideal N–Cu–N angles, one for the tetrahedral

(109.47°) and one for the square planar (90.0°, 180°) geometry. On refinement instead of the ideal tetrahedral values we obtained N–Cu–N angles of 100.4, 84.4, 141.2, 142.0, 99.0, 100.4° and instead of the ideal square planar values we obtained 98.8, 83.5, 148.2, 148.2, 95.8, 98.5° (results in Table VI).

It appears, therefore, that it is possible to reproduce intermediate geometries at metal atom sites using the usual angle bending term with suitably low force constant. There is no need to use a completely different energy term, such as 1,3-non-bonded interactions [30] which is incompatible with the MM2 force-field. However we note that 1,3-interactions for metals have been used recently [31] in an MM2 based force-field and they may well be useful in certain types of low-symmetry coordination spheres.

These results encouraged us to carry out a second set of calculations in which we calculated a steric energy profile for the change from a tetrahedral geometry to a square planar geometry maintaining S_4 symmetry throughout. The reaction coordinate was the angle δ which is the angle each Cu–N bond makes with the CuN$_4$ least squares plane. δ varies from 0° in the square plane to 35.26° in the tetrahedral geometry. The N–Cu–N angles are of two types $\theta_1 = 180 - 2\delta$ (ideal 180, 109.47°) and $\theta_2 = \cos^{-1}(-\cos^2\theta_1/2)$ (ideal 90, 109.47°). We calculated the steric energy at 5° intervals in δ. The bending force constant for N–Cu–N was increased to 10.0 mol Å rad^{-2} before computation.

This increase* overcomes the problem of local energy minima which might have affected our initial calculations. The minima shown in Table VI could be local and there might be minima with square planar or tetrahedral geometry which the refinement did not reach. However, setting a very large value for the N–Cu–N angle bending force constant essentially forces the bond angles concerned to be constrained at their ideal values and therefore the ligand must adapt its conformation accordingly to accommodate a particular copper coordination sphere.

The total steric energy for each value of δ (we took 5° intervals) was then minimised by refining the structure coordinates and Fig. 4 shows a plot of energy against δ. Numerical values are given in the Supplementary Publication.

It can be seen that square planar geometry for the coordination sphere has considerably greater steric energy than has tetrahedral geometry. The minimum energy occurs at $\delta = 17.0°$, $\theta_1 = 146°$, $\theta_2 = 94.9°$ in good agreement with the crystal structure. The agreement is not expected to be closer as S_4 symmetry has been imposed on the reaction path, whereas the crystal structure is only approximately tetrahedral.

TABLE VI. Results of Force Field Calculations Compared to Crystal Structure Dimensions[a]

Parameter[b]	Calculated dimensions via MM2			Observed dimensions in the crystal structure
	(1)	(2)	(3)	
Cu–N(1)	1.984	1.984	1.983	1.977(17)
Cu–N(7)	2.052	2.050	2.062	2.050(17)
Cu–N(1*)	1.985	1.985	1.987	1.977(17)
Cu–N(7*)	2.052	2.051	2.060	2.024(17)
N(1)–Cu–N(7)	100.1	98.5	95.0	98.8(6)
N(1)–Cu–N(1*)	84.4	83.4	94.4	83.6(7)
N(1)–Cu–N(7*)	141.2	148.2	145.8	154.4(5)
N(7)–Cu–N(1*)	142.0	148.0	145.9	154.4(5)
N(7)–Cu–N(7*)	99.0	95.8	95.1	89.9(7)
N(1*)–Cu–N(7*)	100.4	98.8	95.2	98.8(6)
Steric energy terms				
Compression	2.82	2.77	2.97	
Bending	17.05	16.82	16.18	
Stretch-bend	1.08	1.09	1.08	
van der Waals 1, 4	22.72	22.77	22.50	
Other	−11.85	−11.90	−10.70	
Torsional	6.30	6.29	6.14	
Dipole	−0.16	−0.09	−0.16	
Total	37.98	37.76	38.01	

[a] Distances (Å) angles (°) with estimated standard deviations in parentheses. Energies in kcal mol^{-1}. Dimensions in columns (1) and (2) were obtained as follows. Crystal structure coordinates were input, ideal angles subtended at the metal (θ_0) were set at tetrahedral (1) or square planar values (2) and the structure refined. In neither case could the structure be refined significantly towards the ideal geometry. Values in column (3) were taken from the energy minimum (δ = 17°) in Fig. 4. [b] * Denotes the atom in an equivalent position $-x, y, 1.5 - z$ with reference to that at x, y, z.

The result shows clearly that steric effects are responsible for the distortion from square planar geometry in the cation. It is significant that this result is not due to just one or two large repulsive terms and indeed is not apparent from models or from a study of the geometry in the crystal structure. The large increase in steric energy is due to a combination of a large number of terms, bond stretching, angle bending, torsion and van der Waals all of which give slightly higher values in the square planar case. These results show up the strength of the molecular mechanics method where the steric energy is summed over a number of terms (in this case 3673).

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*This technique has recently been used to calculate the 'hole size' of macrocycles. In this case the M–N bond was given a large force constant and the macrocycle conformation was refined to fit in with this value. A plot of M–N bond length against steric energy was then calculated which gave the preferred hole size of the macrocycle.

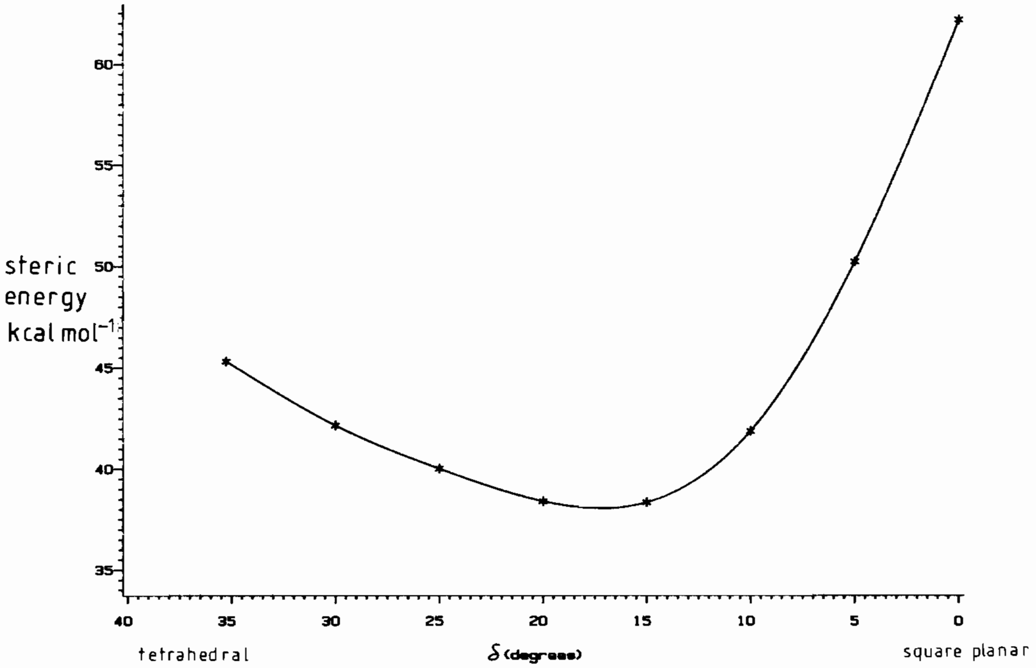

Fig. 4. Plot of steric energy (kcal/mol) of the complex $[CuL^4]^{2+}$ against variations in the metal coordination sphere geometry described by δ, the reaction coordinate for the square planar–tetrahedral reaction path. (δ = 0 for square planar coordination and 35.26° for tetrahedral coordination).

Experimental

Preparation of the Complexes

2,5-Diformylfuran (DFF) was prepared by minor modification of literature methods [32]. 3-Oxapentane-1,5-diamine was prepared as follows.

Phosphorus tribromide (0.53 mol) was added dropwise to a cooled, stirred solution of diethylene glycol (0.68 mol). A white precipitate developed, and the mixture was stirred overnight at room temperature. The precipitate was filtered off and the pale yellow liquid was carefully distilled under water vacuum, yielding 3-oxapentane-1,5-dibromide (140 g, 0.60 mol). The dibromide (0.60 mol), potassium phthalimide (1.35 mol) and diethylamine (3 ml) were heated together at 140 °C for 3 h. On cooling, the solid mass was broken up and washed with hot water (3 l). The solid was then recrystallized from glacial acetic acid with some decolourizing charcoal yielding the cream solid 3-oxa-pentane-1,5-diphthalimide (128 g, 0.35 mol).

The diphthalimide (0.35 mol) was suspended in refluxing methanol (1 l) and hydrazine hydrate (99%) (62 ml) was slowly added producing a brown solution. A white solid was precipitated and after 2 h refluxing, hydrochloric acid 10 M (144 ml) was added. The methanol was distilled off and the white solid filtered out leaving a brown solution. To this solution, sodium hydroxide pellets (200 g) were added slowly. The top brown layer was separated off and extracted with ether (1 l) on a continuous extraction column for 48 h. The ether was removed and the remaining oil was vacuum distilled yielding the clear product (13 g, 0.16 mol) at 90 °C (1 mm Hg) along with morpholine byproduct.

$ML^1(ClO_4)_2\cdot EtOH\cdot H_2O$ (M = Ca, Ba)

$M(ClO_4)_2\cdot xH_2O$ ($x = 3, 4$) (0.01 mol) and DFF (0.01 mol) were dissolved in 500 cm^3 dry ethanol containing ~10% dry acetonitrile. 3-Oxapentane-1,5-diamine (0.01 mol) in 10 cm^3 ethanol was added slowly with stirring and the mixture refluxed for 45 min. The mixture was filtered, rotary evaporated to half volume, and set aside. The crystalline products (beige for M = Ca, pale pink for M = Ba) separated in 60–70% yield. Use of methanol as solvent gave the corresponding methanol solvates.

$ML^2(ClO_4)_2\cdot H_2O$ (M = Ca, Sr)

$M(ClO_4)_2\cdot xH_2O$ (0.002 mol) and DFF (0.002 mol) were dissolved in 100 cm^3 dry ethanol. A solution of 3-oxapentane-1,5-diamine (0.002 mol) in 10 cm^3 ethanol was added with stirring. Stirring was maintained at room temperature for 30 min during which time the white product began to separate out. It was isolated by filtration, washed with cold ethanol and air dried. Yield: 30–50%.

$[Ag_2L^1(H_2O)_2][ClO_4]_2$

$BaL^1(ClO_4)_2 \cdot EtOH \cdot H_2O$ (0.5 mmol) was dissolved in a solvent mixture consisting of 300 cm^3 methanol and 50 cm^3 acetonitrile. An excess (2 mmol) $AgClO_4$ in 10 cm^3 acetonitrile was added dropwise at room temperature. The solution was then concentrated by rotary evaporation to yield the white product in ~65% yield.

$[L^1H][BPh_4]$

To a solution of $[AgL^1(H_2O)_2][ClO_4]_2$ (0.5 mmol) in 30 cm^3 of 3:1 ethanol:acetonitrile solvent mixture was added a solution of $NaBPh_4$ (2 mmol) dissolved in the minimum of acetonitrile at room temperature. After separation of the white precipitate of $AgBPh_4$ the filtrate was evaporated to give white needles of product in low yield.

$CuL^1(ClO_4)_2 \cdot 3H_2O$

An O_2-free solution of $[Cu(MeCN)_4][ClO_4]$ (1.6 mmol) in cold, dry methanol was mixed with an O_2-free solution of $BaL^1(ClO_4)_2 \cdot EtOH \cdot H_2O$ in the same solvent. The result and orange solution (~80 cm^3) was stirred under N_2 until crystallisation started to occur. The yellow crystals were filtered under N_2, washed with cold O_2-free methanol and dried *in vacuo*.

$[Cu_2L^1(pdz)_2][BPh_4]_2$

To a solution of the previous complex in 1:1 O_2-free methanol:acetonitrile was added two equivalents of pyridazine and an excess of $NaBPh_4$. Concentration of the solution produced the red crystalline product in 75% yield.

$[Cu_2L^1(OMe)_2(py)_2][ClO_4]_2 \cdot 2H_2O$

When excess pyridine was added to the orange solution obtained by treating $BaL^1(ClO_4)_2 \cdot EtOH \cdot H_2O$ with $Cu(MeCN)_4ClO_4$ in methanol in the presence of air, the colour turned green and bright green crystals of product separated in ~80% yield.

$[CuL^4][BPh_4]_2$

This complex appears to be the final product obtained whenever L^1 or L^3 or the precursor dialdehyde and diamine are treated with Cu(II) in the presence of $[BPh_4]^-$.

X-ray Crystallography

Crystals of $[CuL][BPh_4]_2$, $C_{72}H_{76}CuN_6O_5B_2$, $M = 1190.6$, monoclinic, space group $C2/c$, $a = 20.12(1)$, $b = 14.48(1)$, $c = 22.37(2)$, $\beta = 110.1(1)°$, $U = 6119.7$ Å^3, $D_m = 1.26(3)$, $D_c = 1.29$ g cm^{-3}, $F(000) = 2459.9$, $\lambda = 0.7107$ Å, μ/cm^{-1} = 6.94.

Precession photographs established the preliminary cell constants and space group. A crystal of size 0.2 × 0.2 × 0.2 mm was mounted to rotate around the *a* axis on a Stoe STADI2 diffractometer and data were collected via variable width ω scan. Background counts were 20 s and a scan rate of 0.0333° s^{-1} was applied to a width of $(2.0 + 0.5 \sin \mu/\tan \theta)$. 5285 independent reflections with $2\theta < 50°$ were measured; but the crystal diffracted poorly and only 1389 of these had $I > 3\sigma(I)$ and these were used in subsequent refinement. The structure was solved

TABLE VII. Atomic Coordinates ($\times 10^{-4}$) with Estimated Standard Deviations in Parentheses

Atom	*x*	*y*	*z*
Cu	0(0)	−926(2)	7500(0)
N(1)	−340(7)	91(11)	7910(8)
C(2)	−600(9)	−83(15)	8418(9)
C(3A)	27(22)	−271(31)	8983(20)
C(3B)	−62(15)	−763(22)	8940(12)
O(4A)	179(16)	−1228(23)	8891(18)
O(4B)	188(10)	−1510(16)	8677(11)
C(5A)	−421(24)	−1845(35)	8738(16)
C(5B)	−272(14)	−2339(21)	8623(11)
C(6A)	−489(26)	−2450(30)	8194(18)
C(6B)	−446(15)	−2698(20)	7978(13)
N(7)	−703(8)	−1928(11)	7542(8)
C(8)	−1317(9)	−2005(13)	7076(11)
C(9)	−1610(11)	−1356(18)	6602(10)
O(10)	−1330(6)	−565(11)	6635(5)
C(11)	−1759(9)	−92(19)	6129(9)
C(12)	−1557(12)	855(27)	6114(12)
N(13)	−1023(10)	1237(12)	6539(10)
C(14A)	−887(18)	2224(27)	6695(18)
C(14B)	952(24)	2097(26)	8680(15)
C(15A)	−141(17)	2540(26)	7015(14)
C(15B)	708(19)	2633(24)	8047(15)
O(16)	46(13)	2188(16)	7672(8)
C(17)	−2212(8)	−1444(19)	6056(10)
C(18)	−2299(11)	−588(22)	5724(8)
B	2707(9)	−30(16)	6439(8)
C(21)	3178(8)	205(13)	6005(7)
C(22)	3477(12)	−477(17)	5747(9)
C(23)	3970(11)	−268(25)	5440(8)
C(24)	4107(12)	618(19)	5319(12)
C(25)	3801(10)	1330(15)	5535(9)
C(26)	3342(11)	1090(17)	5864(8)
C(31)	3199(8)	0(16)	7169(9)
C(32)	3940(9)	8(19)	7380(9)
C(33)	4344(11)	−72(21)	7995(11)
C(34)	4064(12)	−87(14)	8471(9)
C(35)	3332(11)	−140(19)	8297(9)
C(36)	2909(11)	−87(17)	7647(9)
C(41)	2098(9)	745(14)	6274(9)
C(42)	1999(13)	1437(21)	6669(11)
C(43)	1531(13)	2152(17)	6572(11)
C(44)	1079(13)	2231(23)	5953(11)
C(45)	1136(11)	1704(21)	5529(11)
C(46)	1619(13)	980(24)	5671(11)
C(51)	2317(10)	−1049(14)	6234(9)
C(52)	1897(19)	−1301(25)	5631(13)
C(53)	1700(13)	−2262(19)	5472(10)
C(54)	1778(11)	−2814(21)	5881(10)
C(55)	2175(12)	−2596(17)	6469(10)
C(56)	2410(8)	−1719(13)	6643(9)

from the Patterson function. The cation had imposed C_2 symmetry with the Cu atom on the two fold axis. Several atoms in the cation were disordered over two positions. These atoms made up two fragments C(3), O(4), C(5), C(6) and C(14), C(15), O(16). For each fragment, two groups of atoms were included, with bond lengths and 1,3-interactions constrained at expected distances. Each group was given a common isotropic thermal parameter but their common population parameters were allowed to refine subject to the necessary condition that the sum of the two groups was equal to 1.00. Remaining atoms were refined anisotropically. Hydrogen atoms were fixed in trigonal or tetrahedral positions. Hydrogen atoms in the macrocycle were given a common thermal parameter as indeed were hydrogen atoms in the same benzene ring. The hydrogen atoms on the amine N(1) could not be located unequivocally. The structure was refined using full-matrix least squares. The weighting scheme used was $w = 1/(\sigma^2(F) + 0.003F^2)$ where $\sigma(F)$ was taken from counting statistics. This gave equivalent values of $w\Delta^2$ over ranges of F_o and $\sin\theta/\lambda$. Calculations were performed using SHELX76 [33] and local programs on the Amdahl V7/A at the University of Reading. The final R factor was 0.108 ($R_w = 0.115$). Final coordinates are given in Table VII.

Physical Measurements

O_2 and CO gas uptakes were monitored automatically by pressure change using a transducer attached to a thermostatted reaction vessel of fixed volume, as described earlier [34].

Infrared spectra were measured on KBr discs and paraffin mulls using a Perkin-Elmer 598 spectrometer. Electronic spectra were recorded on a Unicam SP 700 instrument and ^{1}H NMR spectra at 250 MHz using a Bruker WM 250 instrument. ESR measurements employed a Varian E9 instrument while magnetic susceptibilities were measured by the Gouy method.

Supplementary Material

Remaining dimensions in cation and anion, thermal parameters, hydrogen atom positions and numerical values used to plot Fig. 4 are available from the authors on request.

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