Dicopper(II) Complexes of a Macrocyclic Ligand containing Single Hydroxo-, Methoxo-, or 1,1-Azido-bridges: Synthesis, Magnetic Properties, Electron Spin Resonance Spectra, and the Crystal and Molecular Structure of a μ-Hydroxo-derivative †

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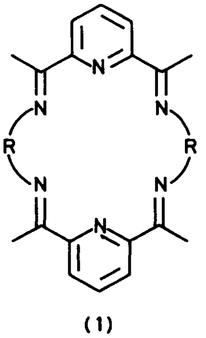
Reaction of 2,6-diacetylpyridine with 1,3-diaminopropane in methanol in the presence of $M[ClO_4]_2$ ($M = Sr^{II}$ or Ba^{II}) in 2:1:1 molar proportions yields the complexes $[ML^2(ClO_4)_2]$ of the new 20-membered macrocyclic tetraimine ligand L^2 derived from the [2 + 2] condensation of 2 mol of diketone with 2 mol of diamine. The single Ba^{2+} in $[BaL^2(ClO_4)_2]$ may be replaced by two Cu^{2+} to afford, depending on the conditions, the complexes $Cu_2L^2(OH)(ClO_4)_3 \cdot 2H_2O$ and $Cu_2L^2(OMe)(ClO_4)_3 \cdot 2H_2O$ formulated as containing two Cu^{2+} linked by, respectively, single hydroxo- and methoxo-bridges. Crystals of the μ-hydroxo-complex are tetragonal with $a = 15.20(1)$, $c = 14.50(1)$ Å, $Z = 4$, and space group $P4_2/n$. 1 191 Reflections above background were measured by diffractometer and refined by Fourier methods to R 0.078. Each copper atom in the binuclear $[Cu_2L^2(OH)(OH_2)]^{3+}$ cation is bonded to the three nitrogen atoms of a trimethine group of the folded macrocycle [Cu–N 1.916(13)—2.066(12) Å]. The approximate co-ordination square plane about each metal atom is completed by a shared oxygen atom, O(1) (presumed to be from OH^-), at 1.916(9) Å. The two Cu atoms are also linked in a shared axial position by a second oxygen atom, O(2) (presumed to be from H_2O), at 2.519(12) Å. The Cu–O(1)–Cu and Cu–O(2)–Cu angles are 110.3(7) and 77.3(4)°, respectively, and the Cu ··· Cu separation is 3.145(4) Å. Magnetic susceptibility measurements in the temperature range 90—300 K establish that the two Cu^{2+} in each binuclear complex are antiferromagnetically coupled with $J = -32$ and -53 cm^{-1} for the μ-hydroxy- and μ-methoxo-derivatives, respectively, where $2J$ is the singlet–triplet separation. The appearance of a ' triplet ' e.s.r. spectrum at $g \approx 2$ and a seven-line $\Delta M = 2$ half-band spectrum at $g \approx 4$ for frozen methanol–dimethyl sulphoxide solutions of the μ-methoxo-complex indicate retention of the bridge in solution. Reaction of $Cu_2L^2(OMe)(ClO_4)_3 \cdot 2H_2O$ with $Na[N_3]$ affords $Cu_2L^2(N_3)(ClO_4)_3$ for which i.r. spectra suggest that the Cu^{2+} are intramolecularly linked by one nitrogen atom of the azide ion (μ-1,1-N_3 bridging mode). E.s.r. spectra of frozen solutions of the monoazide show that the Cu^{2+} are weakly antiferromagnetically coupled. The structures and physical properties of the complexes are discussed in relation to the cavity size of the macrocycle L^2.

Transition-metal complexes of binucleating ligands [1] are of interest because they provide the opportunity to study the intramolecular binding, and possible activation, of small substrate molecules between the metal centres, along with magnetic exchange interactions and multielectron redox reactions. They may also serve as models for certain metalloproteins, particularly those containing copper, for which the biological function is related to the occurrence of the metal centres in pairs. Bovine erythrocyte superoxide dismutase is known to contain an imidazolate-bridged $Cu^{II} \cdots Zn^{II}$ active site.[2] Both imidazolato-[3] and hydroxo-bridges[4] have variously been postulated to link the iron(III) and copper(II) centres in cytochrome c oxidase, and antiferromagnetically coupled copper(II) ions also occur in several other copper proteins including, for example, oxyhaemocyanin.[5] Synthetic macrocyclic ligands having a cavity size large enough to encapsulate two metal ions provide a means whereby the interactions and structural relationships between the metal centres may conveniently be studied in the laboratory.

We have previously described a number of binuclear complexes of several members of the family of macrocyclic tetraimine ligands L^1—L^6 derived from the cyclic [2 + 2] condensation of 2,6-diacetylpyridine with two molecules of diprimary amine.[6] For the dicopper(II) complexes of the 24- and 30-membered rings L^3 and L^6 it was shown that a variety of one-atom, three-atom, and four-atom bridging units (OH^-, 1,3-N_3^-, imidazolate, pyrazine) may be bound intramolecularly between the metal ions, leading to varying degrees of antiferromagnetic coupling.[7,8] The smaller ring systems such as L^1 and L^2 are expected to act as hosts only for the



(1)

L^1, R = $(CH_2)_2$
L^2, R = $(CH_2)_3$
L^3, R = $(CH_2)_2$-S-$(CH_2)_2$
L^4, R = $(CH_2)_2$-NH-$(CH_2)_2$
L^5, R = $(CH_2)_3$-NH-$(CH_2)_3$
L^6, R = $(CH_2)_2$-O-$(CH_2)_2$-O-$(CH_2)_2$

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† *Supplementary data available* (No. SUP 23318, 10 pp.): H-atom positions, thermal parameters, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue. *Non-S.I. units employed:* G = 10^{-4} T; B.M. $\approx 9.27 \times 10^{-24}$ J T^{-1}.

Table 1. Analytical, magnetic, and electrical conductance data for the complexes

Complex	Analysis (%) Found C	Found H	Found N	Calc. C	Calc. H	Calc. N	$\mu_{eff.}$[a]/B.M. 293 K	93 K	Λ[b]/ S cm^2 mol^{-1}
$[BaL^2(ClO_4)_2]$	39.1	4.1	11.2	39.0	4.1	11.4			300
$[SrL^2(ClO_4)_2]$	42.0	4.3	12.0	41.8	4.4	12.2			298
$Cu_2L^2(OH)(ClO_4)_3{\cdot}2H_2O$	32.8	3.7	9.3	32.7	4.0	9.5	1.77	1.54	391
$Cu_2L^2(OMe)(ClO_4)_3{\cdot}2H_2O$	33.4	4.0	9.3	33.5	4.0	9.4	1.71	1.29	409
$Cu_2L^2(N_3)(ClO_4)_3$	38.0	3.9	27.4	38.2	4.0	27.8	1.95	1.90	345

[a] Per Cu atom; corrected for diamagnetism of ligands. [b] For 10^{-3} mol dm^{-3} MeCN solutions at 20 °C.

smaller bridging substrates. The preparation of the complex $Cu_2L^1(OH)(ClO_4)_3{\cdot}H_2O$ has been described.[9] The stoicheiometry of this complex along with the (weak) antiferromagnetism which it exhibits strongly suggest the occurrence of the, rarely observed, single hydroxo-bridge between the metal ions. However, no crystals suitable for *X*-ray structure determination were obtained so that the detailed structure remains unknown. We now report the preparation and magnetic properties of a series of dicopper(II) complexes of the new 20-membered macrocycle L^2 containing single hydroxo-, methoxo-, and azido-bridges, along with the single-crystal *X*-ray structure of the μ-hydroxo-μ-aqua-derivative.

Results and Discussion

Synthesis of the Macrocyclic Complexes.—The macrocycle was prepared by a template reaction in anhydrous methanol of 2 mol of 2,6-diacetylpyridine with 2 mol of 1,3-diaminopropane in the presence of 1 mol of $Ba[ClO_4]_2$ or $Sr[ClO_4]_2$. It was isolated as the strontium(II) or barium(II) complex $[ML^2(ClO_4)_2]$ in 50—65% yield; analytical data are in Table 1. As frequently found in this kind of cyclic Schiff-base condensation, reactions conducted in the absence of metal ion afforded only oils or gums of indefinite composition indicative of mainly oligomeric or polymeric products.

The i.r. spectra of $[ML^2(ClO_4)_2]$ (M = Sr or Ba) showed the expected ν(C=N) and pyridine-ring vibrations at 1 645 and 1 400—1 600 cm^{-1} respectively. No absorptions at 3 200—3 400 or at *ca.* 1 700 cm^{-1} were observed, attesting to the absence of any unreacted primary amine or carbonyl precursor. Distinct splitting of the ν_3 and ν_4 modes of ClO_4^- at *ca.* 1 100 and 620 cm^{-1} indicates co-ordination of the anions in the solid state. The complexes are 2 : 1 electrolytes in MeCN, however.

Treatment of $[BaL^2(ClO_4)_2]$ with an excess of $Cu[ClO_4]_2{\cdot}6H_2O$ in MeOH gave the complex $Cu_2L^2(OMe)(ClO_4)_3{\cdot}2H_2O$ which we formulate (see below) as containing a methoxide bridge between the copper(II) ions. When this material was recrystallized from MeCN the product was $Cu_2L^2(OH)(ClO_4)_3{\cdot}2H_2O$, as proved by a single-crystal *X*-ray structure determination (see below). Although analytical data do not discriminate well between these two complexes, the i.r. spectra in the 2 800—3 700 cm^{-1} region are distinctly different. The product obtained from MeOH shows a strong ν(OH) absorption at 3 440 cm^{-1} with a shoulder at *ca.* 3 500 cm^{-1}, whereas in the spectrum of the material recrystallized from MeCN two well separated ν(OH) vibrations are seen, a strong symmetrical band at 3 450 cm^{-1} and a weaker sharp band at 3 635 cm^{-1}. In addition, the profiles of the spectra in the aliphatic ν(C–H) region (2 800—3 000 cm^{-1}) also differ. First, the overall relative intensity of the multiplet is greater in the case of $Cu_2L^2(OMe)(ClO_4)_3{\cdot}2H_2O$ as expected for a compound containing an extra methyl group. More significantly, a well resolved band occurs at 2 805 cm^{-1} in the spectrum of the complex prepared in MeOH, which we assign to the symmetric ν(C–H) stretch of the OMe group.[10] A second band at *ca.* 2 980 cm^{-1}, attributable to the asymmetric stretch, is discernible also although this is partially overlapped with the rest of the ν(C–H) multiplet. Neither band occurs in the spectrum of the sample recrystallized from MeCN.

While these observations leave no doubt concerning the presence of the OMe group in the complex prepared in MeOH, it is more difficult to decide whether it is present as the methoxide ion or as neutral MeOH, *i.e.* whether the complex should be formulated as μ-methoxo $Cu_2L^2(OMe)(ClO_4)_3{\cdot}2H_2O$ or as μ-hydroxo $Cu_2L^2(OH)(ClO_4)_3{\cdot}MeOH{\cdot}H_2O$. We consider that the bridge is the methoxide ion on the basis of three lines of reasoning. The ν_{sym}(C–H) vibration of the OMe group occurs at 2 805 cm^{-1}, *i.e.* at a significantly lower value than in MeOH itself (2 840 cm^{-1} in the liquid phase) or in complexes containing MeOH co-ordinated to bivalent metal ions. For example, in the complex $[Fe(L')Cl(MeOH)][ClO_4]$,[11] where L′ is another Schiff-base macrocycle, 2,15-dimethyl-7,10-dithia-3,14,20-triazabicyclo[14.3.1]icosa-1(20),2,14,16,-18-pentaene, ν_{sym} of OMe occurs at 2 842 cm^{-1}, while in other binuclear complexes of a related 20-membered macrocycle known from *X*-ray studies to contain bridging OMe^- groups, ν_{sym} is observed at 2 785—2 800 cm^{-1}.[12] Secondly, there is reason to identify the sharp high-frequency ν(O–H) vibration in the spectrum of $Cu_2L^2(OH)(ClO_4)_3{\cdot}2H_2O$, which is absent in the spectrum of the samples obtained from MeOH, with the bridging OH^- group. As will be seen later, the oxygen atom of the OH^- bridge has no contact with another atom, other than metal or hydrogen, of less than 3.36 Å. We may conclude, therefore, that this OH^- group is not hydrogen bonded and that this is the reason for the occurrence of the ν(OH) stretch as a sharp band in the non-hydrogen-bonded region. In contrast, the *X*-ray structure shows that the oxygen atom of one of the two H_2O molecules, also acting as a bridge between the copper(II) ions, is in significantly closer contact (3.01 Å) with a perchlorate oxygen atom. The second H_2O molecule occupies a volume of the unit cell alternatively with a disordered perchlorate anion with an occupancy of 50%. The oxygen atom is 2.91 Å from O(11) and it is therefore probable that this H_2O molecule is also hydrogen bonded. Thirdly, as will be seen, the two complexes differ in their magnetic properties, an observation more readily reconcilable with a change in the nature of the bridge (OH^- or OMe^-) than with a change in the nature of the solvent molecule (H_2O or MeOH) in the crystal lattice.

Attempts to prepare a modification containing an ethoxide bridge by carrying out the transmetallation in EtOH were not wholly successful. Analytical and i.r. data of the products obtained suggested that they were mixtures of $Cu_2L^2(OH)$-

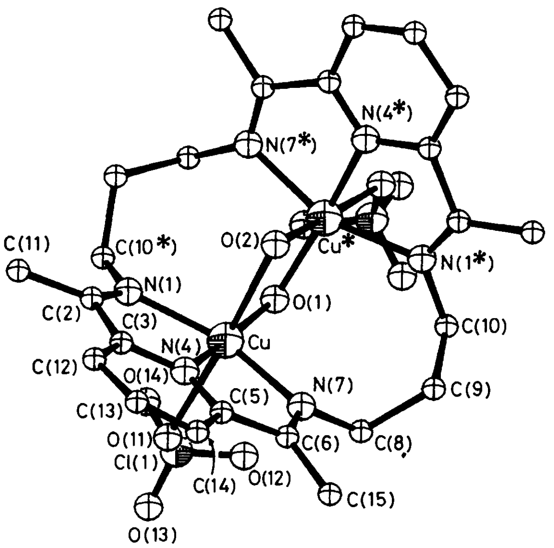


Figure 1. The structure of the $[Cu_2L^2(OH)(OH_2)]^{3+}$ cation

Table 2. Least-squares planes for $[Cu_2L^2(OH)(OH_2)]^{3+}$. Deviations of atoms from the planes are given in Å. Atoms not contributing to the planes are marked with a dagger (†)

Plane 1: Cu, O(1), O(2) 0.00, O(11)† 0.03, N(4)† 0.00
Plane 2: Cu, 0.05, N(1) −0.03, N(4) 0.11, N(7) −0.03, O(1)† 0.40
Plane 3: C(3) 0.01, N(4) −0.00, C(5) −0.00, C(12) −0.00, C(13) −0.00, C(14) 0.01, Cu† 0.19, N(1)† 0.04, C(2)† −0.04, C(6) −0.02, N(7)† 0.11

Angle between plane 2 and its symmetry related ($\frac{3}{2} - x$, $\frac{1}{2} - y$, z) counterpart, 89.5°; between planes 1 and 2, 89.8°.

Table 3. Torsion angles (°) in the macrocycle L^2

O(1)–Cu–N(7)–C(8)	−18.9
Cu–N(7)–C(8)–C(9)	98.1
C(6)–N(7)–C(8)–C(9)	−91.1
N(7)–C(8)–C(9)–C(10)	−96.9
C(8)–C(9)–C(10)–N(1*)	96.4
C(9)–C(10)–N(1*)–C(2*)	92.3
O(2)–Cu–N(1)–C(10*)	104.9
O(1)–Cu*–N(1*)–C(10)	18.5

$(ClO_4)_3{\cdot}2H_2O$ and $Cu_2L^2(OEt)(ClO_4)_3{\cdot}2H_2O$. The intensity of the sharp ν(OH) band at ≈3 630 cm^{-1} was variable as was the profile of the ν(C–H) multiplet. Moreover the magnetic properties also varied somewhat from preparation to preparation. Recrystallization of the crude products from EtOH was not possible due to insolubility in this solvent. Because of the uncertainty in the composition and structure of these modifications they will not be discussed further.

Apart from the differences already discussed the i.r. spectra of $Cu_2L^2(OH)(ClO_4)_3{\cdot}2H_2O$ and $Cu_2L^2(OMe)(ClO_4)_3{\cdot}2H_2O$ are virtually identical. Both showed the expected ν(C=N) and pyridine-ring vibrations at, respectively 1 632 and 1 400—1 600 cm^{-1}. The ClO_4^- ν_3 mode at *ca.* 1 100 cm^{-1} was somewhat broadened while the ν_4 band at *ca.* 620 cm^{-1} was slightly split, suggesting weak co-ordination of at least one of these anions. Both complexes are 3 : 1 electrolytes in MeCN (Table 1) indicating dissociation of the anions in solution and retention of the bridging anion (OH^- or OMe^-). Electronic spectra of the two complexes are very similar each showing a single broad absorption at ≈14 400 cm^{-1} both in the solid state and in MeCN solution, consistent with a ' square '-based ' 4 + 1 ' or ' 4 + 2 ' co-ordination geometry for the copper(II) ions.

Structure of $Cu_2L^2(OH)(ClO_4)_3{\cdot}2H_2O$.—The cation $[Cu_2L^2(OH)(OH_2)]^{3+}$ is shown in Figure 1, together with the atomic numbering scheme. There is a crystallographic two-fold axis passing through the two oxygen atoms which bridge the two copper atoms. Each copper atom is co-ordinated to the three nitrogen atoms of a trimethine group of the macrocycle [2.066(12), 1.916(13), 2.061(13) Å], the shortest bond being to the pyridine nitrogen. Situated *trans* to each pyridine nitrogen and completing the approximate square plane about each copper atom is the bridging oxygen atom O(1) with Cu–O(1) of 1.916(9) Å; the O(1) atom lies 0.40 Å from the CuN_3 plane. The two metal atoms are also linked in a shared axial position by a second oxygen atom O(2). This interaction is a much weaker one, however, since Cu–O(2) is 2.519(12) Å. The stoicheiometry and properties of the complex require that one of the oxygen bridges is an OH^- ion and that the other is a H_2O molecule. While it was not possible to discern hydrogen atoms in a difference-Fourier map there can be little doubt that it is the more basic ligand (OH^-) that occupies the strongly interacting equatorial site. As far as we are aware there are no precedents for a μ-hydroxo-μ-aqua-bridge. There are many examples [13–16] of di-μ-hydroxo-bridges between copper(II) ions but of the 14 such complexes listed in the Cambridge Data Centre files [15] all have the two bridging hydroxo-groups in equatorial positions. Attempts to prepare a di-μ-hydroxo-derivative of the present complex (by treatment with controlled amounts of NaOH) or of a di-μ-aqua-derivative (by treatment with $HClO_4$) were unsuccessful. A perchlorate oxygen atom is positioned in the second axial site at 2.480(13) Å, thus making the co-ordination sphere of each copper(II) an axially elongated octahedron.

The accommodation of the doubly bridged dicopper(II) unit within the relatively small macrocycle ' hole ' requires that the planar $Cu_2(OH)(OH_2)$ moiety is perpendicular to the planes of the trimethine units (Table 2). It also requires that the macrocycle be severely folded, the two symmetry-related trimethine planes intersecting at 89.5°. This leads to a considerable amount of macrocycle strain. Table 3 shows that the torsion angles in the saturated segment of the macrocycle from N(1) to N(7*) are very much distorted from the ideal values of 60 and 180° and, indeed, many are in the range 90—105°. The Cu–O(1)–Cu bond angle is 110.3(7)° while the Cu–O(2)–Cu angle is 77.3(4)°. The Cu ··· Cu distance is 3.145(4) Å. In the di-μ-hydroxo-dicopper(II) structures [15] mean dimensions are Cu–O 1.94 Å, Cu–O–Cu 98°, and Cu ··· Cu 2.88 Å. Thus, in the present structure the Cu–O(1) distance is slightly shorter at 1.916(9) Å while the Cu–O(1)–Cu angle is considerably larger.

Intermolecular distances less than 3.5 Å are listed in Table 4. There are many short distances between atoms not in the same unit cell. Of the true intermolecular contacts that between the axially sited oxygen O(2) and a perchlorate oxygen O(2) is noteworthy. The O(2) ··· O(12) distance of 3.01 Å could represent a hydrogen bond with a postulated O(2)–H ··· O(12) angle of 142° (see discussion above on i.r. spectra).

Magnetic Properties and E.S.R. Spectra of $Cu_2L^2(OH)(ClO_4)_3{\cdot}2H_2O$ *and* $Cu_2L^2(OMe)(ClO_4)_3{\cdot}2H_2O$.—Magnetic susceptibilities of both complexes in the solid state were measured over the temperature range 80—300 K. As can be seen from Table 1 and Figure 2 there is a distinct decrease in $\mu_{eff.}$ per copper(II) ion with decrease in temperature indicating antiferromagnetic superexchange coupling between the paramagnetic centres. The data were fitted to the Bleaney–Bowers

Table 4. Intermolecular distances less than 3.5 Å

(*a*) For disordered atoms not in the same unit cell			
O(500) ··· O(42)	1.90	Cl(4) ··· Cl(4)	1.36
Cl(4) ··· O(500)	1.85		
(*b*) True intermolecular distances			
O(11) ··· O(500)	2.93	O(13) ··· O(2^{III})	3.24
O(500) ··· C(11^{II})	3.40	O(12) ··· C(2^{IV})	3.17
O(11) ··· C(13^{II})	3.36	O(12) ··· C(3^{IV})	3.19
C(6) ··· C(13^{II})	3.19	C(9) ··· O(14^{I})	3.31
O(2) ··· C(13^{III})	3.24	C(8) ··· O(14^{I})	3.42

Roman numeral superscripts indicate the following symmetry related positions: I $y, \frac{1}{2} - x, \frac{1}{2} - z$; II $1 - x, 1 - y, 1 - z$; III $1 - y, -\frac{1}{2} + x, \frac{1}{2} + z$; IV $1 - y, -\frac{1}{2} + x, -\frac{1}{2} + z$.

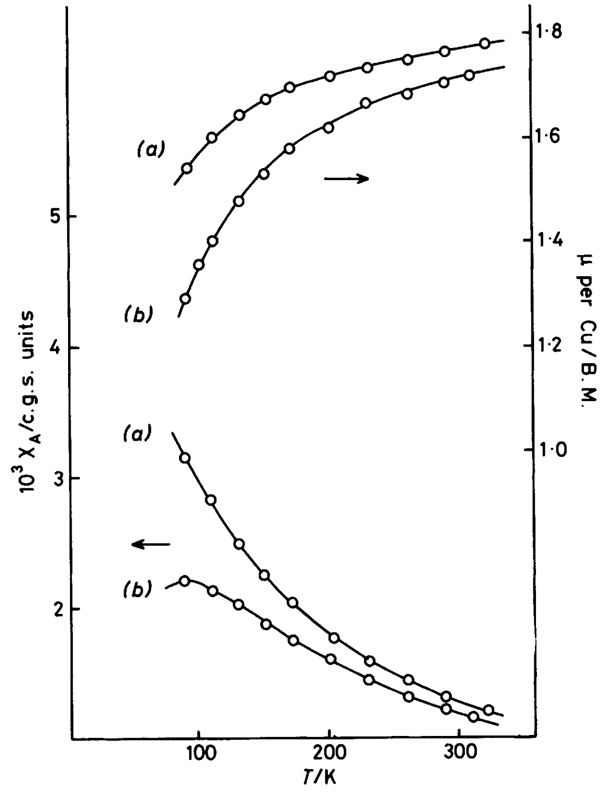


Figure 2. Magnetic susceptibilities and magnetic moments per copper(II) ion as a function of temperature for (*a*) $Cu_2L^2(OH)(ClO_4)_3 \cdot 2H_2O$ and (*b*) $Cu_2L^2(OMe)(ClO_4)_3 \cdot 2H_2O$

equation (1)[17] which expresses the molar susceptibility (χ_A) per copper(II) ion for interacting pairs of $S_1 = S_2 = \frac{1}{2}$ spins in terms of the energy separation ($2J$) between the singlet and triplet states of the binuclear system. Figure 2 compares the

$$\chi_A = \frac{Ng^2\beta^2}{kT}\left[\frac{1}{3 + \exp(-2J/kT)}\right] + N\alpha \qquad (1)$$

observed values (circles) of χ_A and $\mu_{eff.}$ per copper(II) ion with those calculated (full curve) for $J = -32$ cm^{-1} (OH^--bridged complex) and $J = -53$ cm^{-1} (OMe^--bridged complex). A g value of 2.09 determined from the e.s.r. spectrum of a powdered sample of $Cu_2L^2(OMe)(ClO_4)_3 \cdot 2H_2O$ was used in both calculations. The temperature-independent-paramagnetism term $N\alpha$ was taken as 40×10^{-6} c.g.s. units per copper(II) ion.

On the assumption that the complex prepared in MeOH contains a methoxo-bridge between the metal centres, a reasonable although unproved conclusion on the available evidence, it is likely that the difference in antiferromagnetic coupling between the two complexes is a consequence of the change in the nature of the bridge. Theoretical considerations[18] and experimental studies[19] both indicate that an increase in the electron density on the bridging atom should be accompanied by a increase in $-J$. Thus, for the present systems J is expected to be more negative for the OMe-bridged complex, as found.

Binuclear copper(II) complexes containing single bridges are relatively rare.[7,20–26] Recently, however, the *X*-ray structures of four mono-μ-hydroxo-dicopper(II) complexes have been reported.[7,24–26] In three of these,[7,25,26] as in the present complex, the single OH^- bridge is sited in the equatorial plane of the square-pyramidal or tetragonal co-ordination polyhedron of each copper(II) ion ($d_{x^2-y^2}$ ground state). In these three complexes the Cu–O(H)–Cu angles range from 132.2 to 143.7° and the coupling constant from -120 to -500 cm^{-1}. While other factors such as the degree of tetrahedral distortion and the nature of the associated ligands will be important, it is to be expected,[16] as found for the more common di-μ-hydroxo-systems,[13,14,16] that the exchange parameter J is a function of the Cu–O(H)–Cu bridge angle. This expectation is borne out by the present results where the bridge angle is 110.3° (the smallest yet observed in a mono-μ-hydroxo-complex), and the J value is only -32 cm^{-1}.

The *X*-band e.s.r. spectrum of $Cu_2L^2(OMe)(ClO_4)_3 \cdot 2H_2O$ was measured in frozen solutions in dimethyl sulphoxide (dmso)–methanol at ≈80 K. The $\Delta M = 1$ signal obtained in the 2 600—3 700 G region has the appearance of a 'triplet' spectrum[27–30] characteristic of coupled copper(II) ions with approximate values of the zero-field splitting parameters D and E being ≈420 G and ≈45 G, respectively [Figure 3(*a*)]. A half-band ($\Delta M = 2$) transition is seen between 1 100 and 1 800 G which shows a seven-line hyperfine pattern with an average hyperfine spacing of 75 G [Figure 3(*b*)]. These observations confirm the occurrence of superexchange coupling between the copper(II) ions in the binuclear complex and, moreover, that the bridge is retained in solution.

A Complex containing a Single 1,1-*Azido-bridging Group.*—The occurrence of single bridging units in the dicopper(II) complex of L^2 (and also of L^3 and L^6) can logically be traced to the presence in the macrocycle of two rigid, planar, and powerfully co-ordinating trimethine moieties linked by two flexible chains. Each metal ion is thus strongly bound to one trimethine unit with the three nitrogen donors occupying three corners of a square plane. The co-ordinatively unsaturated copper(II) ions may thus complete the co-ordination square plane by the intramolecular binding of a single bridging substrate molecule or ion between the metal centres. As shown earlier the 24- and 30-membered macrocycles L^3 and L^6 are large enough and flexible enough to accommodate bridging ligands of varying size. For the case of the 20-membered ring L^2, on the other hand, molecular models suggest that the cavity size is too small to accommodate other than a single-atom bridging unit. The azide ion is known to act as a bridge between two metal atoms.[31] Two bridging modes have been observed, the end-to-end or μ-1,3-azide bridge [structure (A), following page] and the end-on or μ-1,1-azide bridge [structure (B)]. The 1,3-azido-bridge (A) is the more common and has been observed in the macrocyclic Schiff-base complex $[Cu_2L^6(N_3)_3][ClO_4]$[32] as well as in a dicopper(II) complex of a cryptand ligand.[33] It was thus of interest to see whether

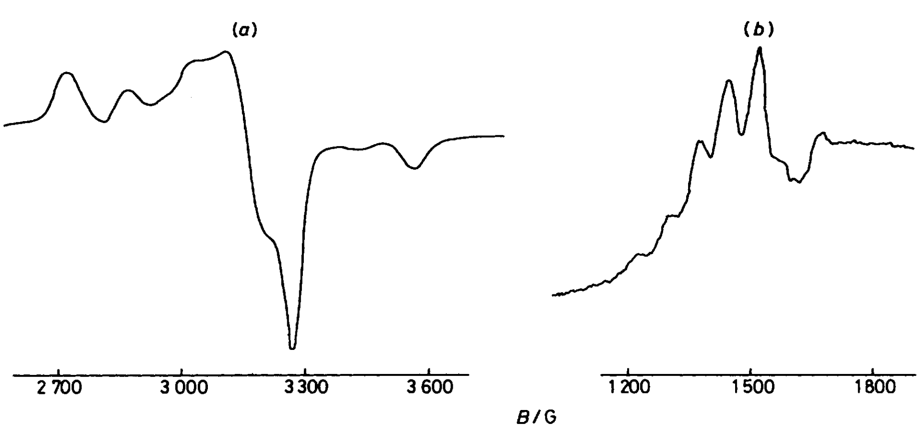


Figure 3. The X-band e.s.r. spectrum of $Cu_2L^2(OMe)(ClO_4)_3{\cdot}2H_2O$ in dmso–MeOH glass at ≈80 K in the $g \approx 2$ and ≈4 regions: (*a*) the $\Delta M = 1$ transition; (*b*) the $\Delta M = 2$ transition

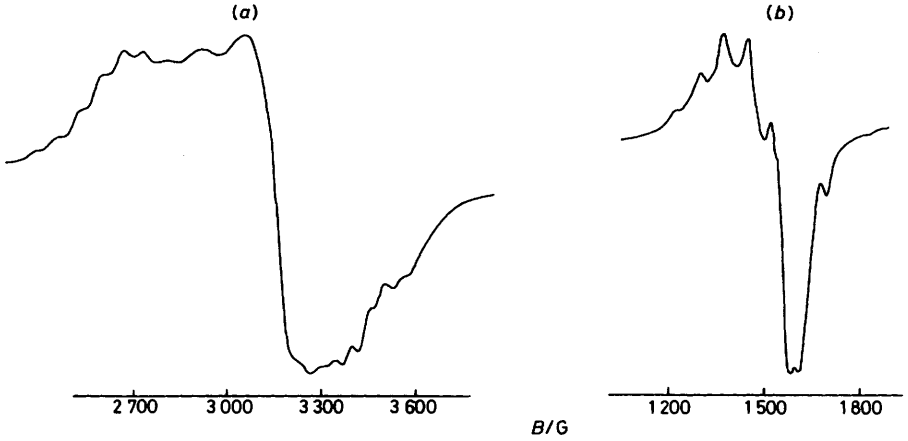
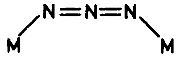


Figure 4. The X-band e.s.r. spectrum of $Cu_2L^2(N_3)(ClO_4)_3$ in the $g \approx 2$ and ≈4 regions; key as in Figure 3

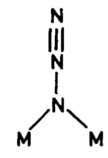
the azide ion could be introduced into the Cu_2L^2 moiety in bridging mode (B).

Reaction of $Cu_2L^2(OMe)(ClO_4)_3{\cdot}2H_2O$ with 1 equivalent of $Na[N_3]$ in MeOH afforded the complex $Cu_2L^2(N_3)(ClO_4)_3$. I.r. spectra confirmed the presence of the unaltered macrocycle. The ν_{asym} asymmetric stretch of the co-ordinated azide ion occurs at 2 070 cm^{-1}. A band at 1 347 cm^{-1}, absent in the spectra of complexes not containing the azide ion, is assigned to the symmetric stretch ν_{sym}. The stoicheiometry of the complex and the occurrence of ν_{sym} as a moderately intense band is evidence for an ' end-on ' (μ-1,1) azide bridge [structure (B)]. The ν_{sym} vibration is expected to be inactive, or of low intensity, in symmetrically bridged 1,3-azido-complexes [structure (A)].

The room-temperature magnetic moment of $Cu_2L^2(N_3)(ClO_4)_3$ is 1.95 B.M. and did not decrease appreciably on cooling to 93 K (Table 1). Thus, magnetic susceptibility measurements in the temperature range available provided no clear indication of antiferromagnetic coupling between the copper(II) ions. However, proof of the occurrence of weak superexchange interaction was obtained from the X-band e.s.r. spectra in dmso–MeOH (3 : 1) glasses at *ca.* 80 K. A broad ' triplet ' spectrum centred at 3 150 G and extending over ≈1 400 G was observed [Figure 4(*a*)]. This spectrum showed two sets of seven-line hyperfine splitting patterns on the wings of the highest-field and lowest-field components of the $\Delta M = 1$ transition. The average value of the hyperfine splitting is 65 G, *i.e.* about half the value expected for mononuclear Cu^{II}. A $\Delta M = 2$ transition of one-tenth intensity at 1 455 G was also seen, this, again, displaying the expected seven-line hyperfine pattern of average spacing 75 G characteristic of coupled copper(II) dimers [Figure 4(*b*)].



(A)



(B)

Experimental

Preparation of the Complexes.—2,6-Diacetylpyridine, 1,3-diaminoethane, and the metal salts were used as supplied commercially without further purification.

$[BaL^2(ClO_4)_2]$. 2,6-Diacetylpyridine (0.015 mol), 1,3-diaminopropane (0.015 mol), and $Ba[ClO_4]_2$ (0.0077 mol) were dissolved in dry methanol (300 cm^3) and refluxed for 1 h. On cooling and standing overnight white crystals of product separated. A further batch of crystals could be obtained on reducing the volume of the filtrate to *ca.* 75 cm^3. Overall yield, 65%.

The complex $[SrL^2(ClO_4)_2]$ was prepared similarly, except that a longer reflux period (*ca.* 2 h) was found advantageous. A lower yield (*ca.* 50%) was obtained.

$Cu_2L^2(OMe)(ClO_4)_3{\cdot}2H_2O$. To a solution of $[BaL^2(ClO_4)_2]$

Table 5. Molecular dimensions, distances in Å, angles in °

(*a*) In the dimeric cation

Cu(1) · · · Cu(1*)	3.145(4)	Cu(1)–N(1)–C(2)	115.5(11)	C(2)–C(11)	1.498(23)	C(12)–C(13)	1.362(22)
Cu(1)–O(11)	2.480(13)	N(1)–C(2)–C(3)	114.5(16)	C(3)–N(4)	1.332(18)	C(13)–C(14)	1.405(23)
Cu(1)–O(1)	1.916(9)	N(1)–C(2)–C(11)	126.7(18)	C(3)–C(12)	1.345(23)	Cl(1)–O(13)	1.322(19)
Cu(1)–O(2)	2.519(12)	C(3)–C(2)–C(11)	118.8(16)	N(4)–C(5)	1.324(19)	Cl(1)–O(14)	1.401(15)
Cu(1)–N(1)	2.066(12)	C(2)–C(3)–N(4)	108.9(15)	C(5)–C(6)	1.510(23)	O(11)–Cl(1)–O(12)	108.1(10)
Cu(1)–N(4)	1.916(13)	C(2)–C(3)–C(12)	127.0(15)	C(5)–C(14)	1.423(23)	O(11)–Cl(1)–O(13)	106.7(13)
Cu(1)–N(7)	2.061(13)	N(4)–C(3)–C(12)	124.0(15)	C(6)–N(7)	1.256(21)	O(12)–Cl(1)–O(13)	108.3(15)
O(11)–Cu(1)–O(1)	98.9(5)	Cu(1)–N(4)–C(3)	122.1(11)	C(6)–C(15)	1.494(22)	O(11)–Cl(1)–O(14)	111.1(9)
O(11)–Cu(1)–O(2)	174.9(3)	Cu(1)–N(4)–C(5)	116.0(11)	N(7)–C(8)	1.488(20)	O(12)–Cl(1)–O(14)	108.6(11)
O(1)–Cu(1)–O(2)	86.2(4)	C(3)–N(4)–C(5)	121.4(15)	C(8)–C(9)	1.537(25)	O(13)–Cl(1)–O(14)	113.9(13)
O(11)–Cu(1)–N(1)	87.0(5)	N(4)–C(5)–C(6)	115.0(16)	C(9)–C(10)	1.534(24)	Cu(1)–O(11)–Cl(1)	126.4(7)
O(1)–Cu(1)–N(1)	101.8(4)	N(4)–C(5)–C(14)	119.4(16)				
O(2)–Cu(1)–N(1)	91.3(4)	C(6)–C(5)–C(14)	125.6(16)				
O(11)–Cu(1)–N(4)	90.3(4)	C(5)–C(6)–N(7)	113.1(15)				
O(1)–Cu(1)–N(4)	170.8(5)	C(5)–C(6)–C(15)	121.1(17)				
O(2)–Cu(1)–N(4)	84.6(4)	N(7)–C(6)–C(15)	125.7(16)				
N(1)–Cu(1)–N(4)	78.4(5)	Cu(1)–N(7)–C(6)	115.1(11)				
O(11)–Cu(1)–N(7)	88.8(5)	Cu(1)–N(7)–C(8)	122.2(11)				
O(1)–Cu(1)–N(7)	99.9(4)	C(6)–N(7)–C(8)	122.1(14)				
O(2)–Cu(1)–N(7)	91.1(4)	N(7)–C(8)–C(9)	112.6(15)				
N(1)–Cu(1)–N(7)	158.2(5)	C(8)–C(9)–C(10)	116.0(15)				
N(4)–Cu(1)–N(7)	80.3(5)	N(1*)–C(10)–C(9)	115.0(14)				
Cu(1)–O(1)–Cu(1*)	110.3(7)	C(3)–C(12)–C(13)	116.1(17)				
Cu(1)–O(2)–Cu(1*)	77.3(4)	C(12)–C(13)–C(14)	123.0(17)				
N(1*)–C(10)	1.461(16)	C(5)–C(14)–C(13)	116.0(16)				
N(1)–C(2)	1.288(21)	Cl(1)–O(11)	1.415(13)				
C(2)–C(3)	1.549(23)	Cl(1)–O(12)	1.405(16)				

(*b*) In the disordered unattached perchlorates

Cl(5)–O(50)	1.37(4)	Cl(4)–O(41)	1.63(4)
Cl(5)–O(51)	1.37(11)	Cl(4)–O(42)	1.42(7)
Cl(5)–O(52)	1.47(5)	Cl(4)–O(41***)	1.63(4)
O(50)–Cl(5)–O(51)	122(6)	Cl(4)–O(42****)	1.42(7)
O(50)–Cl(5)–O(52)	98(3)	O(41)–Cl(4)–O(42)	87(3)
O(51)–Cl(5)–O(52)	72(5)	O(41)–Cl(4)–O(41***)	103(3)
O(50)–Cl(5)–O(52**)	90(3)	O(41)–Cl(4)–O(42****)	101(4)
O(51)–Cl(5)–O(52**)	97(5)	O(42)–Cl(4)–O(41***)	107(4)
O(52)–Cl(5)–O(52**)	151(5)	O(42)–Cl(4)–O(42****)	147(5)
		O(41***)–Cl(4)–O(42****)	102(5)

Atoms marked *, **, ***, **** refer to the following equivalent positions relative to the x,y,z set in Tables 5 and 6: * $\frac{3}{2}-x, \frac{1}{2}-y, z$; ** $\frac{3}{2}-x, \frac{3}{2}-y, z$; *** $x, \frac{1}{2}-y, \frac{1}{2}-z$; **** $\frac{1}{2}-y, x, \frac{1}{2}-z$.

Table 6. Atomic co-ordinates (× 10⁴) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Cu(1)	6 664(1)	3 110(1)	4 055(1)
Cl(1)	5 899(4)	3 702(3)	1 858(4)
O(11)	5 765(9)	3 790(10)	2 819(9)
O(12)	5 939(13)	2 800(11)	1 650(12)
O(13)	6 675(15)	4 055(18)	1 676(17)
O(14)	5 203(13)	4 077(13)	1 361(11)
O(1)	7 500(0)	2 500(0)	3 301(11)
O(2)	7 500(0)	2 500(0)	5 412(11)
N(1)	7 258(8)	4 323(9)	4 212(11)
C(2)	6 923(11)	4 822(12)	4 838(13)
C(3)	6 134(10)	4 412(10)	5 361(13)
N(4)	5 932(8)	3 644(8)	4 973(9)
C(5)	5 267(10)	3 162(12)	5 275(13)
C(6)	5 122(12)	2 310(10)	4 762(13)
N(7)	5 718(9)	2 147(8)	4 186(10)
C(8)	5 664(13)	1 386(11)	3 544(13)
C(9)	6 103(11)	554(11)	3 935(14)
C(10)	7 040(11)	365(12)	3 595(13)
C(11)	7 232(12)	5 722(10)	5 108(16)
C(12)	5 685(10)	4 771(12)	6 066(13)
C(13)	4 993(12)	4 293(12)	6 392(13)
C(14)	4 751(11)	3 472(10)	6 028(13)
C(15)	4 319(12)	1 765(12)	4 924(16)
Cl(5)	7 500(0)	7 500(0)	2 500(0)
O(50)	7 369(36)	7 697(30)	3 408(28)
O(51)	8 291(75)	7 207(79)	2 169(96)
O(52)	8 026(30)	8 273(36)	2 246(44)
Cl(4)	3 103(23)	2 643(35)	2 595(29)
O(41)	2 500(0)	2 500(0)	1 677(35)
O(42)	3 083(51)	3 557(44)	2 398(53)
O(500)	3 970(39)	3 230(41)	3 252(51)

(1.4 mmol) in methanol (400 cm³) was added a methanolic solution of $Cu[ClO_4]_2 \cdot 6H_2O$ (5 mmol). The resulting blue solution was refluxed for 2 h. Blue crystals of product separated in 65% yield on cooling and standing. Experiments conducted in ethanol, in which $[BaL(ClO_4)_2]$ is poorly soluble, gave a blue amorphous product, also insoluble in ethanol, showing variations in the 2 800—3 700 cm⁻¹ region of the i.r. spectrum depending on the preparation (see text).

The complex $Cu_2L^2(OH)(ClO_4)_3 \cdot 2H_2O$ was obtained by recrystallization of the complexes prepared in either methanol or ethanol, from acetonitrile.

$Cu_2L^2(N_3)(ClO_4)_3$. A solution of $Na[N_3]$ (3 mmol in 10 cm³ MeOH) was added dropwise at room temperature to a solution of $Cu_2L^2(OMe)(ClO_4)_3 \cdot 2H_2O$ (6 mmol) in MeCN–MeOH (2 : 1) (350 cm³). The resulting green solution yielded blue-green crystals of product on standing. Yield 51%.

Crystal Data.—$Cu_2L^2(OH)(OH_2)(ClO_4)_3 \cdot H_2O$, $C_{24}H_{35}Cl_3Cu_2N_6O_{15}$, $M = 881.0$, Tetragonal, $a = 15.20(1)$, $c = 14.50(1)$ Å, $U = 3\,351.0$ Å³, $D_m = 1.71$, $Z = 4$, $D_c = 1.74$ g cm⁻³, $F(000) = 1\,800$, $\lambda(\text{Mo-}K_\alpha) = 0.7107$ Å, $\mu(\text{Mo-}K_\alpha) = 16.4$ cm⁻¹, space group $P4_2/n$ from systematic absences $hk0$, $h + k = 2n + 1$ and $00l$, $l = 2n + 1$. A crystal of approximate size 0.3 × 0.3 × 0.3 mm was set up to rotate around c on a Stoe Stadi-2 diffractometer equipped with a graphite monochromator. 3 094 Independent reflections with $2\theta_{max.} < 50°$ were measured using Mo-K_α radiation by ω scan with a width of $(1.0 + \sin\mu/\tan\theta)$ and a scan speed of 0.033° s⁻¹. Backgrounds were measured at the ends of the scan for 30 s. Neither an absorption correction nor an extinction correction was applied. 1 191 Reflections with $I > 2\sigma(I)$ were used in subsequent calculations.

Structure Determination.—The position of one independent copper atom was located from the Patterson map and the positions of all atoms in the dimeric cation were found from subsequent Fourier maps. Hydrogen atoms were fixed in trigonal or tetrahedral positions with thermal parameters equivalent to those of the atoms to which they are bonded. Of the two methyl groups the hydrogen atoms on C(11) were located by rigid-body refinement while those of C(14) were not. Two perchlorate ions were also found, one around Cl(1) in a general position was ordered, the other around Cl(5) in special position (2b) was not. Three oxygen atoms, O(50), O(51) (with $\frac{1}{4}$ occupancy), and O(52) (with $\frac{1}{2}$ occupancy), were refined which together gave 12 oxygen atoms around the chlorine atoms. A set of four gave a very distorted tetrahedron as shown in Table 5. The contents of the unit cell so far located were four $[Cu_2L^2(OH)(OH_2)]^{3+}$ cations and ten (8 + 2) perchlorate anions which leaves two perchlorates unaccounted for. After studying a difference-Fourier map and, in particular, a region of large residual electron density, we concluded that there was a disordered perchlorate with $\frac{1}{4}$ occupancy in general positions Cl(4), O(41), and O(42) and that the region was also occupied, but not simultaneously, by a water molecule O(500) with $\frac{1}{2}$ occupancy. This model, which gave rise to a neutral unit cell, refined successfully and in a final difference-Fourier map no electron density was >0.3 e Å^{-1}. The weighting scheme was $\sqrt{w} = 1/[\sigma^2(F) + 0.001\ F^2]$ where $\sigma(F)$ was taken from counting statistics. The final R value was 0.078 ($R' = 0.080$) and in the last cycle of refinement no shift was $>0.1\sigma$. Calculations were carried out using the SHELX-76 package[34] at the University of Manchester Computer Centre. Scattering factors and dispersion corrections were taken from International Tables.[35] Table 6 lists the final atomic co-ordinates and Table 5 the bond lengths and angles.

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