Binuclear Macrocyclic Copper(II) Complexes as Receptors for Small Bridging Ligands: *X*-Ray Crystal and Molecular Structure of a μ-Azido Complex

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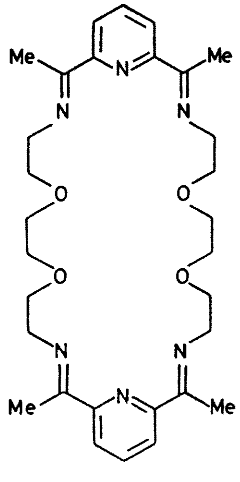
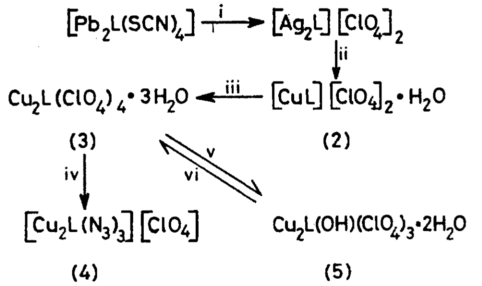
Summary In two binuclear copper(II) complexes of a 30-membered Schiff's base macrocyclic ligand the macrocycle adopts a folded conformation which allows intramolecular linkage of the metal atoms *via* small bridging ligand (N_3^- or OH^-); the structure of the μ-azido complex has been solved by *X*-ray analysis.

THE synthesis in high yield of the potentially decadentate 'N_6O_4' macrocycle L (**1**) [isolated as its dilead(II) complex] has been reported.[1] Binuclear metal complexes are of interest in regard to metal–metal exchange interaction, electron transfer properties, and as synthetic analogues for some metalloproteins, particularly those of copper, in which the metal centres occur in pairs.[2] It was therefore of interest to synthesise binuclear transition metal complexes of the macrocycle (**1**).



(1)

While it has not so far proved possible to isolate (**1**) in the unco-ordinated state we have had success in replacing the Pb^{II} ions by means of exchange reactions carried out in solutions containing a second metal ion. The Scheme summarizes some reactions leading to a mononuclear Cu^{II} complex (**2**), believed to have a pseudo-octahedral 'CuN_6' structure in which the oxygen atoms of L (**1**) are unco-ordinated, and to several binuclear Cu^{II} complexes.† Two of these (**4**) and (**5**) are shown to contain single intramolecular bridging units between the metal centres. The structure of complex (**4**) has been solved by single crystal *X*-ray analysis.



SCHEME. i, $AgClO_4$; ii, $Cu(ClO_4)_2 \cdot 6H_2O$; iii, excess $Cu(ClO_4)_2 \cdot 6H_2O$; iv, NaN_3; v, NaOH; vi, $HClO_4$.

Crystal data: $[Cu_2L(N_3)_3]\ ClO_4$, $C_{30}H_{42}ClCu_2N_{15}O_8$, $M = 902{\cdot}9$, $a = 17{\cdot}891(7)$, $b = 10{\cdot}939(11)$, $c = 20{\cdot}361(13)$ Å, $\beta = 106{\cdot}10(8)°$, $U = 3828{\cdot}6$, $Z = 4$, $D_c = 1{\cdot}57$, $D_m = 1{\cdot}56$, $\mu = 12{\cdot}1\ cm^{-1}$, space group $P2_1/n$. 2394 reflections above background were measured on a G.E. XRD5 diffractometer. The structure was solved by Patterson and Fourier methods and refined to *R* 0·075. An –O–C– linkage in the cation was disordered and two positions with half occupancy were refined for each atom. The perchlorate ion was also disordered and three ClO_4^- tetrahedra, sharing a common Cl–O bond, were refined with relative occupancies of 1/3.‡

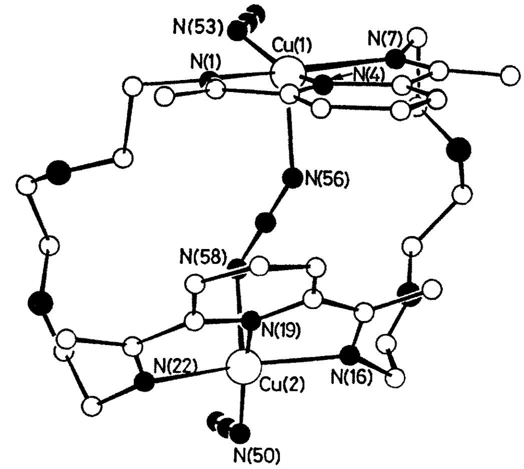


FIGURE. The structure of $[Cu_2L(N_3)_3]^+$. Selected bond distances and angles are: Cu(1)–N(1), 2·09(2); Cu(1)–N(4), 1·92(3); Cu(1)–N(7), 2·05(2); Cu(1)–N(53), 1·94(3); Cu(1)–N(56), 2·25(2); Cu(2)–N(16), 2·07(2); Cu(2)–N(19), 1·93(2); Cu(2)–N(22), 2·06(2); Cu(2)–N(50), 1·93(2); and Cu(2)–N(58), 2·20(3) Å; ∠Cu(1)–N(56)–N(57), 143(2) and ∠Cu(2)–N(58)–N(57), 114(2)°.

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† All the complexes gave satisfactory analyses for C, H, N, and Cu.

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The Figure shows the folded conformation of the macrocycle. The geometries of the two Cu^{II} ions are similar and are best considered as square-pyramids with each metal ion bonded to three imino nitrogens and to a terminal azide ion in the basal plane, with the Cu atoms 0·19 and 0·28 Å out of plane. The two metal atoms are linked *via* a third, bridging, azide ion in the axial positions. The Cu · · · Cu distance is 6·02 Å and the angle between the two equatorial N$_4$ planes is 54·6°. The oxygen atoms of the macrocycle are not bonded to the metal ions.

The persistence of the azide bridge in solution (MeCN, CH$_2$Cl$_2$) was established by the close correspondence between solid and solution electronic spectra and by the univalent electrolyte behaviour. The magnetic moment, per Cu^{II} ion, falls from a value of 1·88 B.M. at 293 K to 1·74 B.M. at 93 K, indicating only a relatively weak antiferromagnetic interaction.

While the detailed structure of complex (**5**) is not known evidence for an intramolecular bridge in this case also is inferred from (i) the stoicheiometry, (ii) the occurrence of a medium intensity, fairly sharp, O–H stretching mode at 3440 cm^{-1} in the i.r. spectrum (superimposed on a separate, broader, OH absorption), (iii) the antiferromagnetic properties, and (iv) the reversible formation of the complex from the magnetically normal [μ_{eff}(293 K) = 1·95 B.M., μ_{eff}(93 K) = 1·90 B.M.] tetra-perchlorate (**3**) by treatment with 1 equiv. (per two Cu ions) of NaOH. Application of the theory[3] for antiferromagnetically coupled Cu^{II} dimers gave an acceptable fit with the experimental data (93—293 K) for complex (**5**) for the exchange energy $J = -120$ cm^{-1} (where $2J$ = the singlet–triplet separation), $g = 2{\cdot}1$, and $N\alpha = 60 \times 10^{-6}$ cgsu. While dihydroxo-bridged Cu^{II} complexes are well known, only in the case of [Cu$_2$(tren)$_2$(OH)]X$_3$ (tren = 2,2′,2″-triaminotriethylamine; X = PF$_6^-$ or ClO$_4$) has a single hydroxo bridge been reported.[4] Here, considerably larger values of the exchange parameter were observed. As with the dihydroxo-bridged species the magnitude of J is expected to be strongly dependent on the Cu–O(H)–Cu bridge angle.[5] The only previous report of a single 1,3-azido bridge is of a Ni^{II} dimer of *N*-tetramethylcyclam.[6] In both these systems the bridges are formed by intermolecular association in the solid state. The binuclear macrocyclic complexes described here differ in the important respect that the bridge is intramolecular and therefore very much less vulnerable to cleavage on dissolution.

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