The Copper-promoted Oxidative Dehydrogenation and Inner Ring Rearrangement of a Macrocyclic Ligand: the *X*-Ray Crystal Structure of the Resultant Complex

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The (7 + 12 + 7) inner ring system of a polycyclic Schiff base rearranges with accompanying oxidative dehydrogenation to a (15 + 6 + 3) inner ring system on reaction with $Cu(ClO_4)_2.6H_2O$ in the presence of dioxygen in order to accommodate the Cu^{II} ion within the 15-membered ring.

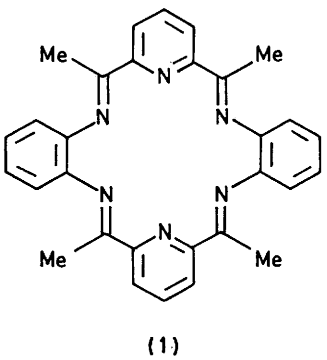
The cyclic Schiff base L^1 derived from the condensation of 2,6-diacetylpyridine with *o*-phenylenediamine has been shown[1] to have the structure (**2**) and not structure (**1**) as proposed previously.[2] We now report a very unusual inner ring rearrangement on reaction of L^1 with $Cu(ClO_4)_2.6H_2O$ in MeOH in the presence of dioxygen.

Treatment of L^1 with an excess of $Cu(ClO_4)_2.6H_2O$ in refluxing MeOH in the presence of air afforded dark green crystals $[CuL^2(H_2O)][ClO_4]_2.H_2O$ (**3**) in 45% yield. I.r. spectra indicated the presence of co-ordinated pyridine and imine (1630 cm^{-1}) groups but the ν(NH) vibration present in L^1 was absent. The magnetic moment (1.86 μ_B at 293 K) was virtually temperature independent and the X-band e.s.r. spectrum in frozen MeCN solution was of the axial type typical of mononuclear square pyramidal Cu^{II} ($g_{\parallel} = 2.21$, $g_{\perp} = 2.05$, $A_{\parallel} = 162$ G), as was the ligand field spectrum (single broad band at 15 300 cm^{-1}). The structure was solved by *X*-ray analysis.

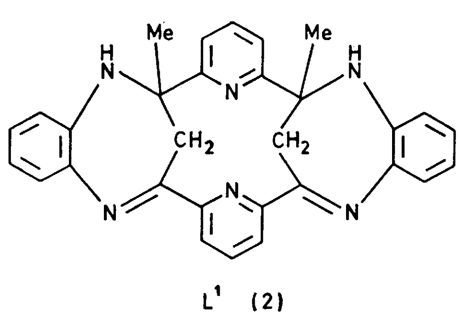
Crystal data: $[CuL^2(H_2O)][ClO_4]_2.H_2O$, $C_{30}H_{28}N_6O_{10}Cl_2Cu$, $M = 766.7$, orthorhombic, space group *Pbna* (No. 60), $a = 16.40(1)$, $b = 14.39(1)$, $c = 26.50(1)$ Å, $U = 6253.9$ Å^3 $D_m = 1.62$, $D_c = 1.62$ g cm^{-3}, $Z = 8$, $\mu = 9.70$ cm^{-1}. 752 Reflections above background were measured by diffractometer and refined to *R* 0.11.† The structure contains discrete $[CuL^2(H_2O)]^{2+}$ cations, disordered ClO_4^- anions, and a lattice water molecule.

As can be seen from L^2 and Figure 1 the L^1 ligand has rearranged from a structure containing a (7 + 12 + 7) inner ring system to one containing a (15 + 6+ 3) inner ring system, with loss of two hydrogen atoms. The Cu^{II} ion is contained within the 15-membered ring being bonded to the two pyridine nitrogen atoms and the two imino nitrogen atoms [Cu–N, 1.94(4)—2.09(4) Å], and sitting 0.37 Å above the N_4 plane in the direction of an apical water molecule [Cu–O, 2.28(4) Å]. The co-ordination geometry is thus a distorted square pyramid. The N(1)–Cu–N(10) angle is 113.2° and the macrocycle is folded so that the plane of the phenyl ring adjacent to N(4) and N(7) intersects the 'N_4' co-ordination plane at 78.2°.

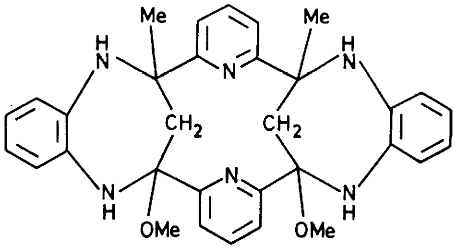
Two important features of the L^1 to L^2 rearrangement may be noted. One is the reversal of the $C=CH_2$ to C=N addition



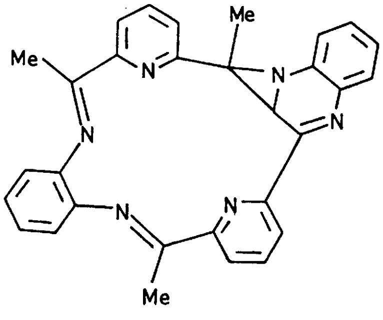
(**1**)



L^1 (**2**)



L^3



L^2

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

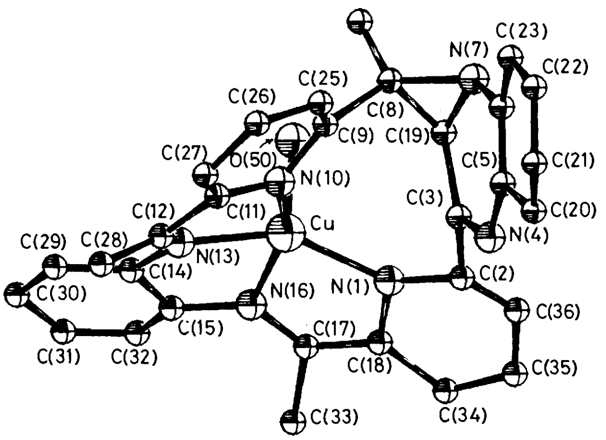

Figure 1. The structure of the $[CuL^2(H_2O)]^{2+}$ cation.

described in the previous Communication[1] and the second is the aziridine ring formation *via* dehydrogenation at N(7) and C(19). The observation of a rather positive reversible one-electron reduction ($E_f = +0.155$ V *vs.* standard calomel electrode, hanging drop Hg electrode, in MeCN) for (**3**) would be consistent with a $Cu^{II} \rightarrow Cu^{I} \rightarrow Cu^{II}$ redox cycle in the oxidative dehydrogenation. It seems clear that the driving force for the rearrangement is the stability gained by providing a suitably sized macrocycle cavity for the metal ion.

Confirmation of the necessity for dioxygen in the ligand rearrangement is the observation that when the reaction was carried out in the absence of dioxygen the product was the brown microcrystalline complex $CuL^3(ClO_4)_2.H_2O$ (**4**) where L^3 is the product of addition of two molecules of MeOH across the two azomethine bonds of L^1. The i.r. spectrum of (**4**) differed from that of L^1 in showing two well-separated ν(NH) bands at 3350 and 3230 cm^{-1}, a new band at 2820 cm^{-1}, assigned to the symmetric ν(CH) of OMe which shifted to 2068 cm^{-1} when CD_3OD was used as reaction medium, a new band at 1120 cm^{-1}, assigned to ν(C–O) of OMe, but no absorption at 1600—1660 cm^{-1} attributable to ν(C=N). Moreover, the profile of the pyridine ring vibrations in the 1400—1600 cm^{-1} region was characteristic of unco-ordinated pyridine.[3] Molecular models show that unlike L^1 the dimethanol adduct L^3 has sufficient flexibility to fold so as to bring the four secondary amine groups into a square planar arrangement with the lone pairs directed inwards towards a centrally co-ordinated metal ion leaving one axial site available for the attachment of a fifth ligand (H_2O or ClO_4^-). In agreement with the predictions of the i.r. spectra this conformation (C_{2v}) of L^3 does not permit co-ordination of the pyridine groups, these being disposed roughly parallel to each other. Physical properties of (**4**) are fully consistent with the predicted square pyramidal co-ordination geometry, *viz.*, $\mu_{eff} = 1.92\ \mu_B$ at 293 K, $\nu_{max} = 13\,100$ cm^{-1}, $g_{\parallel} = 2.227$, $g_{\perp} = 2.079$, $A_{\parallel} = 164$ G in DMSO–MeOH at *ca.* 80 K. Significantly, 'recrystallization' of (**4**) from O_2-free MeCN led to recovery of the free L^1 macrocycle.

$[CuL^2(H_2O)][ClO_4]_2.H_2O$ (**3**)

$CuL^3(ClO_4)_2.H_2O$ (**4**)

We are at present unable to suggest a plausible structure for the product of the reaction of L^2 with $Cu(NO_3)_2$, formulated as $Cu_2L(NO_3)_4$‡ by Stotz and Stoufer.[2] However, in view of the results presented in this and the preceding Communication this material is unlikely to contain the ligand in the form [*i.e.* structure (**1**)] suggested.[2]

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References

1 J. de O. Cabral, M. F. Cabral, M. G. B. Drew, F. S. Esho, O. Haas, and S. M. Nelson, preceding communication.
2 R. W. Stotz and R. C. Stoufer, *Chem. Commun.*, 1970, 1682.
3 M. M. da Mota, J. Rodgers, and S. M. Nelson, *J. Chem. Soc.*, 1969, 2038.

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‡ This formulation may not be correct; we find the nitrogen content to be consistently 1—2% low.