Isolation of a Stable Binuclear Copper Complex Containing a Copper–Copper Bonded Unit. *X*-Ray Structure Determination of {(7,8,15,16,17,18,25,26,33,34,35,36-Dodecahydrotetrabenzo[*e*,*m*,*s*,*a*′][1,4,8,11,15,18,22,25]octa-azacyclo-octacosine)dicopper} Triperchlorate

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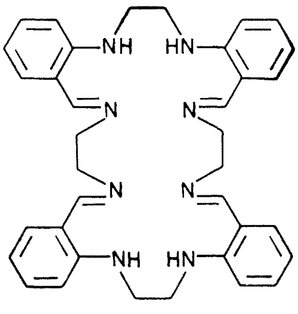
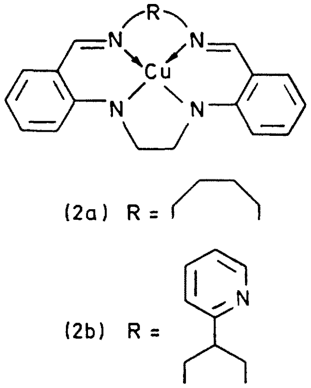
Summary The *X*-ray crystal structure of the title octa-azamacrocycle with a 28-membered ring shows that it is capable of incorporating a symmetrical copper–copper bonded unit which contains a short Cu–Cu bond [2.445(4) Å], the compound is paramagnetic with $\mu_{eff} = 1.87\,\mu_B$ at 300 K, exhibiting a single line at $g = 2.09$ in the *X*-band e.s.r. spectra of solid samples or of frozen acetonitrile solutions (77 K).

A number of dinucleating ligands have been used[1,2] recently to bring two copper atoms into close proximity, thus providing models for the 'Type 3 Coppers' in the multi-copper oxidases.[2] These copper sites are characterized[3] by an ability to act as two-electron acceptor–donor systems and contain two Cu^{2+} ions which are strongly antiferromagnetically coupled. In most of these model systems the two copper atoms are separated by bridges containing one[1] or more[2] atoms. We report here the preparation of a dinuclear complex which contains a direct Cu–Cu bond.



(1)



Treatment of a suspension of the octa-azamacrocycle (1)[4] in tetrahydrofuran with a methanolic solution of copper(II) perchlorate resulted in almost complete dissolution of (1). After filtration, the green solution slowly deposited green prisms of the title complex, $[Cu_2(\mathbf{1})](ClO_4)_3$. The presence of a tricationic complex was unexpected and could have arisen either (i) by the transfer of a single electron to the dicopper centre, (ii) by the loss of one of the anilino-protons from the ligand (a common form of co-ordination for related tetra-azamacrocycles),[5] (iii) by the reduction of the copper ions and simultaneous mono-oxidation of the macrocyclic ligand, or (iv) from a bonded pair of copper(II) ions with a reduced ligand. The second possibility can be excluded on the basis of an *X*-ray structure determination which shows that all four anilino-nitrogen atoms have approximately tetrahedral geometry (Figure), rather than a trigonal planar arrangement which has been found[6] for the deprotonated anilino-nitrogen atoms in the neutral complexes (2).

A magnetic-moment determination by the Faraday method on a solid sample at room temperature (300 K) yielded $\mu_{eff} = 1{\cdot}87\ \mu_B$, thus confirming the expected paramagnetism of the $[Cu_2(\mathbf{1})]^{3+}$ formulation.

The two copper atoms have very similar co-ordination geometries (Table) and the cation has approximate 2-fold symmetry about an axis which passes through the mid-point of the Cu–Cu bond and relates the ligand portion A to C and B to D (see the Figure). The similarity of the environments of Cu(1) and Cu(2) and the short bond [2·445(4) Å] between them suggest that the copper atoms should not be assigned the discrete formal oxidation states +1 and +2, but that the single unpaired electron is delocalised over both metal centres, or that the metal centres are identical and the unpaired electron resides on the ligand.

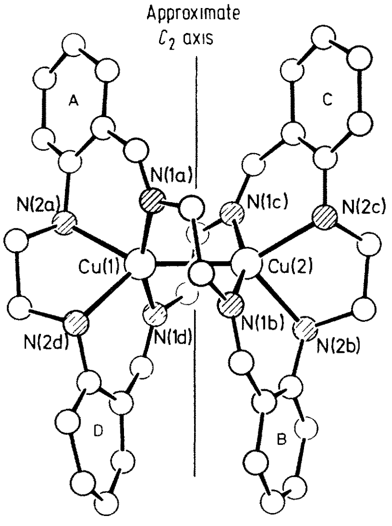


FIGURE.

TABLE. Geometry about the copper atoms Cu(1) and Cu(2).

	Cu(1)		Cu(2)	
	Part A	Part D	Part B	Part C
Bond-lengths/Å				
Cu–N(1)	1·95(2)	1·88(2)	1·91(2)	1·97(2)
Cu–N(2)	2·18(2)	2·20(2)	2·19(2)	2·15(2)
Angles/°				
N(1)–Cu–N(2)	91·8(9)	92·5(7)	93·7(9)	92.2(8)
N(1)–Cu–N(1)[a]	159·8(7)	—	158·0(9)	—
N(1)–Cu–N(2)[a]	106·1(7)	98·3(9)	101·2(9)	105·0(8)
N(2)–Cu–N(2)[a]	83·5(8)	—	84·6(8)	—
N(1)–Cu–Cu[b]	81·0(6)	80·6(7)	78·7(7)	80·5(6)
N(2)–Cu–Cu[b]	144·6(5)	131·8(7)	129·0(5)	146·4(6)

[a] Denotes an atom in the alternative quarter of the ligand which is co-ordinated to the same Cu atom. [b] Denotes the Cu atom in the other half of the complex.

The e.s.r. spectra, at the *X*-band, of a powdered sample or of a frozen acetonitrile solution (77 K) exhibited one line at $g = 2{\cdot}09$ with a peak line width of 80—90 G. These data do not unambiguously support the immediate conclusions from the *X*-ray structural study that the copper ions are equivalent and that this is a 'type 3A' mixed-valence compound.[7] The single line could arise from exchange-narrowing between sites with life-times which are very short on the e.s.r. time-scale or from inherently narrow lines arising from isotropic, nuclear, hyperfine coupling-constants of the order of $40 \times 10^{-4}\ cm^{-1}$, as estimated from the line width. Such small coupling-constants are known for the 'blue' copper proteins[3] as well as a variety of typical co-ordination compounds of copper(II).[8] It is well established that a 4s and 4p orbital admixture in the ground state leads to small, hyperfine coupling-constants[9] and single line e.s.r. spectra. The magnetic susceptibility and e.s.r. data clearly indicate that the formulation of the compound as $[Cu_2L](ClO_4)_3$ is correct and the *X*-ray structural results are most readily interpreted in terms of a copper–copper bond since the Cu–Cu distance is very short[10] for a dinuclear complex and compares with values found in other metal–metal bonded systems.

An E.S.C.A. spectrum was obtained with a PHI 548 spectrometer using a magnesium anode and a precision energy analyser. A single copper $^2P_{3/2}$ line at 935·6 eV and a $^2P_{3/2}$–$^2P_{1/2}$ separation of 20·3 eV are compelling pieces of evidence for the assignment of equal oxidation states to the two copper ions.

The compound undergoes reduction rapidly in a variety of solvents including tetrahydrofuran–methanol solutions, but is relatively stable in acetonitrile, thus permitting a range of electrochemical and optical studies on a new chemical system.

Crystal data. $[Cu_2(\mathbf{1})](ClO_4)_3$, $C_{36}H_{40}Cl_3Cu_2N_8O_{12}$, $M = 1010·2$, monoclinic, space group *Cc*, $a = 22·577(7)$, $b = 11·016(4)$, $c = 20·909(8)$ Å, $\beta = 118·96(2)°$, $U = 4550·0$, $Z = 4$, θ-range 3—35°, $R = 0·080$ for 1815 data with $I/\sigma(I) > 3·0$ obtained on a Philips PW1100 diffractometer with Mo-K_α radiation (two of the perchlorate ions show extensive disorder).†

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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 Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] D. Earl Fenton and R. L. Lintvedt, *J. Am. Chem. Soc.*, 1978, **100**, 6367; A. W. Addison, *Inorg. Nucl. Chem. Lett.*, 1976, **12**, 899; David E. Fenton, N. Bresciani Pahor, M. Calligaris, G. Nardin, and L. Randaccio, *J. Chem. Soc., Chem. Commun.*, 1979, 39; R. R. Gagné and C. L. Spiro, *J. Am. Chem. Soc.*, 1980, **102**, 1443.

[2] K. D. Karlin, D. M. Keller, and L. T. Dipierro, 1979, April ACS Meeting Hawaii, INOR 205; Chi Lin O'Young, J. C. Dewan, H. R. Lilienthal, and S. J. Lippard, *J. Am. Chem. Soc.*, 1978, **100**, 7291; M. G. B. Drew, M. McCann, and S. M. Nelson, *J. Chem. Soc., Chem. Commun.*, 1979, 481.

[3] J. A. Fee, *Struct. Bonding* (*Berlin*), 1975, **23**, 1.

[4] P. G. Owston, R. Peters, and P. A. Tasker, unpublished work.

[5] D. St. C. Black, C. H. Bos Vanderzalm, and L. C. H. Wong, *Aust. J. Chem.*, 1979, **32**, 2203.

[6] D. Losman, L. M. Englehardt, and M. Green, *Inorg. Nucl. Chem. Lett.*, 1973, **9**, 791; K. Henrick and P. A. Tasker, *Inorg. Chim. Acta*, in the press.

[7] M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 247.

[8] J. R. Wasson, H. W. Richardson, and W. E. Hatfield, *Z. Naturforsch., Teil B*, 1977, **32**, 551.

[9] A. J. Freeman and R. E. Watson, 'Magnetism,' Vol. 11A, eds. G. T. Rado and H. Suhl, Academic Press, New York, 1965, p. 67 ff; M. Sharnoff, *J. Chem. Phys.*, 1963, **42**, 3383; K. J. Stanley and K. W. H. Stevens, *Proc. Phys. Soc., London*, 1963, **79**, 73.

[10] M. Corbett, B. F. Hoskins, N. J. McLeod, and B. P. O'Day, *Aust. J. Chem.*, 1975, **28**, 2377.