Oxidative Coupling of Phenylacetylene by a Di-copper(i1) Complex of a Macrocyclic Ligand and the X-Ray Structure of a Tetra-copper(i) Phenylacetylide Complex

Michael G. B. Drew,*a Ferida S. Esho,b and S. Martin Nelson*b

^a*Department of Chemistry, The University, Reading RG6 2AD, U.K.*

^b*Department of Chemistry, The Queen's University of Belfast, Belfast BT9 5AG, N. Ireland, U.K.*

Reaction of phenylacetylene with a di- μ -hydroxo-di-copper(ii) complex of a macrocyclic ligand affords diphenyldiacetylene together with a tetranuclear copper(i) complex containing a Cu₄-phenylacetylide core in which the terminal carbon atom is five-co-ordinate.

Current interest in the active sites of Type 3 copper proteins' and in bimetallic redox catalysts² has stimulated efforts towards the design of binucleating ligands³ capable of holding two metal ions in juxtaposition. Control of the metal . . . metal separation *via* appropriate ligand design may allow the incorporation of bridging substrate molecules and ions of varying size and chemical nature between the metal centres and may also allow the study of magnetic superexchange and substrate activation *via* electron transfer. We here report the oxidative coupling of phenylacetylene by a di- μ -hydroxo-di-copper (II) complex of the 20-membered macrocyclic ligand (L) and the structure of a tetranuclear copper(r) complex of phenylacetylide.

> $Ba(L)(ClO₄)₂ \cdot ROH$ $Cu^H₂(L)(OH)₂(ClO₄)₂ \cdot H₂O$ **(1)** (2) $\text{[Cu}_4^I(L)_2$ (CCPh)] $\text{[ClO}_4]_3$.0.5dpda **(3)**

The macrocycle (L) was prepared from 2,5-diformylfuran and 1,3-diaminopropane in MeOH or EtOH using $Ba(CIO₄)₂$ as template and isolated as the complex Ba(L)(ClO₄)₂·ROH(1)(R $=$ Me or Et) in $>70\%$ yield. Treatment of (1) with Cu^{II}- $(CIO₄)₂$ -6H₂O in EtOH afforded the di-Cu¹¹ complex Cu₂⁻¹ $(L)(OH)₂(ClO₄)₂·H₂O$ (2) in 55% yield. The occurrence of the di- μ -hydroxo-di-Cu^{II} structural unit in (2) was inferred from the antiferromagnetic behaviour ($\mu_{\text{eff}}/Cu = 1.37 \mu_{\text{B}}$ at 293 K and 0.70 μ_B at 93 K). Reaction of (2) with phenylacetylene in a 2 : **1** MeCN : MeOH solvent mixture at reflux for 15 min gave orange crystals of $\left[\text{Cu}_{4}^{1}(\text{L})_{2}(\text{CCPh})\right]\left[\text{ClO}_{4}\right]_{3}\cdot 0.5d$ pda **(3) (dpda** $=$ diphenyldiacetylene) followed by white crystals which were shown by chemical analysis and mass and **lH** n.m.r. spectra to be dpda. The total recovered yield of reacted phenylacetylene, *i.e.* $[CCPh]^-$ + dpda, was 0.95 mol per Cu atom. The **'H** n.m.r. spectrum of **(3)** in MeCN showed the expected features of the co-ordinated macrocycle together with a pair of nultiplets (2H + 3H) at δ 7.57 and 7.44 identical in position 2nd contour with those occurring in a spectrum of dpda, and **i** multiplet (5H) at δ 7.10 attributable to the co-ordinated Jhenylacetylide group. The structure of **(3)** was determined by .Y-ray analysis.

Crystal data: $C_{52}H_{50}O_{16}N_8Cl_3Cu_4$, $M = 1400.9$, triclinic, C_{52} and \overline{M}_{12} \overline{C}_{22} and C_{52} \overline{C}_{12} \overline{C}_{12} \overline{C}_{12} \overline{C}_{12} \overline{C}_{12} \overline{C}_{12} \overline{C}_{12} \overline{C}_{12} \overline{C}_{12 space group \overline{PI} , $\overline{Z} = 2$, $\overline{a} = 12.43(1)$, $\overline{b} = 16.67(1)$, $\overline{c} =$ 3079.9 \AA^3 , $d_e = 1.51$, $d_m = 1.49$ g cm⁻³. 1615 Independent reflections above background were measured by the diffractometer and refined to *R* 0.10. The asymmetric unit contains one discrete $\text{[Cu}^{\text{I}}_{4}(\text{L})_{2}(\text{CCPh})$ ³⁺ cation, three ClO₄⁻ anions (one disordered), and one-half of a centrosymmetric dpda molecule.[†] 15.37(1) \hat{A} , $\alpha = 83.3(1)$, $\beta = 103.1(1)$, $\gamma = 92.8(1)^\circ$, $U =$

Each macrocycle is bonded to a pair of copper atoms *via* the four imino-nitrogen atoms [Cu-N $1.94(3)$ -2.14(3) Å]. The conformation of each ' $Cu₂N₄$ ' moiety is such that the two metal atoms sit outside the approximate $'N_4'$ plane on the open face of the saddle-shaped macrocycle (Figure I). The four nitrogens of each macrocycle are planar to within 0.13 **A;** Cu(1A) and Cu(2A) lie $+0.77(1)$, and $+0.82(1)$ Å, respectively, from the 'N₄' plane of macrocycle A while Cu(1B), and Cu(2B) lie $+0.62(1)$ and $+0.79(1)$ Å from the 'N_a' plane of macrocycle B. The two pairs of copper atoms are linked *via* the *C-C* bond [1.38(5) A] of the phenylacetylide ion. The furan oxygen atoms are not co-ordinated: Cu . . . $O > 2.76$ Å.

The bonding of the two pairs of copper atoms to the acetylide group is different (Figure 2 and Table 1). The two copper atoms Cu(1A) and Cu(2A) of macrocycle **A** each have short contacts **[I** .93(3)-2.18(3)A] with both **C(30)** and C(31) and are clearly π -bonded to the C(30)–C(31) triple bond, the

Figure 1. The structure of the $[Cu_4(L)_2(CCPh)]^{3+}$ cation,

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.

	Cu(1A)	Cu(1B)	Cu(2A)	C(30)	C(31)
Cu(1A)				2.18	2.14
Cu(1B)	4.26		--	2.12	2.63
Cu(2A)	2.95	2.98		2.04	1.93
Cu(2B)	3.09	2.88	3.44	1.83	3.18

Table 1. Copper-copper and copper-carbon distances **(A).**

Figure 2. The structure of the 'Cu₄(CCPh)' core.

dihedral angle between the $Cu(1A)-C(30)-C(31)$ and $Cu(2A)$ $-C(30)-C(31)$ planes being 82(1)°. Cu(2B) is σ -bonded to the terminal carbon atom [Cu(2B)-C(30), 1.83(3) **A]** with the Cu(2B)-C(30)-C(31) bond angle $167(3)$ °. The situation with $Cu(1B)$ is less clear. This atom is strongly bonded to $C(30)$ at 2.12(3) **A.** It is also 2.63(3) A distant from C(31), but this cannot represent other than a very weak interaction. The Cu(1B)-C(30)-C(31) bond angle is 95(2)° compared to 66(2)° and $70(2)^\circ$ for the corresponding angles involving the two π bonded copper atoms of macrocycle **A.** Moreover, since the π -bonding capacity of the acetylenic triple bond would appear to be satisfied by $Cu(1A)$ and $Cu(2A)$ we therefore regard the Cu(1B)–C(30) bond as predominantly σ in nature. Thus, while the geometry around $C(31)$ is a distorted tetrahedron, $C(30)$ **is** formally five-co-ordinate with a very irregular polyhedron.

Of the six Cu . . . Cu distances (Table l), four fall between 2.88(1) and 3.09(1) Å *i.e.* at the high end of the range of Cu ... Cu separations observed in other di- and poly-nuclear $Cu¹$ complexes.^{4,5} Molecular orbital calculations⁴ on Cu_n⁺ $(n =$ 2-4) model systems have shown that while there will be closed shell repulsions between the d¹⁰ shells, these may be overlaid by slight attractive interactions through mixing of metal s- and p-orbitals. However, it is unlikely that direct metal-metal bonding, as in transition metal-acetylide clusters,⁶ plays any major role; rather, it is the bridging acetylide ion that is largely responsible for the aggregate structure.

The expected lengthening^{6} of the acetylenic triple bond $[{\rm C}(30) - {\rm C}(31), 1.38(5)$ Å is particularly marked in this complex. The deviation from linearity of $C(30)$ -C(31)-C(32) is 34(3)^o and the C(31)–C(32) bond distance is 1.47(5) Å.

Received, 16th August 1982; Corn. 984

References

- 'The Biochemistry of Copper,' eds. J. Peisach, P. Aisen, and W. Blumberg, Academic Press, New York, 1966; **J. A.** Fee, *Struct. Bonding (Berlin),* 1975, **23, 1** ; **H.** Beinart, *Coord. Chem. Rev.,* 1980,33,55; M. E. Winkler, **K.** Lerch, and **E. I.** Solomon, *J. Am. Chem. Soc.,* 1981, **103,** 7001.
- J. P. Collman, C. M. Elliott, T. R. Halbert, and B. **S.** Tourog, *Proc. Natl. Acad. Sci., USA,* 1977, **74,** 18.
- U. Cassellato, **P. A.** Vigato, D. **E.** Fenton, and M. Vidali, *Chem. Soc. Rev.,* 1979, **8,** 199.
- P. **K.** Mehrotra and R. Hoffmann, *Inorg. Chem.,* 1978, **17,** 2187, and references therein.
- A. Avdeef and **J.** P. Fackler, *Inorg. Chem.,* 1978, **17,** 2182, and references therein.
- See, for example, **A.** J. Carty, *Pure Appl. Chem.,* 1982, **54,** 113.