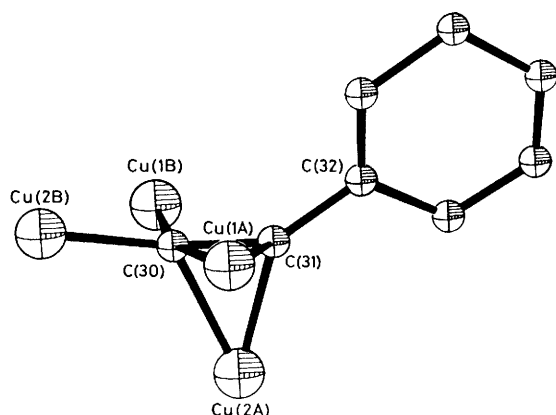


Table 1. Copper-copper and copper-carbon distances (Å).

	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

**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) Å] 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) Å. It is also 2.63(3) Å 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)° 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 1), 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 Cu^I 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 lengthening⁶ of the acetylenic triple bond [C(30)–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)° and the C(31)–C(32) bond distance is 1.47(5) Å.

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