A Tetranuclear Cluster Complex of Copper(I) with Bridging Aryl Ligands: the Crystal Structure of (4-Methyl-2-cupriobenzyl)dimethylamine

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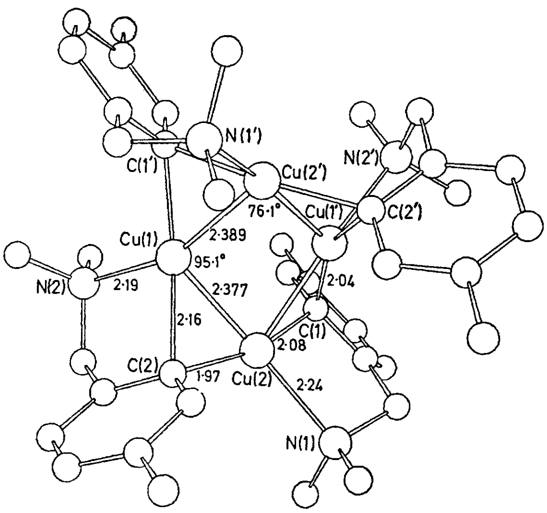
Summary An X-ray diffraction analysis of (4-methyl-2-cupriobenzyl)dimethylamine establishes its tetranuclear nature; the aryl ligands bridge copper atoms separated by 2·38 Å.

The synthesis of stable aryl copper(I) complexes has been described[1] but their structures are not known with certainty; phenylcopper is supposed to be polymeric[2] while a cubic arrangement with mobile-bridging benzotrifluoride groups has been proposed for the octameric *m*-(trifluoromethyl)-phenylcopper(I).[3] (4-Methyl-2-cupriobenzyl)dimethylamine exists in solution as discrete tetramers[1] which suggests that its structure is based on a tetranuclear cluster similar to that of $[CuI(AsEt_3)]_4$.[4] Our present crystallographic results define the arrangement.



Figure

Crystals (from benzene) are monoclinic with $a = 18{\cdot}02$, $b = 11{\cdot}35$, $c = 19{\cdot}58$ Å, $\beta = 97{\cdot}6°$; space group $C2/c$; $Z = 4$. Structural analysis was based on Fourier and least-squares analysis of 1424 reflexions observed on a PAILRED diffractometer (Mo-K_α) and having $F^2 \geqslant 2{\cdot}0\ \sigma(F^2)$. R has converged to 0·07. The complex has C_2 symmetry in the crystal, its stereochemistry being illustrated in the Figure; e.s.d.'s in the bond lengths average 0·003 Å (Cu–Cu), 0·015 Å (Cu–C and Cu–N), and 0·02 Å (C–C and C–N).

The observation of an aryl group bridging transition metals has a precedent only in an osmium trinuclear complex.[5] As in Al_2Ph_6 and $Al_2Me_4Ph_2$,[6] the aryl ligand has its plane oriented perpendicular to the metal–metal bond but it is only in the osmium complex that the M–C–M bond angle approaches 90°. The maximum overlap and alternative 'explanations' of acute M–C–M bond angles in alkyl- and aryl-bridged electron deficient molecules are discussed elsewhere.[7] We prefer to describe the bonding in the present complex in terms of the metal using only *s* and *p* valence orbitals to any significant extent and to rule out direct metal–metal bonding in spite of the very short Cu–Cu distances; each copper atom then has a distorted trigonal planar stereochemistry. An alternative description would be to imagine that each metal ion obeys the rare-gas rule when it becomes necessary to regard the direct bond between the bridged copper atoms as of order two. Such extensive use of metal *d* orbitals seems to us to be unlikely on promotion energy considerations.

The copper atoms form a distorted 'butterfly' arrangement. The origin of this distortion from a more regular cluster arrangement is not clear at the present time.

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