Crystal Structure (at $-40°$) of Tetrakis[trimethylsilylmethylcopper(I)], an Alkyl Bridged, Square Planar, Tetranuclear Copper(I) Cluster

By John A. J. Jarvis,* Barry T. Kilbourn, and Ronald Pearce
(*Imperial Chemical Industries Limited, Corporate Laboratory, P.O. Box* 11, *The Heath, Runcorn, Cheshire* WA7 4QE)

and Michael F. Lappert
(*School of Molecular Sciences, University of Sussex, Brighton* BN1 9QJ)

Summary $(Me_3SiCH_2Cu)_4$ consists of discrete, centrosymmetric, tetrameric units containing a square plane of copper atoms (Cu–Cu 2·42 Å), with the methylene carbons lying in the same plane and bridging the edges.

No crystal structures have yet been reported of copper alkyls although *X*-ray analyses of copper(I) aryls[1] have revealed tetra- or hexa-meric copper clusters with aryl groups bridging the edges. We have now determined the structure of the d^{10} complex, tetrakis[trimethylsilylmethylcopper(I)],[2] that is found to contain an unusual square planar arrangement of copper atoms.

Crystal data: $C_{16}H_{44}Cu_4Si_4$, colourless, $M = 603{\cdot}0$, $a = 6{\cdot}355(4)$, $b = 12{\cdot}636(7)$, $c = 17{\cdot}938(11)$ Å, $\beta = 90{\cdot}84(5)°$, $U = 1440(1)$ Å^3, space group $P2_1/c$, $D_c = 1{\cdot}390$ for $Z = 2$, $F(000) = 624$, Mo-K_α radiation (Nb filter), $\mu = 31{\cdot}8$ cm^{-1}. After preliminary photography to identify the space group, full three-dimensional data ($2\theta \leqslant 50°$) were collected using a Picker automatic diffractometer. The crystal was kept at *ca.* −40° while being oriented and during data collection by using special diffractometer attachments.[3] The structure was refined to $R = 0{\cdot}051$ for 2044 reflections.

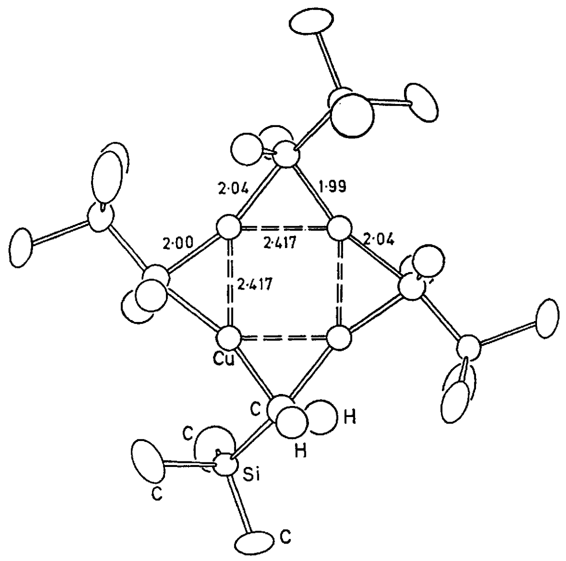

FIGURE. *The molecular structure of tetrakis[trimethylsilylmethylcopper*(I)]. *The positions of the methyl hydrogens are not shown.*

The crystal contains discrete, centrosymmetric, tetrameric units with a square plane of copper atoms (Figure). The methylene carbons bridge the edges and lie in the Cu_4 plane (deviations from the plane, 0·06 and 0·02 Å). One of the silicon atoms is slightly out of this plane (deviation 0·68 Å) while the other is in the plane (deviation 0·08 Å). The positions of the hydrogen atoms bound to the methylene carbons have been determined and the co-ordination at these carbon atoms can be considered as tetrahedral with the fourth bonding vector intersecting the Cu–Cu axis off centre. We propose that the alkyl bridge involves a three-centre, two-electron bond with linear co-ordination at copper and that copper–copper bonding is relatively unimportant. In such three-centre bonds the bonding orbitals do not lie along the internuclear axes (see *e.g.* Al_2Me_6)[4] and consequently in the present complex the C–Cu–C angle of 164° does not preclude linear co-ordination at copper. The apparent pinching-in of the copper atoms from a regular Cu_4C_4 square arises from a description using inter-nuclear vectors and is not due to Cu–Cu interactions.

Bridging alkyls are found in compounds of the Groups IA to IIIA metals but to our knowledge this is the first such example in the transition-metal series. Further, a square-planar arrangement of metals is unusual in transition-metal clusters,[5] although a planar configuration of four coppers has been reported in tetrakis[1,3-dimethyltriazenocopper-(I)].[6]

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