A Unique Six-membered Ring in a Sulphur Bridged Trigonal Copper(I) Trimer: The Crystal Structure of *cyclo*-Tris-μ-(trimethylphosphine sulphide)-tri-[chlorocopper(I)]

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Summary The molecular structure of $[Cu(Me_3PS)Cl]_3$ consists of a six-membered ring of copper and sulphur atoms in which trigonally co-ordinated copper atoms are bonded to two bridging sulphur atoms and a terminal chlorine atom.

WE report the crystal structure of $[Cu(Me_3PS)Cl]_3$ which verifies that a new class of polymeric Cu^I complexes has been isolated and characterized. The compounds $[CuLX]_n$ (X = Cl, Br, I, SCN; L = a tertiary phosphine sulphide) can be isolated when phosphine sulphides are combined with CuX salts or when a co-ordinating anion is added to the $[CuL_3]^+$ complexes in a non-aqueous solvent such as ethanol or acetonitrile. The $[CuLX]_n$ compounds are fairly insoluble and ν_{P-S} is shifted $\sim$50 cm^{-1} to lower energy as compared to ν_{P-S} of the free ligand†. The insolubility and the large $\Delta\nu_{P-S}$ suggest a polymeric compound possibly containing a bridging phosphine sulphide group. Polymeric structural precedents are known for Cu^I complexes of the type $[CuLX]_4$[1] and $[CuL_2X]_2$,[2] where X = halide or pseudohalide and L = neutral ligand such as a tertiary phosphine or arsine. This paper reports the first structure for a trimeric Cu^I complex.

The compound $[Cu(Me_3PS)Cl]_3$ was prepared by adding LiCl to a solution of $[Cu(Me_3PS)_3]BF_4$ in MeCN.

Crystal data: $[Cu(Me_3PS)Cl]_3$, $M = 621{\cdot}36$, colourless crystals (MeCN), monoclinic, space group *Im* (an alternate setting of Cs^3-Cm), $a = 6{\cdot}294(3)$, $b = 20{\cdot}399(11)$, $c = 9{\cdot}271(5)$ Å, $\beta = 99{\cdot}04(2)°$, $Z = 2$, $D_m = 1{\cdot}75$, $D_c = 1{\cdot}755$ g cm^{-3}. A set of 2501 independent non-zero reflections was obtained by counter methods. The structure was solved by the heavy atom method, and has been refined by least-squares techniques to a final *R* factor of 0·024.

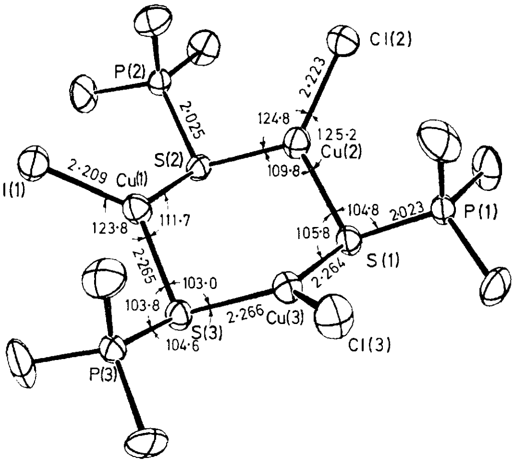

FIGURE. *A perspective drawing of* $[Cu(Me_3PS)Cl]_3$. *Atoms with designations of* (2) *and* (3) *are equivalent and related to each other by the crystallographic mirror plane.*

The structure of the trimer consists of a six-membered ring of alternating Cu atoms and bridging S atoms (Figure), with a crystallographic mirror plane bisecting the ring. The ring has the chair conformation with approximate C_{3v} symmetry, and the trimethylphosphine groups of the

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† The P–S stretching frequency usually shifts 15–35 cm^{-1} to lower energy when the phosphine sulphide ligand forms a non-bridging u^I complex.

bridging phosphine sulphides occupy equatorial positions. The co-ordination geometry around copper is planar, even though the S–Cu–S angles average 111°, a distortion from the idealized trigonal value of 120°. This leads to the chlorine atoms occupying positions intermediate between axial and equatorial. The ring angles at sulphur are smaller, averaging 105°, and this requires considerable puckering of the ring. There is no evidence for direct metal–metal interactions, with the Cu(1)–Cu(2) and Cu(2)–Cu(3) distances being 3·545 and 3·610 Å, respectively. The Me_3PS geometry is similar to that found in the free ligand and in $[Cu(Me_3PS)_3]ClO_4$,[3] with nearly tetrahedral co-ordination of sulphur and phosphorus. The sulphur bridge is symmetric, and the geometry around the sulphur atom is pyramidal with all bond angles being approximately 105°.

This structure is the first showing a bridging phosphine sulphide, although other sulphur ligands form bridges.[4] A bridging phosphine sulphide is remarkable in the presence of a terminal chlorine atom, as a halide often acts as a bridging atom with Cu^{I}.[2,5] It is a property of the bridging sulphur atom that is most likely responsible for the existence of a trimer rather than a more common dimer involving a four-membered ring. The smaller ring would require sulphur ring angles to be highly strained (less than 90°). Similar considerations were used to explain the formation of a trimeric palladium complex with a mercapto-ligand, although the corresponding nickel complex is a dimer.[6]

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