The Crystal Structure of a Trigonal Planar Copper(I) Complex

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Summary Crystals of tris(trimethylphosphine sulphide)-copper(I) perchlorate have been shown by *X*-ray diffraction to contain monomeric, trigonally co-ordinated cations, the free ligand being little changed in geometry upon co-ordination.

We report the crystal and molecular structure of tris(trimethylphosphine sulphide)copper(I) perchlorate, [Cu-$(SPMe_3)_3]ClO_4$. This compound was first prepared by Meek and Nicpon in the course of their studies on the co-ordination chemistry of trialkyl- and triaryl-phosphine sulphides.[1,2] The reaction of these compounds with copper(II) salts usually involves reduction to copper(I) and formation of complex cations of the type CuL_4^+. However, in the case of trimethylphosphine sulphide, a product was isolated and characterized as the novel salt, $[Cu(SPMe_3)_3]ClO_4$, which would involve three-co-ordinate copper. It appeared that an *X*-ray diffraction study would be particularly useful, since structural studies on trigonal planar co-ordination compounds are still rare.[3,4]

Crystal data: $CuS_3P_3C_9H_{27}$ ClO_4, $M = 511{\cdot}96$, colourless platelets, from acetone; monoclinic, space group $P2_1/c$; $a = 6{\cdot}207(2)$, $b = 16{\cdot}465$ (5), $c = 22{\cdot}144$ (7) Å, $\beta = 97{\cdot}63$ (3)°; $Z = 4$; $D_m = 1{\cdot}44(1)$, $D_c = 1{\cdot}448$ g/cm³. 2600 non-zero reflections were obtained by the equi-inclination Weissenberg technique; least-squares refinement of a model with 150 variables reduced R to 0·11; refinement continues. The structure consists of discrete, well separated $Cu(SPMe_3)_3{}^+$ cations and perchlorate counterions. Thus, the closest Cu · · · Cl contact is 6·9 Å, while the shortest Cu · · · Cu distance is 6·21 Å. The perchlorate ions are apparently disordered in a way not yet understood. The structure and dimensions of the cation are shown in the Figure. Co-ordination about copper is indeed close to trigonal planar with the ligands bonded through sulphur. The copper atom is co-planar with the three sulphur atoms, while the phosphorus atoms P(1), P(2), and P(3) lie only −0·46, +0·28 and +0·76 Å, respectively, from this plane. Bond angles about copper are close to the idealized value of 120°. The Cu–S distances are similar to those found in copper(I) thiourea complexes.[5,6] Although the Cu–S distances are somewhat shorter than the sum of covalent tetrahedral radii for Cu and S (2·39 Å),[7] they are not sufficiently short to suggest appreciable metal–sulphur multiple bonding.[8]

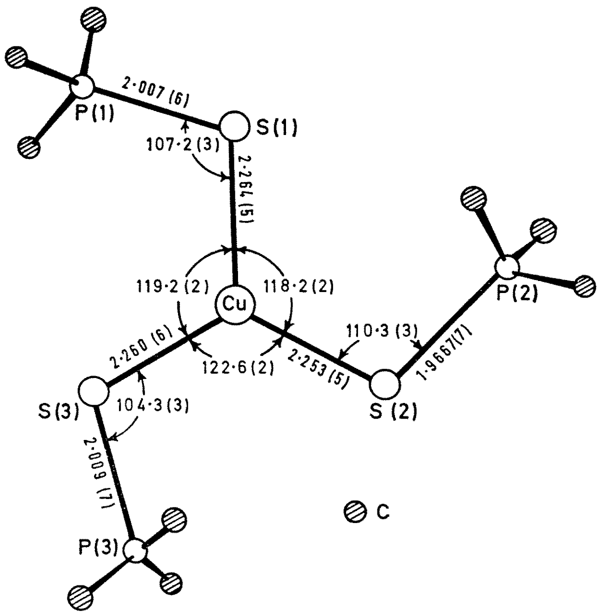

FIGURE. *View of* $[Cu(SPMe_3)_3]$ *down the pseudo-threefold axis. The plane of the sulphur atoms is inclined* 23° *to the* bc *plane.*

Although there is some scatter among individual values, the average bond angle about sulphur (107·3°) is quite close to tetrahedral, suggesting formal sp^3 hybridization for sulphur.

We have also determined, by counter methods, the structure of free trimethylphosphine sulphide. Crystal data: SPC_3H_9, $M = 108{\cdot}08$, colourless plates, from methanol; monoclinic, space group $P2_1/m$; $Z = 2$; $a = 6{\cdot}266(2)$, $b = 7{\cdot}588(5)$, $c = 6{\cdot}642(4)$ Å, $\beta = 90{\cdot}36(5)$°; $D_m = 1{\cdot}14$, $D_c = 1{\cdot}139$ g/cm³; least-squares refinement of a model with 28 variables has reduced R to 0·05 for 500 independent reflections. The molecules lie on a mirror plane. The geometry of trimethylphosphine sulphide changes little upon co-ordination. The P–S distance in the free ligand, [1·959 (2) Å] is only slightly shorter than the average value found in the complex [1·994(17) Å], suggesting little change in the S–P bond order upon co-ordination. P–C distances are 1·798(2) Å in the free ligand, and range from 1·756(10) to 1·809(10) Å in the complex [average 1·793(8) Å]. S–P–C angles range from 112·9° to 113·8° in the free ligand [average 113·2(3)°] and from 108·9° to 114·1° in the complex [average 111·6(6)°].

The lack of change in the trimethylphosphine sulphide ligand upon co-ordination and the tetrahedral angles at sulphur in the complex suggest that sulphur is bonded to the metal by simple σ-donation of a filled sp^3 orbital.[†]

The structures of other three-co-ordinate copper(I) complexes involving thiourea,[5] phosphine,[8] halide,[8] cyanide,[9] olefinic,[10] and acetylenic[11] ligands, have been reported. However, in each case the structure is polynuclear with bridging ligand groups. To our knowledge, the tris(trimethyl phosphine sulphide)copper(I) cation is the first structure reported of a trigonal monomeric copper complex.

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[†] However, we have just determined the crystal structure of the methyl iodide adduct of trimethylphosphine sulphide, $[Me_3PSMe]I$. This compound is ionic, with the fourth methyl group bonded to sulphur. The P–S distance, which should correspond to a single P–S bond, has increased to 2·05(1)Å, while the P–S–C angle is 101°.

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