The Molecular Structure of 2-(Diphenylphosphine oxide)ethyldiethylammonium Dichlorocuprate(I): Single-crystal *X*-Ray Analysis[1]

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Summary The product formed upon reaction of 2-(diphenylphosphino)ethyldiethylamine and copper(II) chloride in ethanol has been shown to be an ionic compound, 2-(diphenylphosphine oxide)ethyldiethylammonium dichlorocuprate(I) by single-crystal *X*-ray analysis: this is the first *X*-ray analysis of a discrete dichlorocuprate(I) anion.

WHILE attempting to prepare a stable copper(II) complex containing a Cu^{II}–P^{III} bond by reacting ethanolic copper(II) chloride with the "mixed" nitrogen–phosphorus bidentate ligand, 2-(diphenylphosphino)ethyldiethylamine, Ph_2PCH_2-CH_2NEt_2, we have discovered an interesting reaction in which simultaneous oxidation of the tertiary phosphine to the phosphine oxide, reduction of copper(II) to copper(I), and quaternization of the amine function takes place. We can find no precedent in the literature for this behaviour although it is known that the reaction of tertiary phosphines with copper(II) halides leads to either copper(I) tertiary phosphine complexes[2] or copper(II) complexes with the oxide of the parent phosphine.[3] The complex has been formulated as the dichlorocuprate(I) salt of the 2-(diphenylphosphine oxide)ethylammonium cation. This compound may also be prepared by reacting copper(I) chloride with the chloride of this cation.[4] We report the results of a single-crystal *X*-ray diffraction study of this salt.

The pale yellow needles of the salt crystallized from ethanol. A single crystal (approximately 0·15 mm × 0·15 mm × 0·90 mm) was selected and mounted inside a glass capillary and sealed from the atmosphere. Precession photographs (Mo-K_α, $\lambda = 0{\cdot}7107$) revealed a monoclinic crystal system mounted along the unique axis, *b*: $a = 12{\cdot}54$ Å, $b = 9{\cdot}12$ Å, $c = 21{\cdot}73$ Å, $\beta = 123{\cdot}1°$; D_c for $CuCl_2C_{18}H_{24}NPO$ and $Z = 4$ 1·39, D_m (flotation) of 1·37 g/cm.[3] Systematic extinctions uniquely indicated space group $P2_1/c$.

Three-dimensional intensity data were recorded on a Weissenberg camera using Cu-K_α radiation ($\lambda = 1{\cdot}5418$) and multiple film equi-inclination techniques. Diffraction maxima were estimated visually with the aid of a standard intensity strip produced from the same crystal. In all, 2663 unique non-zero reflections were recorded and used in the analysis. Initial attempts to locate the position of the copper atom from the Patterson map were unsuccessful. The data were then phased by application of the symbolic addition procedure.[5] The resulting *E*-maps indicated positions for the copper and the two chlorine atoms. From this point, the analysis followed the heavy-atom procedure[6] eventually revealing the positions of all non-hydrogen atoms. Full-matrix least-squares refinement of all atomic positions and isotropic temperature factors for carbon, nitrogen, oxygen, and phosphorus atoms and anisotropic temperature factors for copper and chlorine atoms, using all observed reflections, gave a conventional *R* value of 11·0%.

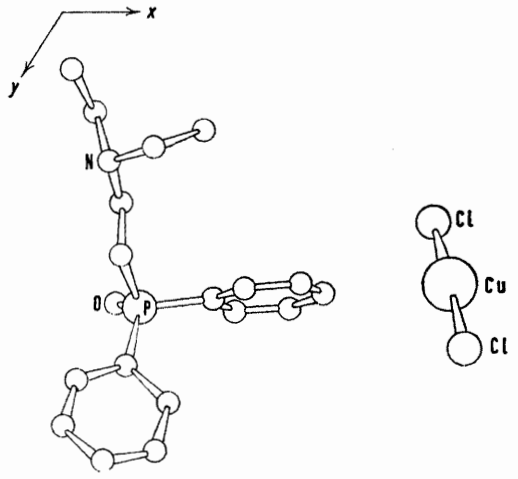

FIGURE. *Projection of the molecular structure on to the* ac *plane.*

The projection of one molecular unit on to the *ac* plane is shown in the Figure. The structure is clearly composed of two separate units: a linear dichlorocuprate(I) anion and the 2-(diphenylphosphine oxide)ethyldiethylammonium cation. The closest anion–cation contact distance is 3·87 Å between one of the chlorine atoms of the anion and the nitrogen of the cation. The average Cu–Cl distance is 2·09 Å. We were unable to find any previous report of an *X*-ray structural determination of a discrete dichlorocuprate(I) anion; this appears to be the first measurement of a Cu–Cl distance in such a species.[7]

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