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A Cationic Trinuclear Copper(I) Complex. The Structure of the 1:1 Derivative of CuCl with Bis-(diphenylphosphino)methane

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Recently we have reported[1] the structure of the 2/1 reaction products of copper(I) halides and bis(diphenylphosphino)methane (DPM), which are characterized by a planar Cu_4 core with two copper atoms in a tetrahedral and the other two in a trigonal geometry.

However, the above reagents, under suitable conditions, may give a series of compounds $(CuX)_n$-DPM_m with different m/n ratio.[2] This prompted us to rationalize the formation of the different species on the basis of structural results of the most representative compounds of such series. The structure of the compound (CuCl)DPM is now reported.

Crystal data

Monoclinic $P2_1/m$, $a = 13.355(6)$, $b = 22.383(9)$, $c = 14.743(7)$; $\beta = 123.1(1)$, $Z = 6$, $Dc = 1.35$ g/cm^3 (as monohydrate), $Dm = 1.38(2)$ g/cm^3 (by flotation). Mo$K\alpha$ $\lambda = 0.7107$ $\mu = 12.0$ cm^{-1}. A crystal 0.3 × 0.4 × 0.4 mm was mounted on an automated SIEMENS diffractometer and intensity data collected by θ–2θ scan technique to $2\theta \leqslant 50°$ with Mo$K\alpha$. A total of 3150 independent reflections were found to be statistically above background ($I > 3\sigma(I)$) and these were used to solve and refine the structure after correction for Lorentz and polarization factors. No absorption correction was applied because the transmission factor does not significantly vary in the θ range of interest. The structure was solved by standard heavy atom methods and refined by least-squares method with anisotropic temperature factors for copper and phosphorus atoms to a final conventional R of 0.092. Refinement and geometrical parameters of the compound obtained in both the $P2_1$ and $P2_1/m$ space groups suggested the choice of the latter.

The crystal structure may be described as built of discrete anions Cl^- and trinuclear cations $[Cu_3Cl_2DPM_3]^+$. The cation is shown in Fig. 1 with some bond lengths and angles of interest. The crystallographic mirror plane imposes C_s symmetry in the trimeric unit, so that Cu(1), Cl(1) and Cl(2) atoms lie on the mirror plane. Similar trinuclear units have been found in other compounds,[3] such as $(CuCl)_3(Me_3PS)_3$, where the chlorine atoms act as mono-dentate ligands. The Cu_3Cl_2 core may be described as a distorted trigonal bipyramid with the three copper and the two chlorine atoms at the equatorial and axial vertices respectively. Each DPM molecule bridges one of the three sides of the copper triangle with Cu(1)–Cu(2) and Cu(2) . . . . Cu(2)′ distances of 3.175(4) and 3.281(3) Å respectively.

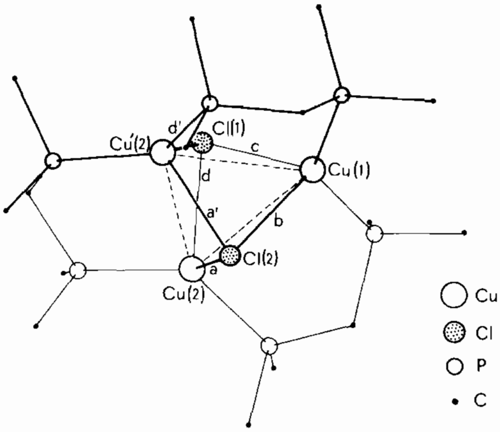
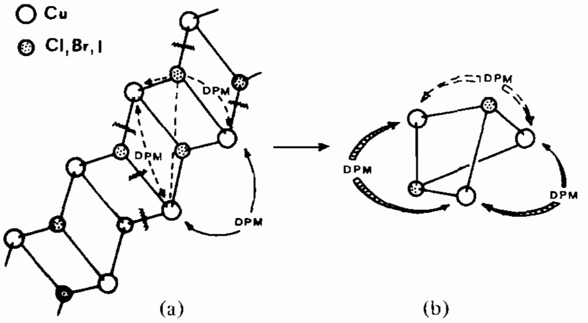


Fig. 1. A perspective view of the $[Cu_3ClDPM]^+$ cation. Some bond lengths and angles are: $a = 2.438(4)$, $b = 2.678(6)$, $c = 2.407(7)$, $d = 2.598(3)$ Å, aa′ = 84.6, ab = 76.6, cd = 78.6, cd′ = 78.3° (all ± 0.1°).

Thus the copper atoms are tetracoordinate, each being bonded to two chlorine and two phosphorus atoms. The two chlorine atoms are tricoordinated in a way similar to those already found in $(CuCl)_2DPM$[1b] and $(CuCl)_3(C_3H_6S_3)$.[4] However, in the latter compound the CuCl distances are nearly all equal (from 2.332(6) to 2.366(6) Å), whereas they are significantly different with respect to the former compound (from 2.315(6) to 2.740(4) Å). In the present complex the Cl(2) atom binds the copper atoms with two short bond lengths (2.438(4) Å) and one long (2.678(6) Å), whereas Cl(1) binds the copper atoms with one short (2.407(7) Å) and two long (2.598(3) Å) bonds. These differences seem due, as already suggested,[1b] to the influence of steric hindrance of the chlorine atoms with the CH_2 group of DPM ligand. Finally the Cu–P bond lengths (mean 2.257(4) Å) appear significantly longer than those (2.196(4) Å) found in $(CuCl)_2DPM$ as well as those found in $(CuBr)_2DPM$ (2.19(1) Å)[1c] and $(CuI)_2DPM$ (2.224(8) Å).[1a]

We will report[1c] elsewhere a simple interpretation of the structure of this and other compounds of general formula $(CuX)_nL_m$ starting from a common parent structure, the double stranded chain of Figure 2(a), already found in $(CuX)_nL_m$ complexes with non-bulky L ligands.[5] However, when L is a bulky ligand this chain is broken down mainly because of steric ligand–ligand and chain–ligand interactions. Figure 2 sketches the formation of the ionic species $[(Cu_3Cl_2)DPM_3]^+$.



(a) (b)

Fig. 2. A possible interpretation of the formation of $[(Cu_3Cl_2)DPM_3]^+$ species from the double-stranded chain.

The structural results are in good agreement with conductivity measurements[2] in dichloroethane solutions, which suggest the (CuX)DPM compounds to behave as uni-univalent electrolytes, probably dissociated as:

$$(CuCl)_3DPM_3 \longrightarrow Cl^- + [Cu_3Cl_2DPM_3]^+$$

(in the case of the chlorine derivative).

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References

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