Molecular Structure of Di-μ-chlorotris-(*trans*-cyclo-octene)dicopper(I)

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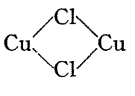
Summary The crystal structure of the title compound has been determined, and conformational parameters for the cyclo-octene units are reported.

As part of a programme devoted to the correlation of the physicochemical properties of cyclo-olefins and their conformations, a structural investigation of a complex of CuCl with *trans*-cyclo-octene has been undertaken.

Colourless crystals (m.p. 73°—76° with dec.) were prepared from *trans*-cyclo-octene [1] and $CuCl_2$ in methanolic and/or ethanolic dilute solution by reduction with SO_2.[2] The analysis is in accordance with the formula $CuCl(C_8H_{14})_{1\cdot5}$. The compound is insoluble in most organic solvents and loses olefin on standing. Two possibilities should be considered: either the true formula corresponds to a ratio Cu : olefin = 1 : 1 so that there are olefin molecules clathrated in the crystal, *i.e.* one olefin molecule to every two $CuCl(C_8H_{14})$ units; or $CuCl\ (C_8H_{14})_{1\cdot5}$ is the true empirical formula but in this case two differently co-ordinated copper atoms are probably present in the crystal.

X-Ray diffraction studies of single crystals of the complex showed it to be triclinic; space group $P\bar{1}$ (later confirmed by the structural analysis) with unit-cell dimensions $a = 14{\cdot}95$; $b = 11{\cdot}50$; $c = 11{\cdot}20$ Å; $\alpha = 119°\ 15'$; $\beta = 114°\ 2'$; $\gamma = 101°\ 40'$. D_o ranges between 1·25 and 1·35 g.cm.$^{-3}$ ($D_c = 1{\cdot}32$ g.cm.$^{-3}$) indicating the presence of two formula units $Cu_2Cl_2(C_8H_{14})_3$ per unit cell. Intensities of 2029 independent non-zero *hkl* reflexions were obtained with normal Weissenberg techniques. A three-dimensional Patterson vector map yielded the position of copper and chlorine atoms and demonstrated the presence of the bridged nonplanar system



(I)

in the molecule. Fourier synthesis calculation showed the location of carbon atoms. The molecules of the complex $Cu_2Cl_2(C_8H_{14})_3$ have no symmetry element (see Figures 1

and 2, and Table). Cu(1) shows an almost undistorted trigonal-pyramidal co-ordination. The apical position is occupied by a chlorine atom weakly bonded to Cu(1) at 2·96 Å; another chlorine atom belonging to a centrosym-

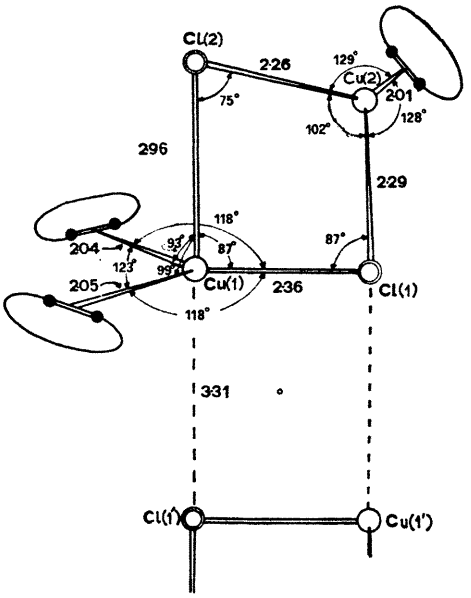


FIGURE 1. *Conformational parameters of the bridged system* (I)

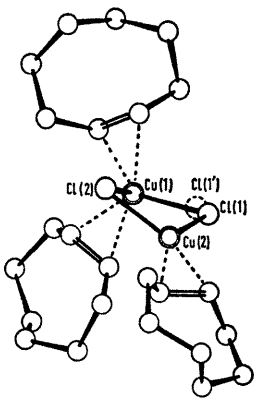


FIGURE 2. *The molecular structure of* $[Cu_2Cl_2(C_8H_{14})_3]$

metrical molecule lies at 3·3 Å in the opposite apical direction (Figure 1). An analogous situation was found in case of the $[CuCl(C_8H_8)]_n$ and $[(C_7H_6)CuCl]_4$, in which all the Cu atoms are geometrically equivalent.[3] Cu(2) shows a trigonal co-ordination, the apical positions are in this case not occupied (Figure 1). It is apparent that two olefin molecules are π-bonded to one copper atom and only one olefin to the other copper atom of the bridged system. The type of co-ordination of the copper atoms is not the same. The presence of differently co-ordinated cuprous atoms in the same molecule was never observed. At the present stage of three-dimensional refinement ($R = 0{\cdot}13$) performed with block-matrix least squares, the standard deviations for the bond lengths are *ca.* 0·03 Å; for the bond angles *ca.* 2°.

TABLE

Interatomic distances, bond angles, and torsional angles of the bridged system (I)

Cu(1)–Cl(1)	..	2·36 Å	Cu(1)–Cl(1)–Cu(2)	.. 87°
Cu(1)–Cl(2)	..	2·92 Å	Cl(1)–Cu(2)–Cl(2)	.. 102°
Cu(2)–Cl(1)	..	2·29 Å	Cu(2)–Cl(2)–Cu(1)	.. 75°
Cu(2)–Cl(2)	..	2·26 Å	Cl(2)–Cu(1)–Cl(1)	.. .. 84°
Cu(1) · · · Cu(2)		3·21 Å	Cu(1)–Cl(1)–Cu(2)–Cl(2)	31°
Cl(1) · · · Cl(2)	..	3·55 Å	Cl(1)–Cu(2)–Cl(2)–Cu(1)	−25°
Cu(1) · · · Cl(1)′		3·34 Å	Cu(2)–Cl(2)–Cu(1)–Cl(1)	24°
Cu(1)–(C=C)(1)		2·04 Å	Cl(2)–Cu(1)–Cl(1)–Cu(2)	−23°
Cu(1)–(C=C)(2)		2·05 Å		
Cu(2)–(C=C)(3)		2·01 Å		

The three cyclo-olefins of the structural unit have, within the standard deviations, a C_2 symmetry; their conformation has no pseudo-mirrors as might be expected for the cyclo-octene.[4] Figure 3 shows the conformational parameters

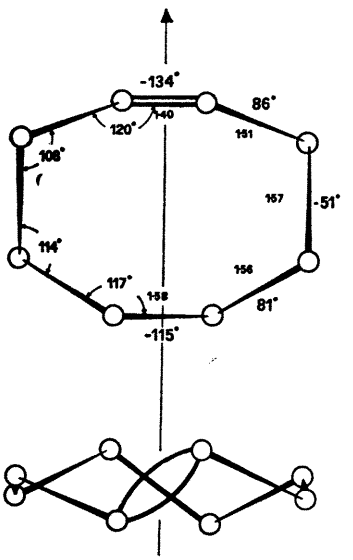


FIGURE 3. *Averaged internal conformational parameters of the cyclo-octene rings of* $[Cu_2Cl_2(C_8H_{14})_3]$

averaged on the three cyclo-octene molecules. Considering the almost exact C_2 symmetry, averaged data are given only for the asymmetrical part of the molecule.

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[4] J. D. Dunitz, "Perspectives in Structural Chemistry," Wiley, New York, Vol. II, 1968, 49.