The crystal and molecular structure of the dichloroethane solvate of the 2:1 derivative of copper(I) chloride and bis(diphenylphosphino)methane.

By G. Nardin and L. Randaccio, *Istituto di Chimica, Università di Trieste, 34127 Trieste, Italy*

$C_{49}H_{42}Cl_4Cu_4P_4.xC_2H_4Cl_2$ is monoclinic, space group $C2/c$, $Z=8$, with $a=26\cdot42$, $b=12\cdot30$, $c=21\cdot58$ Å and $\beta=129\cdot1°$. The crystal structure was refined by least-squares to an R of $0\cdot105$ for 2230 reflexions. The crystal is built up of discrete tetranuclear $(CuCl)_4DPM_2$ and dichloroethane molecules. The $(CuCl)_4$ core has a stepped geometry with two Cu atoms trigonally surrounded by two Cl and one P atom, the other two being surrounded by three Cl and one P atom in distorted tetrahedral geometry. The bond lengths are: Cu–Cl $2\cdot270$ (4)–$2\cdot740$ (4) Å; Cu–P $2\cdot195$ (4)–$2\cdot197$ (5) Å.

Introduction

It has been reported (Marsich, Camus & Cebulec, 1972) that copper halides react with diphosphine ligands such as bis(diphenylphosphino)methane (DPM) giving compounds with several stoichiometries $(CuX)_nDPM_m$, where X = Cl, Br, I.

We have already reported the structure of $(CuI)_2DPM$ (Marsich, Nardin & Randaccio, 1973). We report here the results for an analogous chloride.

Experimental

Cell parameters determined from Weissenberg photographs and on a three-circle automated Siemens diffractometer (Mo $K\alpha$, $\lambda=0\cdot7107$Å) are $a=26\cdot42$, $b=12\cdot30$, $c=21\cdot58$Å and $\beta=129\cdot1°$, $Z=8$,* $D_c=1\cdot58$, $D_m=1\cdot56$ g cm^{-3}, space

---

* The unit formula is assumed to be $(CuCl)_2DPM$ $0\cdot5CH_2Cl-CH_2Cl$ in agreement with the elemental analysis. Such a formulation implies 100 % occupancy of the fourfold dichloroethane (DCE) sites. Actually, both refinement of the occupancy factor and electron-density measurements suggest for the *particular crystal used* a stoichiometry near $(CuCl)_2DPM.0\cdot25ClCH_2.CH_2Cl$.
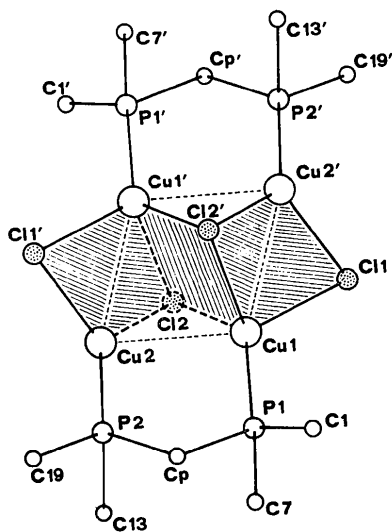

Fig. 1. A view of the molecule. Only the first carbon atom of each phenyl group is shown.

group $C2/c$ (from the Patterson function and from the structure refinement), $\mu=21$cm^{-1}. 2230 independent reflexions with $I>3\sigma(I)$ were collected with the diffractometer. The structure was solved by the heavy-atom technique and refined by block-diagonal least-squares. Only Cu, Cl and P atoms were treated anisotropically. The hydrogen atoms were neglected. The final R was $0\cdot105$.

It was not possible to locate the carbon atom of the dichloroethane molecule either from Fourier or $(F_o - F_c)$ syntheses. In fact,* the CH_2Cl-CH_2Cl molecules are arranged on the twofold axes of the space group with an occupancy of $0\cdot5$ for the independent –CH_2–Cl half of the molecule. In addition such molecules may have different

Table 1. *Fractional coordinates* ($\times 10^4$) *and temperature factors with estimated standard deviations in parentheses*

The anisotropic temperature factors ($\times 10^5$) are in the form:

$$\exp\left[-(B_{11}h^2+B_{12}hk+B_{13}hl+B_{22}k^2+B_{23}kl+B_{33}l^2)\right].$$

	x	y	z	B
Cu(1)	810 (1)	179 (2)	833 (1)	
Cu(2)	−92 (1)	−1396 (2)	658 (1)	
Cl(1)	1082 (2)	1774 (4)	527 (3)	
Cl(2)	−109 (2)	516 (4)	714 (2)	
Cl(3)	940 (5)	1899 (10)	3599 (7)	
P(1)	1634 (2)	−915 (4)	1653 (2)	
P(2)	695 (2)	−2497 (4)	1550 (2)	
C(P)	1421 (7)	−2379 (14)	1614 (8)	4·0 (3)
C(1)	2208 (7)	−981 (15)	1496 (9)	4·3 (4)
C(2)	1954 (9)	−904 (20)	676 (12)	6·7 (5)
C(3)	2391 (10)	−935 (21)	484 (12)	7·0 (6)
C(4)	3058 (9)	−1047 (20)	1089 (11)	6·5 (5)
C(5)	3297 (9)	−1101 (19)	1847 (11)	6·3 (5)
C(6)	2896 (8)	−1071 (17)	2091 (10)	5·3 (4)
C(7)	2131 (7)	−506 (14)	2707 (9)	4·1 (3)
C(8)	2588 (7)	−1202 (16)	3354 (9)	4·9 (4)
C(9)	2981 (8)	−774 (18)	4119 (10)	5·8 (5)
C(10)	2934 (9)	307 (19)	4270 (11)	6·0 (5)
C(11)	2462 (8)	962 (18)	3616 (10)	5·8 (5)
C(12)	2059 (7)	567 (16)	2830 (9)	4·8 (4)
C(13)	1029 (7)	−2333 (15)	2616 (9)	4·3 (4)
C(14)	1432 (8)	−3098 (18)	3190 (10)	5·7 (5)
C(15)	1666 (9)	−2941 (20)	3956 (11)	6·7 (5)
C(16)	1508 (9)	−2047 (21)	4166 (12)	7·3 (6)
C(17)	1135 (10)	−1257 (22)	3604 (12)	7·8 (6)
C(18)	844 (8)	−1407 (18)	2784 (10)	5·8 (4)
C(19)	491 (7)	−3917 (14)	1356 (9)	4·4 (4)
C(20)	767 (8)	−4662 (17)	1126 (10)	5·5 (4)
C(21)	534 (8)	−5746 (19)	929 (10)	6·3 (5)
C(22)	64 (9)	−6079 (20)	930 (11)	7·0 (5)
C(23)	−184 (11)	−5427 (23)	1175 (14)	8·0 (7)
C(24)	−10 (8)	−4272 (18)	1362 (11)	5·9 (5)

Table 1 (cont.)

	B_{11}	B_{12}	B_{13}	B_{22}	B_{23}	B_{33}
Cu(1)	217 (4)	219 (15)	308 (7)	905 (18)	516 (20)	469 (7)
Cu(2)	228 (4)	257 (15)	304 (7)	966 (18)	405 (19)	385 (6)
Cl(1)	298 (10)	−149 (32)	303 (18)	741 (34)	120 (41)	460 (16)
Cl(2)	221 (7)	98 (28)	335 (12)	847 (33)	48 (35)	367 (11)
Cl(3)	406 (22)	−309 (75)	649 (39)	1057 (86)	445 (99)	798 (40)
P(1)	188 (7)	125 (28)	234 (13)	769 (33)	243 (36)	297 (12)
P(2)	205 (8)	96 (28)	236 (14)	641 (29)	138 (35)	297 (12)

conformations with C_{2v} symmetry in the same site with their carbon atoms spread out over a large number of positions.

Atomic fractional coordinates and temperature factors are given in Table 1.*

Discussion

The structure, shown in Fig. 1, is similar to that found for the iodide, the tetranuclear $(CuCl)_4.DPM_2$ molecules being arranged on the crystallographic symmetry centre. The geometry of the centrosymmetric $(CuCl)_4$ core may be described as a 'step' formed by the strictly planar Cu(1), Cu(1'),Cl(2), Cl(2') ring with the two Cu(1), Cu(2'), Cl(1), Cl(2') and Cu(2), Cu(1'), Cl(2), Cl(1') 'butterfly rings' the primed atoms being those related by the symmetry centre. With the exception of the larger distortion from planarity of the last two rings [the angle between the Cu(2), Cu(1'), Cl(2) and Cu(1'), Cu(2), Cl(1') planes is 41·7°], the structure is very similar to that found in $(CuBr.PPh_3)_4$ (Churchill & Karla, 1973). The large deviation from planarity in the present case is certainly due to the bite of the DPM bidentate ligand which causes Cu(1) and Cu(2) to come close together [Cu(1)–Cu(2) = 2·908 (4) Å]. Thus Cu(1) has a distorted tetrahedral geometry, bonding one phosphorus and three chlorine atoms, whereas only two chlorine and one phosphorus atom are trigonally arranged around Cu(2). Such stepped geometry is however completely different from the cubane-type structure found in $(CuCl.PPh_3)_4$ (Churchill & Karla, 1973) in which each of the four copper atoms has a distorted tetrahedral geometry. The above arrangements

---

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30342 (9pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

(CuCl·PPh₃)₄   (CuBr PPh₃)₄   (CuCl)₄DPM₂

○ Cu
○ Br or Cl
● P

Fig. 2. A comparison of the $(CuX)_4$ core found in tetranuclear compounds with phosphine ligands.

are sketched in Fig. 2. Furthermore the cubane $CuCl_4$ core is characterized by larger Cu–Cl distances which range from 2·362 (2) to 2·505 (2) Å, whereas in the present case

Table 2. Bond lengths (Å) and angles (°) with their standard deviations in parentheses

For the mean values the average of individual standard deviations is reported in parentheses.

(a) Individual values

Cu(1)–Cu(2)	2·908 (4) Å
Cu(1)–Cu(2)	2·915 (3)
Cu(1)–Cl(1)	2·324 (6)
Cu(2)–Cl(1)	2·270 (4)
Cu(1)–Cl(2)	2·315 (6)
Cu(2)–Cl(2)	2·358 (6)
Cu(1)–Cl(2)	2·740 (4)
Cu(1)–P(1)	2·197 (5)
Cu(2)–P(2)	2·195 (4)
P(1)—C(P)	1·872 (18)
P(2)—C(P)	1·840 (22)
P(1)—C(1)	1·752 (24)
P(1)—C(7)	1·840 (16)
P(2)—C(13)	1·885 (19)
P(2)—C(19)	1·798 (18)
Cu(2)–Cu(1)–Cu(2')	106·9 (1)°
Cl(1)–Cu(1)–P(1)	114·8 (2)
Cl(1)–Cu(1)–Cl(2)	108·0 (2)
Cl(1)–Cu(1)–Cl(2')	90·5 (2)
P(1)—Cu(1)–Cl(2)	129·6 (2)
P(1)—Cu(1)–Cl(2')	110·8 (2)
Cl(2)–Cu(1)–Cl(2')	93·8 (2)
Cu(1)–Cu(2)–Cu(1')	73·1(1)
Cl(2)–Cu(2)–Cl(1')	102·5 (2)
Cl(2)—Cu(2)–P(2)	127·5 (2)
P(2)—Cu(2)–Cl(1')	130·0 (2)
Cu(1)–P(1)—C(1)	114·3 (6)
Cu(1)–P(1)—C(7)	113·6 (6)
C(7)—P(1)—C(P)	106·2 (8)
Cu(1)–P(1)—C(P)	115·9 (4)
C(1)—P(1)—C(P)	102·7 (9)
C(1)—P(1)—C(7)	102·8 (8)
Cu(2)–P(2)—C(P)	112·6 (5)
Cu(2)–P(2)—C(13)	117·4 (6)
Cu(2)–P(2)—C(19)	114·6 (4)
C(P)—P(2)—C(13)	103·7 (8)
C(P)—P(2)—C(19)	103·9 (9)
C(13)–P(2)—C(19)	103·2 (9)
P(1)—C(P)—P(2)	110·4 (10)
Cu(1)–Cl(1)–Cu(2')	78·8 (2)

(b) Mean values

C–C [Ph–C(1)]	1·42 (3) Å
C–C [Ph–C(7)]	1·40 (3)
C–C [Ph–C(13)]	1·38 (3)
C–C [Ph–C(19)]	1·40 (4)
C–C–C [Ph–C(1)]	120 (2)°
C–C–C [Ph–C(7)]	120 (2)
C–C–C [Ph–C(13)]	120 (2)
C–C–C [Ph–C(19)]	120 (2)

they range from 2·270 (4) to 2·358 (6) Å if we exclude the long Cu(1)–Cl(2) bond of 2·740 (4) Å. This observation is in agreement with the different hybridization states of the copper atoms in the two structures. As far as the long Cu–Cl bond is concerned a comparison with the analogous iodide shows that the three-coordinate iodine atom is nearly equidistant from its three copper atoms, the Cu–I distances varying from 2·721 (6) to 2·784 (5) Å. On the contrary Cl(2) is involved in two short and one long Cu–Cl bond, the difference amounting to 0·4 Å. This results in a strengthening of the Cu(1)–Cu(2) distance [3·108 (7) Å for I and 2·908 (4) for Cl] and, correspondingly, in a lengthening of Cu(1)–Cu(2′) [2·682 (7) Å for I and 2·915 (3) Å for Cl]. It is not clear whether these differences are due to steric and/or electronic factors.

No significant differences are found in the Cu–P bond lengths of all these complexes. Bond lengths and angles are given in Table 2. The structure found in the solid state is in agreement with molecular weight measurements (Marsich, Camus & Cebulec, 1972) in CHCl₃ and C₂H₄Cl₂

solutions and conductivity measurements in $C_2H_4Cl_2$. The values of the molecular weight suggest that a dimeric species is present in solution whereas the non-conducting solution in $C_2H_4Cl_2$ indicates that no dissociation into ions occurs. These results, as already suggested (Marsich, Nardin & Randaccio, 1973), indicate that the compounds have the same structure in the solid state and in solutions of slightly polar solvents.

References

CHURCHILL, M. R. & KARLA, K. L. (1973). *J. Amer. Chem. Soc.* **95**, 5772–5773.

MARSICH, N., CAMUS, A. & CEBULEC, E. (1972). *J. Inorg. Nucl. Chem.* **34**, 933–946.

MARSICH, N., NARDIN, G. & RANDACCIO, L. (1973). *J. Amer. Chem. Soc.* **95**, 4053–4054.

Données cristallographiques sur la phase ordonnée du *p*-terphényle à –160°C.

Par JEAN-LOUIS BAUDOUR et GUY-PAUL CHARBONNEAU, *Département de Physique Cristalline et Chimie Structurale, E.R.A. au CNRS n° 15, Université de Rennes, avenue du Général Leclerc, 35031-Rennes Cedex, France*

Crystal data are given for the ordered phase of *p*-terphenyl at $-160°C$: $a = 16·01$ (3); $b = 11·09$ (3), $c = 13·53$ (3) Å, $\beta = 92·0$ (2)°, $Z = 8$.

Les calculs d'énergie potentielle effectués par Rietveld, Maslen & Clews (1970) montrent que les mouvements de libration des cycles benzéniques du *p*-terphényle, autour de l'axe long de la molécule, se font dans un puits double de potentiel. La configuration quasi plane obtenue par diffraction X (Dejace, 1969) n'étant alors qu'une moyenne, ne correspond pas à un équilibre stable. A basse température les spectres infrarouge (Wincke, Hadni & Gerbaux, 1970) ainsi que les spectres Raman (Marqueton & Decamps, 1970) montrent plus de bandes que n'en laisse prévoir le groupe spatial centrosymétrique $P2_1/a$. Le spectre de diffusion inélastique de neutrons réalisé à 130°K par Reynolds & White (1972) renforce l'hypothèse d'une légère perturbation à basse température de la symétrie du groupe spatial. Enfin, une comparasion des tenseurs de libration du *p*-terphényle et de la forme dimère de l'isocyanate de phényl qui sont isomorphes (Baudour, Delugeard & Sanquer, 1974) permet aussi de conclure à une configuration d'équilibre non plane. On pouvait espérer, les molécules se stabilisant dans cette configuration d'équilibre à – 160°C, observer les modifications correspondantes par diffraction X.

Des clichés d'oscillation et de Weissenberg effectués à – 160°C avec l'appareillage Renaud-Fourme (Renaud & Fourme, 1967) montrent l'existence d'une surstructure monoclinique ayant les paramètres suivants:

$a = 16,01$ (3), $b = 11,09$ (3), $c = 13,53$ (3) Å, $\beta = 92,0(2)°$; $Z = 8$ molécules par maille.

Par rapport à la maille primitive les paramètres a et b sont doublés, c est inchangé, à la contraction thermique près.

Les indices des réflexions satisfont à la condition : $h + k = 2n$, ce qui indique que la maille est centrée sur la face (001).

Il n'est pas possible, à ce stade, de choisir avec certitude le groupe d'espace. Les intensités des réflexions de surstructure sont très faibles, car probablement à – 160°C, l'ordre n'est pas totalement réalisé, et les changements dans la structure cristalline sont peu importants.

Des mesures à trois dimensions sont en cours.

Références

BAUDOUR, J. L., DELUGEARD, Y. & SANQUER, M. (1974). *Acta Cryst.* B**30**, 691–696.

DEJACE, J. (1969). *Bull. Soc. Fr. Minér. Crist.* **92**, 141–159.

MARQUETON, Y. & DECAMPS, E. A. (1970). *C.R. Acad. Sci. Paris*, **271**, 644–647.

RENAUD, M. & FOURME, R. (1967). *Acta Cryst.* **22**, 695–698.

REYNOLDS, P. A. & WHITE, J. W. (1972). *J. Chem. Soc. Faraday*, **8**, 1434–1438.

RIETVELD, H. M., MASLEN, E. N. & CLEWS, C. J. B. (1970). *Acta Cryst.* B**26**, 693–706.

WINCKE, B., HADNI, A. & GERBAUX, X. (1970). *J. Phys. Radium*, **31**, 893–898.