SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
VEIDIS, M. V., PALENIK, G. J., SCHAFFRIN, R. & TROTTER, J. (1969). *J. Chem. Soc A*, pp. 2659–2666.
WOJTCZAK, A., JASKÓLSKI, M. & KOSTURKIEWICZ, Z. (1988). *Acta Cryst.* C**44**, 1179–1181.
YAMANE, T., ASHIDA, T. & KAKUDO, M. (1973). *Acta Cryst.* B**29**, 2884–2891.

Acta Cryst. (1989). C**45**, 33–35

Structure of Tetraphenylphosphonium Trichlorocuprate

BY D. TRAN QUI

Laboratoire de Cristallographie, CNRS, Laboratoire associé à l'Université J. Fourier, 166 *X,*
38042 *Grenoble CEDEX, France*

AND A. DAOUD AND T. MHIRI

Laboratoire de l'état solide, ENIS BPW Sfax, Tunisia

(*Received* 10 *June* 1988; *accepted* 5 *August* 1988)

Abstract. $[P(C_6H_5)_4][CuCl_3]$, $M_r = 509{\cdot}3$, monoclinic, $P2_1/n$, $a = 13{\cdot}601\,(2)$, $b = 19{\cdot}272\,(3)$, $c = 9{\cdot}216\,(2)$ Å, $\beta = 107{\cdot}9\,(1)°$, $V = 2297{\cdot}8$ Å^3, $Z = 4$, $D_x = 1{\cdot}47$ g cm^{-3}, $\lambda(\text{Ag}\,K\alpha) = 0{\cdot}56087$ Å, $\mu = 7{\cdot}1$ cm^{-1}, $F(000) = 1036$, $T = 298$ K, $R = 0{\cdot}049$, $wR = 0{\cdot}062$ for 1432 reflexions $>2\sigma(F)$. The structure consists of segregated stacks of the non planar $[Cu_2Cl_6]^{2-}$ anions and of the respective cations, $[Ph_4P]^+$. The isolated copper dimers, $[Cu_2Cl_6]^{2-}$, are bibridged over the inversion center. The average Cu—Cl bond lengths are 2·191 (terminal) and 2·310 Å (bridging) with bridging Cu—Cl—Cu angle averaging 93·1°. The P atom in the tetraphenylphosphonium cation, $[Ph_4P]^+$, is tetrahedrally coordinated by four phenyl C atoms with $\langle P—C\rangle = 1{\cdot}796$ Å; the phenyl rings of the tetraphenylphosphonium are planar, with $\langle C—C\rangle$ in the four phenyl rings ranging from 1·384 to 1·389 Å.

Introduction. Halide transition-metal complexes aroused particular interest owing to their magnetic properties which are good examples for magnetostructural correlation in exchange coupled systems. Thus, $[N(CH_3)_4][MnCl_3]$ constitutes a typical example where the antiferromagnetic behavior of manganese ions in the $MnCl_3$ chain is entirely predictable by the Heisenberg interaction model and to some lesser extent the observed ferromagnetic exchange between Cu ions in $[N(CH_3)_4][CuCl_3]$ can also be understood by the same theoretical basis (Landée & Willett, 1979; Peersy, Morigin & Smara, 1973).

More recently another copper complex, piperazinium hexachlorodicuprate, has been synthesized and its crystal structure determined; in this compound the trichlorocuprate groups are condensed into infinite $[Cu_2Cl_6]^{2-}$ chains zigzagging along the *a* axis. Magnetic susceptibility as a function of temperature, maximum at $T = 15$ K and then tending to zero, has been successfully predicted, $S = \frac{1}{2}$, as an alternating antiferromagnetic exchange with a relatively small value of J_1/K, $-12{\cdot}5$ K, and with an alternation parameter, (J_2/J_1) close to 0·6, in good agreement with the structural data (Daoud, Ben Salah, Chappert, Renard, Cheikhrouhou, Tran Qui & Verdaguer, 1986). In a continuation of magnetostructural correlation studies of transition-metal complexes a new tetraphenylphosphonium chlorocuprate, $[P(Ph)_4][CuCl_3]$, is synthetized and its crystal structure is reported in this paper.

Experimental. Red-yellow needle-shaped crystals of the title compound were grown by slow evaporation at ambient temperature in an aqueous saturated equimolar solution of $(Ph)_4PCl$ and $CuCl_2$. Several recrystallizations in saturated HCl solution were necessary to obtain single crytals suitable for X-ray analysis: CAD-4 diffractometer, crystal size $0{\cdot}08 \times 0{\cdot}07 \times 0{\cdot}14$ mm, $\lambda(\text{Ag}\,K\alpha)$, random orientation, no absorption correction, ω scan, 2° min^{-1}, scan range $= 1{\cdot}1°$, $2\theta_{\text{max}} = 20°$, $-15 \le h \le 15$, $-23 \le k \le 23$, $0 \le l \le 11$. Unit-cell parameters from 24 reflexions with $10 \le 2\theta \le 18°$, 3672 reflexions measured, averaged to 1432 unique reflexions $\ge 2\sigma(F)$, internal agreement factor was 3·7%. Three standard reflexions, no intensity variation.

The structure was solved using the Patterson heavy-atom method which revealed the positions of Cu, Cl and P atoms. The remaining atoms were located by succeeding difference Fourier syntheses. H positions, unsuccessfully determined by the Fourier method, were assigned according to the phenyl geometry. Three final cycles including H positions showed no improvement in

0108-2701/89/010033-03$03.00

R, *wR* or *S* factors; no hydrogen bonding will therefore be discussed in the following section. Function minimized $\sum w||F_o| - |KF_c||^2$, $w = [\sigma^2(F_o) + 0{\cdot}01|F_o|^2]^{-1}$. f, f' and f'' from *International Tables for X-ray Crystallography* (1974). Final *R* and *wR* (Cu, Cl and P anisotropic and C isotropic) are 4·9% and 6·2%, $(\Delta/\sigma)_{\max} = 0{\cdot}03$, $|\Delta\rho|_{\max} < 0{\cdot}3$ e Å^{-3} on final difference Fourier map.. *SDP-Plus* package of programs (Frenz, 1983) was used on MicroVAX for structure solution and refinement.

Discussion. The crystal structure of the title compound consists of a monoclinic cell, containing four $[\mathrm{Ph_4P}]^+$ and two $[\mathrm{Cu_2Cl_6}]^{2-}$ groups. Fig. 1 shows the geometry of the tetraphenylphosphonium and its chlorocuprate counterion. Table 1 contains the final positional parameters while selected interatomic distances and bond angles appear in Table 2.* The P atom is tetrahedrally coordinated by four C atoms [C(1), C(7), C(13) and C(19)]. The observed P—C bond distances lie in the range 1·793 to 1·819 Å and are slightly shorter than those recently observed in triphenylphosphonium in $[\mathrm{PClPh_3}][\mathrm{MoCl_6}]$ (Richards, Shortman, Povey & Smith, 1987). The four phenyl rings are planar within 0·06 Å; the C—C bond distances and C—C—C angles (Table 2) indicate no distortion for these groups. The C thermal factors are relatively high denoting a certain flexibility of the phenyl rings in the $\mathrm{Ph_4P}$ group.

Table 1. *Final atomic coordinates and equivalent isotropic thermal factors*

Standard deviations are in parentheses.

$B_{\mathrm{eq}} = \frac{4}{3}\sum_i\sum_j B_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	*y*	*z*	B_{eq}(Å^2)
Cu	0·5978 (2)	0·0475 (1)	0·9781 (2)	3·38 (4)
Cl(1)	0·0914 (5)	0·3538 (3)	0·3589 (5)	5·8 (1)
Cl(2)	0·5588 (4)	−0·0038 (2)	0·1779 (4)	4·1 (1)
Cl(3)	0·2652 (4)	0·4716 (2)	0·5590 (5)	4·4 (1)
P	0·5147 (4)	0·2947 (2)	0·3400 (4)	3·0 (1)
C(1)	0·447 (1)	0·6697 (9)	0·471 (2)	3·5 (4)
C(2)	0·377 (1)	0·7042 (9)	0·352 (2)	3·6 (4)
C(3)	0·349 (1)	0·676 (1)	0·206 (2)	4·1 (4)
C(4)	0·391 (2)	0·614 (1)	0·181 (2)	5·1 (5)
C(5)	0·462 (2)	0·579 (1)	0·301 (2)	5·5 (6)
C(6)	0·491 (2)	0·607 (1)	0·447 (2)	4·3 (5)
C(7)	0·866 (1)	0·7831 (9)	0·207 (2)	3·4 (4)
C(8)	0·839 (2)	0·7185 (9)	0·250 (2)	4·2 (5)
C(9)	0·747 (2)	0·712 (1)	0·282 (2)	4·6 (5)
C(10)	0·682 (2)	0·768 (1)	0·272 (2)	5·0 (5)
C(11)	0·712 (1)	0·834 (1)	0·234 (2)	4·3 (5)
C(12)	0·803 (1)	0·842 (1)	0·200 (2)	4·1 (5)
C(13)	0·047 (1)	0·7121 (9)	0·168 (2)	3·4 (4)
C(14)	0·101 (1)	0·6841 (9)	0·312 (2)	3·7 (4)
C(15)	0·142 (2)	0·6186 (9)	0·321 (2)	3·9 (4)
C(16)	0·133 (1)	0·5805 (9)	0·191 (2)	4·3 (4)
C(17)	0·079 (2)	0·607 (1)	0·048 (2)	4·4 (5)
C(18)	0·038 (1)	0·6728 (9)	0·036 (2)	4·1 (4)
C(19)	0·075 (1)	0·8496 (9)	0·292 (2)	3·8 (4)
C(20)	0·170 (2)	0·863 (1)	0·275 (2)	4·4 (5)
C(21)	0·242 (2)	0·902 (1)	0·380 (2)	5·0 (5)
C(22)	0·214 (2)	0·933 (1)	0·502 (2)	5·5 (6)
C(23)	0·118 (2)	0·921 (1)	0·516 (2)	5·5 (5)
C(24)	0·048 (2)	0·879 (1)	0·411 (2)	4·6 (5)

Table 2. *Selected bond distances* (Å) *and angles* (°)

Standard deviations are in parentheses.

$[\mathrm{Cu_2Cl_6}]^{2-}$ dimers			
Cu—Cu	3·353 (4)	Cl(1)—Cu—Cl(2)	96·7 (2)
Cu—Cl(1)	2·186 (5)	Cl(1)—Cu—Cl(3)	101·1 (2)
Cu—Cl(2)	2·292 (5)	Cl(1)—Cu—Cl(2)	142·8 (2)
Cu—Cl(2)	2·328 (5)	Cl(2)—Cu—Cl(2)	86·9 (2)
Cu—Cl(3)	2·197 (5)	Cl(2)—Cu—Cl(3)	97·3 (2)
		Cl(2)—Cu—Cl(3)	143·5 (2)
P atom			
P—C(1)	1·793 (8)	C(1)—P—C(7)	105·2 (7)
P—C(7)	1·819 (9)	C(1)—P—C(13)	111·8 (7)
P—C(13)	1·793 (8)	C(1)—P—C(19)	111·6 (8)
P—C(19)	1·779 (7)	C(7)—P—C(13)	108·9 (8)
		C(7)—P—C(19)	112·6 (8)
		C(13)—P—C(19)	106·6 (8)
Phenyl rings			
⟨C(1)—C(6)⟩	1·389 (5)	⟨C(1)—C—C(6)⟩	120·0 (2)
⟨C(7)—C(12)⟩	1·389 (5)	⟨C(7)—C—C(12)⟩	119·5 (4)
⟨C(13)—C(18)⟩	1·388 (5)	⟨C(13)—C—C(18)⟩	120·1 (3)
⟨C(19)—C(24)⟩	1·384 (5)	⟨C(19)—C—C(24)⟩	120·3 (3)

The $\mathrm{CuCl_3}$ groups are bridged together over the inversion center forming a copper dimer $[\mathrm{Cu_2Cl_6}]^{2-}$. Unlike the $\mathrm{C_4H_{12}Cu_2Cl_6}$ salt, in which the $[\mathrm{Cu_2Cl_6}]^{2-}$ dimers are linked together to form $\mathrm{Cu_2Cl_6}$ chains (Daoud *et al.*), the chlorocuprate counterions in the present complex are isolated groups. The average Cu—Cl bond distances, 2·390 (bridging) and 2·191 Å (terminal), are significantly different to those observed in $\mathrm{K_2CuCl_3}$ and $\mathrm{(NH_4)_2CuCl_3}$ salts (Willett, Dwiggins, Kruh & Rundle, 1963). Moreover, inspection of the Cl—Cu—Cl angles (Table 2) indicates substantial deviation of the copper neighbors from the usual Cu$^{\mathrm{II}}$ square-planar coordination as observed in the $\mathrm{K_2CuCl_3}$

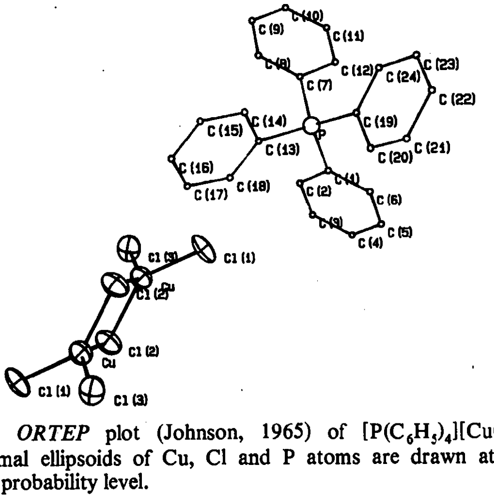

Fig. 1. *ORTEP* plot (Johnson, 1965) of $[\mathrm{P(C_6H_5)_4}][\mathrm{CuCl_3}]$. Thermal ellipsoids of Cu, Cl and P atoms are drawn at the 50% probability level.

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51313 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

and $(NH_4)_2CuCl_3$ salt structures. Constrained by the inversion center symmetry, the distortion of the $[Cu_2Cl_6]^{2-}$ dimer, which is crucial for magnetic behavior of this complex, is of a twisting mode, *i.e.* the plane defined by a Cu atom and two terminal Cl atoms, Cu/Cl(1)/Cl(3), is twisted by an angle of 45° with respect to the Cu—Cl(2)—Cu—Cl(2) plane.

References

Daoud, A., Ben Salah, A., Chappert, C., Renard, J. P., Cheikhrouhou, A., Tran Qui, D. & Verdaguer, M. (1986). *Phys. Rev. B*, **33**(9), 6253–6260.

Frenz, B. A. (1983). *Enraf–Nonius Structure Determination Package*; *SDP Users Guide*, version 1.1. Enraf–Nonius, Delft, The Netherlands.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Landée, C. P. & Willett, R. D. (1979). *Phys. Lett.* **46**, 463–469.

Peersy, P. S., Morigin, B. & Smara, G. A. (1973). *Phys. Rev. B*, **8**, 3378–3388.

Richards, R. L., Shortman, C., Povey, D. C. & Smith, G. W. *Acta Cryst.* (1987). C**43**, 2309–2311.

Willett, R. D., Dwiggins, C. Jr, Kruh, R. H. & Rundle, R. E. (1963). *J. Chem. Phys.* **38**, 2429–2436.

Acta Cryst. (1989). C**45**, 35–37

1,1,2,2,4,4,5,5-Octamethyl-1,2,4,5-tetrastannacyclohexane

By Hans Preut and Terence N. Mitchell

Fachbereich Chemie, Universität Dortmund, Postfach 50 05 00, *D*-4600 *Dortmund* 50,
Federal Republic of Germany

(*Received* 13 *June* 1988; *accepted* 30 *September* 1988)

Abstract. $C_{10}H_{28}Sn_4$, $M_r = 623{\cdot}09$, monoclinic, $P2_1/c$, $a = 20{\cdot}095\ (6)$, $b = 6{\cdot}492\ (2)$, $c = 16{\cdot}067\ (7)$ Å, $\beta = 112{\cdot}88\ (3)^\circ$, $V = 1931\ (1)$ Å^3, $Z = 4$, $D_x = 2{\cdot}143$ Mg m^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0{\cdot}71073$ Å, $\mu = 5{\cdot}12$ mm^{-1}, $F(000) = 1152$, $T = 291\ (1)$ K, final $R = 0{\cdot}070$ for 1243 unique observed $[F \geq 4{\cdot}0\sigma(F)]$ diffractometer data. The molecule is in the boat conformation. The Sn—Sn bond lengths are 2·791 (3) and 2·780 (3) Å; this small difference, which is greater than three times the corresponding standard deviation, parallels the two different values for the one-bond Sn–Sn coupling constant observed in the ^{119}Sn solid-state spectrum of the compound.

Introduction. Previous work (Meunier-Piret, Van Meerssche, Gielen & Jurkschat, 1983; Preut, Bleckmann, Mitchell & Fabisch, 1984) has shown that 1,2,4,5-tetrastannacyclohexanes can exist in both chair and boat forms: the chair form is observed for the octaphenyl derivative, while the *cis*-dodecamethyl derivative exists in a boat structure. In order to obtain more information on the factors determining which structure is preferred, we decided to determine the crystal structure of 1,1,2,2,4,4,5,5-octamethyl-1,2,4,5-tetrastannacyclohexane. The high-resolution solid-state ^{119}Sn NMR spectrum of this compound reveals four non-equivalent Sn signals (Harris, Mitchell & Nesbitt, 1985) with two different one-bond Sn–Sn coupling constants (Mitchell, 1986): these may be related to differences in the Sn—Sn bond length.

Experimental. Title compound prepared by treating 1,3-dibromo-1,1,3,3-tetramethyl-1,3-distannapropane with sodium in liquid ammonia; colourless crystals obtained by vacuum sublimation, m.p. 372–373 K, yield 73% (Mitchell, Fabisch, Wickenkamp, Kuivila & Karol, 1986). Crystal size 0·06 × 0·06 × 0·38 mm. The external form of the crystals and the X-ray photographs indicated poor quality of the crystals which diffracted weakly. $\omega/2\theta$ scan, scan speed 2·5–14·6° min^{-1} in θ, Nicolet $R3m$/V diffractometer, graphite-monochromated Mo $K\alpha$; lattice parameters from least-squares fit with 22 reflections up to $2\theta = 24{\cdot}3^\circ$; six standard reflections recorded every 2·5 h showed up to 52% intensity loss; 4773 reflections measured, $1{\cdot}5 \leq \theta \leq 21{\cdot}0^\circ$, $-17 \leq h \leq 17$, $0 \leq k \leq 7$, $-21 \leq l \leq 21$; after averaging ($R_{\text{int}} = 0{\cdot}061$): 2099 unique reflections, 1243 with $F \geq 4{\cdot}0\sigma(F)$; Lorentz–polarization correction, decay correction, no absorption correction; systematic absences ($h0l$) $l = 2n + 1$, ($0k0$) $k = 2n + 1$ conform to space group $P2_1/c$; structure solution *via* Patterson function, ΔF syntheses and full-matrix least-squares refinement with anisotropic temperature factors for all non-H atoms and a common isotropic temperature factor for H atoms, which were placed in geometrically calculated positions (C—H 0·96 Å); refinement on F with 1243 reflections and 128 refined parameters; $w = 1{\cdot}0/[\sigma^2(F) + 0{\cdot}0005F^2]$; $S = 1{\cdot}62$, $R = 0{\cdot}070$, $wR = 0{\cdot}060$, $(\Delta/\sigma)_{\max} = 0{\cdot}30$, no extinction correction; largest peak in final ΔF map $\pm 1{\cdot}4\ (6)$ e Å^{-3}, atomic

0108-2701/89/010035-03$03.00