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The Structure of Tetramethylphosphonium Dicopper Pentachloride

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Abstract. $[(CH_3)_4P]Cu_2Cl_5$, $M_r = 395{\cdot}46$, monoclinic, $P2_1/n$, $a = 10{\cdot}967\,(1)$, $b = 12{\cdot}023\,(1)$, $c = 10{\cdot}211\,(1)$ Å, $\beta = 109{\cdot}86\,(7)°$, $V = 1266{\cdot}3\,(2)$ Å^3, $Z = 4$, $D_x = 2{\cdot}074$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 45{\cdot}22$ cm^{-1}, $F(000) = 776$, $T = 293$ K, $wR = 0{\cdot}024$ for 2176 reflections. The compound consists of chains of edge-sharing $CuCl_5$ pyramids, with approximate site symmetry C_{4v}. One Cl of each pyramid bridges to a neighbouring chain. In this way planes of interconnected chains are formed, which are held together by the large tetramethylphosphonium (TMP) cations.

Introduction. Part of the investigations carried out in our group are focused on structural and magnetic properties of ternary halides in the system AX–BX_2 and more specifically of compounds with the formula ABX_3, the hexagonal perovskite (2*L*). In the systems under consideration, $B = Cu^{2+}$, $X = Cl^-$ and $A = Rb^+$, Cs^+, $(CH_3)_4N^+$ (Crama & Maaskant, 1983; Weenk & Spek, 1976). In these compounds the *A* ion is important for the manifestation of the cooperative $E \otimes \varepsilon$ Jahn–Teller effect of the $CuCl_6$ octahedra. In order to investigate the effect of a still larger cation, $(CH_3)_4P^+$ was used. The synthesis yielded a new compound with the composition $[(CH_3)_4P]Cu_2Cl_5$ in which copper is coordinated to five chlorines.

Experimental. Single crystals were grown from an aqueous solution, acidified with concentrated hydrochloric acid, containing equimolar amounts of (TMP)-Cl and $CuCl_2$. The solution yielded reddish-brown and yellow oblique crystals. From the crystal structure determination it was found that the reddish-brown TMP compound was $(TMP)Cu_2Cl_5$. It is known that the composition of this kind of crystal depends on the concentration of both hydrochloric acid and starting materials (Weenk, 1976).

Reddish-brown oblique crystals, $0{\cdot}43 \times 0{\cdot}17 \times 0{\cdot}14$ mm, Enraf–Nonius four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation, 24 reflections used for determination of unit-cell dimensions ($-14{\cdot}25 < \theta < 14{\cdot}25°$), from systematic absence of $hk0$, $h + k = 2n$, and $00l$, $l = 2n$, it was concluded that the space group is $P2_1/n$, 7691 reflections measured $2 < \theta < 30°$, 3852 independent reflections, $R_{\rm int} = 0{\cdot}036$, 2176 significant, 584 non-significant [observed, $I > 2\sigma(I)$], 1092 unobserved reflections, h -15 to 15, k 0 to 16, l -14 to 14, 3 standard reflections ($\bar{4}35$, $\bar{6}06$, $2\bar{6}3$), decay scattering power $5{\cdot}77\%$, observed reflections were corrected for this variation; e.s.d. of standard reflections $1{\cdot}4\%$. Lp correction, absorption correction (de Graaff, 1973), min. and max. transmission $0{\cdot}6097$, $0{\cdot}7351$, scattering factors from *International Tables* *for X-ray Crystallography* (1974) with correction for real and imaginary parts of anomalous dispersion. Function minimized during least-squares refinement $\sum w(|F_{\rm obs}| - |F_{\rm calc}|)^2$, $w = 1/\sigma(F)^2$, $\sigma(F)$ e.s.d. calculated from counting statistics and errors in the aforementioned corrections. For all calculations both *SHELX*76 (Sheldrick, 1976) and computer programs written or modified by Rutten-Keulemans and de Graaff were used on the Leiden University Amdahl V 7B computer.

The determination of the crystal structure was started by solving a Patterson map for the heavy atoms. As a result it appeared that pseudosymmetry was present in the distances between different ions in the crystal structure. Owing to this pseudosymmetry it was difficult to solve the Patterson map. *SHELX* least squares and Fourier $\Delta\rho$ maps were used to find all ions in $P2_1/n$. Refinement of all Cu, Cl, P and C positional and anisotropic thermal parameters resulted in $wR = 0{\cdot}043$. 12 H atoms were included to supply the remaining electron density to the asymmetric unit. Isotropic refinement of the H atoms (C—H = 1·00 Å), hydrogens belonging to one carbon were coupled, resulted in $wR = 0{\cdot}0242$ ($R = 0{\cdot}0268$, $S = 1{\cdot}1816$). The ratio of the maximum least-squares shift to e.s.d. is smaller than 0·012. The maximum and minimum heights in the final difference Fourier synthesis are 0·40 and 0·28 e Å^{-3} respectively (statistical height: 0·19 e Å^{-3}). From the final differences between $F_{\rm obs}$ and $F_{\rm calc}$ it was concluded that corrections for extinction effects were negligible.

Discussion. The structural parameters of (TMP)Cu$_2$Cl$_5$ are presented in Tables 1 and 2.* Fig. 1 shows a projection of the structure on the *ab* plane and Fig. 2 a projection of half a unit cell on the *ac* plane. The Cu atoms are surrounded by five chlorines in an approximate square pyramid. In the case of Cu(1) four chlorines lie in the equatorial plane with the Cu ion 0·31 Å above it. The equatorial chlorines surrounding Cu(2) are not coplanar.

The deviation from ideal square-pyramidal geometry, found in this compound for the Cu(1) environment, has been described before in other systems by Bacci (1979), who ascribes this distortion to the pseudo-Jahn–Teller effect in the ground state of a C_{4v} complex.

The structure consists of chains of coupled pyramids. Projected on the *ac* plane, the Cu ions lie on a straight line which bisects the monoclinic angle (Fig. 2). In the direction of the unique axis (Fig. 1) the chain has a wave form. Each unit cell contains two chains above each other as shown in Fig. 1. In this way planes

Table 1. *Fractional coordinates and equivalent isotropic thermal parameters* (Å^2)

$B_{\rm eq} = 8\pi^2U_{\rm eq}$.

	x	y	z	$B_{\rm eq}$
Cu(1)	0·63499 (3)	0·29469 (3)	0·64152 (3)	2·06 (1)
Cu(2)	0·36167 (3)	0·38143 (3)	0·37832 (3)	2·13 (1)
Cl(1)	0·54181 (7)	0·27348 (6)	0·40430 (7)	2·69 (2)
Cl(2)	0·78733 (7)	0·16062 (6)	0·64250 (7)	2·69 (2)
Cl(3)	0·76960 (7)	0·46995 (6)	0·64131 (8)	2·69 (2)
Cl(4)	0·44843 (7)	0·39722 (7)	0·61758 (7)	2·72 (2)
Cl(5)	0·67755 (7)	0·26756 (6)	0·87088 (7)	2·78 (2)
P	0·82449 (7)	0·45639 (7)	0·22063 (8)	2·82 (2)
C(1)	0·8800 (3)	0·5720 (3)	0·3337 (3)	2·63 (2)
C(2)	0·9149 (3)	0·4501 (3)	0·1055 (3)	3·23 (1)
C(3)	0·6563 (3)	0·4715 (3)	0·1243 (4)	4·36 (1)
C(4)	0·8494 (3)	0·3331 (3)	0·3217 (4)	4·54 (1)

Table 2. *Relevant distances* (Å) *and angles* (°) *in the structure*

Cu(1)—Cl(1)	2·3010 (8)	Cu(2)—Cl(4)	2·3088 (8)
Cu(1)—Cl(2)	2·3193 (8)	Cu(2)—Cl(5)	2·6810 (8)
Cu(1)—Cl(3)	2·5734 (8)	Cu(1)—Cu(2)	3·9003 (5)
Cu(1)—Cl(4)	2·3293 (7)	Cu(1)—Cu(2)	3·4383 (4)
Cu(1)—Cl(5)	2·2509 (8)	P—C(1)	1·777 (3)
Cu(2)—Cl(1)	2·3026 (8)	P—C(2)	1·778 (3)
Cu(2)—Cl(2)	2·3205 (8)	P—C(3)	1·781 (3)
Cu(2)—Cl(3)	2·2605 (8)	P—C(4)	1·773 (4)
C(1)—P—C(2)	108·53 (16)	C(2)—P—C(3)	110·15 (16)
C(1)—P—C(3)	109·94 (16)	C(2)—P—C(4)	109·81 (16)
C(1)—P—C(4)	108·96 (17)	C(3)—P—C(4)	109·42 (18)

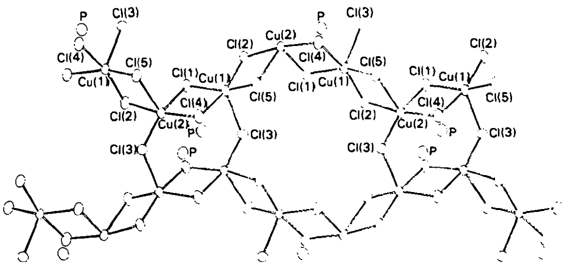

Fig. 1. Projection of the structure on the *ab* plane. The carbon atoms of the TMP groups are omitted for clarity.

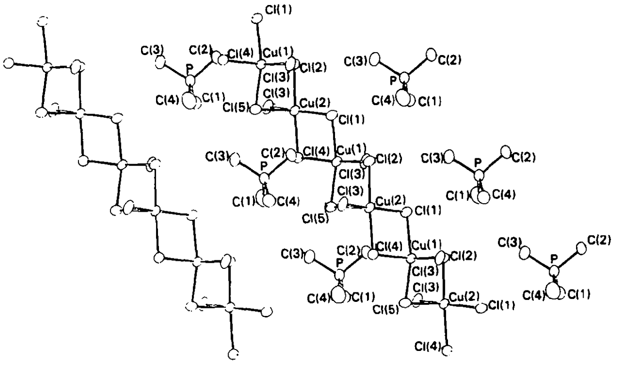

Fig. 2. Projection of half a unit cell on the *ac* plane.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43096 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

parallel to $(10\bar{1})$ are formed. These planes 'sandwich' the TMP groups. Magnetic measurements will be carried out in due course as this compound is a possible candidate for a low-dimensional magnetic system.

A compound with similar composition, tetramethylammonium dicopper pentachloride, has been reported before (Weenk, 1976). The structure of this compound is unknown.

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Structure of Dipyridinebis(2,4,6-trichlorophenolato)copper(II)

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Abstract. $[\mathrm{Cu(C_6H_2Cl_3O)_2(C_5H_5N)_2}]$, $M_r = 614{\cdot}6$, triclinic, $P\bar{1}$, $a = 8{\cdot}292\,(2)$, $b = 9{\cdot}002\,(2)$, $c = 9{\cdot}587\,(2)$ Å, $\alpha = 85{\cdot}91\,(2)$, $\beta = 72{\cdot}44\,(2)$, $\gamma = 63{\cdot}48\,(2)^\circ$, $V = 608{\cdot}9$ Å^3, $Z = 1$, $D_x = 1{\cdot}68$ g cm^{-3}, $F(000) = 306{\cdot}96$, $\lambda(\mathrm{Mo}\,K\alpha) = 0{\cdot}71069$ Å, $\mu = 15{\cdot}9$ cm^{-1}, $T = 293$ K. 2158 unique reflections, of which 1819 had $I \geq 3\sigma(I)$, were refined to a final R of 0·046 ($R = 0{\cdot}036$ for the 3σ data set and $wR = 0{\cdot}032$). The structure consists of discrete centrosymmetric molecules with the stoichiometric formula indicated in the title. The $\mathrm{CuO_2N_2}$ coordination sphere is *trans* planar [Cu—O = 1·909 (2), Cu—N = 2·036 (3) Å] with the fifth and sixth coordination sites blocked by chlorine atoms from the phenoxide ions [Cu—Cl = 2·912 (1) Å].

Introduction. The oxidation and polymerization of phenols is catalyzed by the presence of copper chloride and pyridine (Finkbeiner, Hay, Blanchard & Endres, 1966, and references therein). In methanol solution, the active species has been identified as $\mathrm{Cu_2Cl_2(OH)(OCH_3)(py)_2}$ (Davies & El-Sayed, 1983). The crystal structure of the bis(methoxide) complex, $\mathrm{Cu_2Cl_2(OCH_3)_2(py)_2}$, has been shown to contain dibridged methoxide dimers (Willett & Breneman, 1983). As part of a further study of this system, we have determined the structure of the copper(II) substrate complex in the presence of pyridine.

Experimental. Brown prismatic crystals separated out upon cooling of a saturated solution of the complex prepared as described by Blanchard, Finkbeiner & Russell (1962). A small crystal with maximum dimension 0·3 mm was selected for data collection. Data were collected on a Nicolet *R*3*m*/*E* diffractometer system with Mo $K\alpha$ radiation and a graphite monochromator (Campana, Shepherd & Litchman, 1980). Agreement between equivalent reflections: $R = 0{\cdot}019$. The triclinic unit cell and orientation matrix were defined by least-squares refinement of 25 accurately centered high-angle ($34^\circ < 2\theta < 39^\circ$) reflections. Empirical absorption corrections assuming an ellipsoidally shaped crystal (minimum transmission = 0·61, maximum transmission = 0·79). Data collected for all h and k, $l \geq 0$ (maximum values of $h, k, l = 8, 10, 11$). Three standards monitored every 50 reflections, variation within counting statistics. 2158 unique reflections ($2\theta \leq 50^\circ$); 1819 reflections with $I > 3\sigma(I)$. The Patterson function yielded positions of the Cu, O, N, and a Cl atom. Subsequent difference maps, starting with these positions, yielded all other atom positions. Final refinement on F of all positional parameters with anisotropic thermal parameters for the non-hydrogen atoms and isotropic thermal parameters for the H atoms gave a final value of $R = 0{\cdot}036$ and $wR = 0{\cdot}032$ with an average $\Delta/\sigma = 0{\cdot}034$ for all observed reflections

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