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Crystal and Molecular Structure of Tetraphenylphosphonium Trichlorocuprate(II), $(C_6H_5)_4PCuCl_3$, a Complex Containing Nonplanar Dimeric $[Cu_2Cl_6]^{2-}$ Units

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The crystal structure of tetraphenylphosphonium trichlorocuprate(II), $(C_6H_5)_4PCuCl_3$, has been determined by conventional Patterson, Fourier, and least-squares refinement techniques with data collected on an automated four-circle diffractometer. The complex crystallizes in the centrosymmetric space group $P2_1/c$ with $a = 9.226$ (8) Å, $b = 19.301$ (15) Å, $c = 13.842$ (15) Å, $\beta = 111.26$ (6)°, and $Z = 4$. The structure was refined to a conventional discrepancy factor of 0.032 for 1189 observed reflections. The function minimized during the refinement process was $\Sigma w(|F_o| - |F_c|)^2$. All atoms including the hydrogens of the phenyl rings have been located. The structure contains completely isolated $[Cu_2Cl_6]^{2-}$ dimers with two bridging and four terminal chlorines and a Cu–Cu distance of 3.355 (1) Å. The dimeric units are distinctly nonplanar, the angle between the plane defined by the copper and the two terminal chlorines and the plane defined by the copper and the two bridging chlorines being 50°. The coordination about each copper is between a planar and a tetrahedral arrangement of four chloride ligands. The Cu–Cl bond distances to the terminal chlorines (2.200 (2) and 2.179 (3) Å) are considerably shorter compared to the bridging ones (2.292 (2) and 2.321 (2) Å). Both terminal and bridging chlorines are significantly displaced from a symmetrical position relative to the copper central atoms. The shortest distance of about 9 Å between different $[Cu_2Cl_6]^{2-}$ dimers rules out any further coordination about the copper atom by additional chlorine atoms. The $(C_6H_5)_4P^+$ cations are separated from the dimeric units by normal van der Waals contacts (shortest Cl–C distance 3.54 Å). Tetraphenylarsonium trichlorocuprate(II), $(C_6H_5)_4AsCuCl_3$, is isomorphous with $a = 9.298$ (8) Å, $b = 19.596$ (11) Å, $c = 13.743$ (9) Å, and $\beta = 111.60$ (5)°. Electronic reflection spectra and the expected magnetic behavior of the complexes under study are briefly discussed.

Introduction

Ludwig and Textor[1] reported on spectroscopic studies of chloro and bromo complexes of copper(II) formed in noncoordinating organic solvents such as methylene chloride at various concentrations of copper(II) and halide ions. In the special case where the ratio $[Cu^{2+}]:[X^-] = 1:3$ (X = Cl, Br) only one complex species exists in observable concentration. Molecular weight determination, as well as electronic and infrared spectra, favored the assumption of a monomeric three-coordinate complex $[CuX_3]^-$. From these solutions it is possible to isolate complex salts of the type (cation)CuX_3, where cation stands for the bulky tetraphenylphosphonium, tetraphenylarsonium, or tetrabutylammonium group.

Structural investigations on complexes of the same stoichiometry, but with smaller cations like the garnet-red $KCuCl_3$,[2] NH_4CuCl_3,[2] and $(CH_3)_2NH_2CuCl_3$,[3] have been shown to contain discrete planar $[Cu_2Cl_6]^{2-}$ ions. The dimers in $KCuCl_3$ and NH_4CuCl_3 are stacked above each other in such a way that each copper is bonded to a chlorine atom in the dimer above it and to a chlorine atom in the dimer below it. In this manner the copper atom completes its distorted octahedral coordination. The situation in $(CH_3)_2NH_2CuCl_3$ is comparable, except for the sixth position of the distorted octahedral configuration remaining unoccupied, which results in formally five-coordinate copper(II).

Spectral investigations in the visible and ultraviolet regions of $(C_6H_5)_4PCuCl_3$, $(C_6H_5)_4AsCuCl_3$, and $(C_4H_9)_4NCuCl_3$[1] showed that there is no striking similarity to those complexes containing the planar $[Cu_2Cl_6]^{2-}$ mentioned above. This holds especially for the ligand field part of the spectra, which contains in the case of the former complexes with bulky cations a band at some 8 kK and a shoulder at 11.1 kK while the known planar dimers exhibit one broad absorption at about 12.9 kK with a weak shoulder in the range of 10.5-11.5 kK,[4] typical for an octahedrally distorted environment of copper(II).

While one could not expect the presence of three-coordinate copper(II) in the solid complexes under investigation, the energy of their ligand field transitions pointed to a new local symmetry about the copper somewhere between a planar and a tetrahedral coordination.

Experimental Section

Preparation of $(C_6H_5)_4PCuCl_3$. Saturated solutions of $(C_6H_5)_4PCl$ and $CuCl_2$ in absolute ethanol were poured together in equimolar proportions. Red-brown platelike crystals separated immediately and were collected. They were recrystallized from hot absolute ethanol and dried in a vacuum desiccator. *Anal.* Calcd for $(C_6H_5)_4PCuCl_3$: C, 56.60; H, 3.96; Cu, 12.48. Found: C, 56.75; H, 4.03; Cu, 12.38.

Growth of Single Crystals. An ethanolic solution of $(C_6H_5)_4PCuCl_3$ saturated at 50° is slowly cooled to room temperature over a 48-hr period. The resulting prismatic crystals are stable to air and do not decompose upon exposure to X-rays.

Unit Cell and Space Group. Weissenberg photographs taken on a Nonius camera with Cu Kα radiation and precession photographs taken on a Buerger precession camera with Mo Kα radiation indicated that the crystals belong to the monoclinic system. The systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$ are consistent with the centrosymmetric space group $P2_1/c$ (C_{2h}^5). Accurate unit cell dimensions were calculated from X-ray powder photographs registered on a Guinier–de Wolff focusing camera using Cu Kα radiation and high-purity potassium chloride as an internal standard. The lattice constants refined by least-squares methods from 30 powder reflections are $a = 9.226$ (8) Å, $b = 19.301$ (15) Å, $c = 13.842$ (15) Å, and $\beta = 111.26$ (6)°. The unit cell volume is 2297 Å^3. The pycnometrically measured density ($\rho_{obsd} = 1.46 \pm 0.01$ g cm^{-3}) is in good agreement with the calculated value $\rho_{calcd} = 1.47$ g cm^{-3} and $Z = 4$.

Collection and Reduction of the X-Ray Diffraction Data. A $(C_6H_5)_4PCuCl_3$ single crystal with approximate dimensions 0.17 × 0.13 × 0.08 mm was chosen for data collection on an automated four-circle Picker diffractometer using Mo Kα radiation (pyrolytic graphite monochromator, 002). Intensity data were collected by a conventional moving-crystal, moving-counter θ–2θ scan over a 2θ range of 1.5° with a scan speed of 0.25°/min. Background counts of 100 sec were taken at each side of the peak.

Three selected standard reflections were measured after every 10 reflections and used for an internal scaling of the data by least-squares methods. The average standard deviations of the intensities from the

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(1) W. Ludwig and M. Textor, *Helv. Chim. Acta*, **54**, 1143 (1971).

(2) R. D. Willett, C. Dwiggins, R. F. Kruh, and R. E. Rundle, *J. Chem. Phys.*, 38, 2429 (1963).

(3) R. D. Willett, *J. Chem. Phys.*, **44**, 39 (1966).

(4) R. D. Willett and O. L. Liles, *Inorg. Chem.*, **6**, 1666 (1967).

fit with the regression lines are 1.0, 0.6, and 1.2% for the three standard reflections. Intensities were collected up to $2\theta \leqslant 35°$. Of the 2098 reflections measured (including standards), 1460 remained after averaging equivalent reflections and 1189 were judged to be observed according to the criterion $I \geqslant 2\sigma(I)$, $\sigma(I)$ being the estimated standard deviation in the net intensity based on counting statistics. The intensities were reduced to F_o in the usual way by applying Lorentz and polarization factors. Absorption corrections ($\mu = 14.0$ cm^{-1} for Mo Kα) were made by an enlarged version[5] of the program ORABS 2[6] and resulted in a significantly better agreement between intensities of measured equivalent reflections. The calculated transmissions varied from 0.842 to 0.898.

Solution and Refinement of the Structure. A three-dimensional Patterson synthesis revealed the positional parameters of the copper, two chlorine, and the phosphorus atoms. The unweighted discrepancy factor $R(\Sigma||F_o| - |F_c||/\Sigma|F_o|)$ at this point was about 0.39. By two successive three-dimensional difference Fourier syntheses the positions of the still missing chlorine atom and of all carbon atoms were detected. Full-matrix isotropic least-squares refinement on the positional and thermal parameters of all nonhydrogen atoms resulted in an unweighted R value of 0.087 and a weighted discrepancy factor of $R_w = 0.091$, where $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where w is the weight derived from counting statistics and defined as $w = 1/\sigma^2(F_o)$. Refinement was continued using anisotropic thermal parameters. Three cycles of refinement of thermal and two cycles of positional parameters converged to $R = 0.053$ and $R_w = 0.058$. A subsequent three-dimensional difference Fourier map showed 20 peaks with peak heights between 0.7 and 1.0 e/Å^3, which could be attributed to the hydrogens of the phenyl rings. The variation of the positional parameters of the hydrogens resulted in a substantial improvement of the C–H distances and C–C–H angles. Inclusion of the hydrogen atoms decreased R to 0.042 and R_w to 0.041. The isotropic thermal parameter B for all the hydrogen atoms was chosen as 6.0 Å^2 and held invariant during the refinement process. A further refinement cycle of the thermal and positional parameters of all nonhydrogen atoms yielded the final values[7] $R = 0.032$ and $R_w = 0.024$. The largest ratio of the shifts of the atomic positional parameters to the standard deviations in the last full-matrix refinement cycle was <0.4.

Structure factors were calculated using the atom scattering factors for Cu(2+), Cl(1−), C(0), and H(0) and interpolated values for P(1+) tabulated in "International Tables for X-Ray Crystallography" (1962). No corrections for anomalous scattering were applied. All the computations, including refinement of the structure, were performed using the program system XRAY 67,[8] which was enlarged and modified for use on a CDC 6400-6500 computer system by Schwarzenbach.[5]

Description of the Structure

Final atomic positions and anisotropic thermal parameters are listed in Tables I and II; intramolecular distances and angles together with their estimated standard deviations are collected in Tables III and IV.

The principal feature of the crystal structure is the existence of essentially isolated $[Cu_2Cl_6]^{2-}$ dimers (shown in Figures 1 and 2) with a copper-copper distance of 3.355 (1) Å. By space group symmetry requirements the dimers need only have a center of symmetry which is at the same time the center of the dimer and connects equivalent pairs of Cu, Cl1, Cl2, and Cl3, respectively. The $[Cu_2Cl_6]^{2-}$ units are decidedly nonplanar, the angle between the plane defined by the copper and the two terminal chlorines Cl1 and Cl2 and the plane defined by the copper and the two bridging chlorines being 50° (see Figure 2). The coordination about each copper is intermediate between a planar and a tetrahedral arrangement of four chlorine ligands and can crudely be approximated as D_{2d}. Distances to the terminal chlorines (2.200 (2) and 2.179 (3) Å) have significantly different values and are substantially shorter than the distances to the bridging chlorines (2.292 (2) and 2.321 (2) Å). The bridging chlorines are also displaced considerably from a symmetrical position respective to the copper atoms.

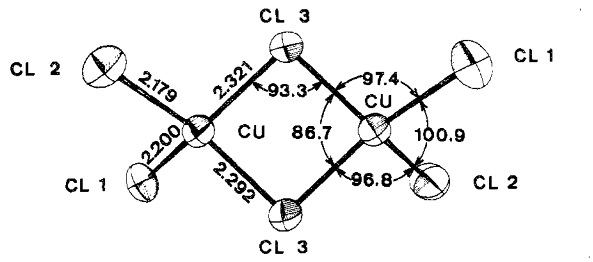

Figure 1. The $[Cu_2Cl_6]^{2-}$ ion. View is perpendicular to the plane Cu–Cl3–Cu.

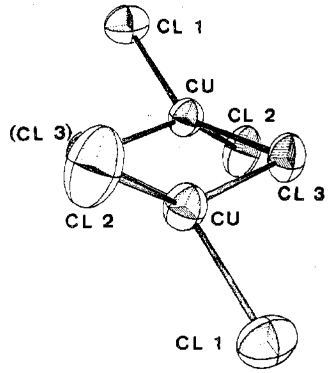

Figure 2. The $[Cu_2Cl_6]^{2-}$ ion viewed approximately along the Cu–Cu direction. The angle between the planes Cu–Cl1–Cl2 and Cu–Cl3–Cu is 50°.

The copper central atoms in the dimers have no further long-range coordination, the next atom apart from the chlorines being a hydrogen (H(25)) at a distance of 3.25 Å.

The anisotropic mean-square amplitudes of vibration of the terminal chlorines are, as can be seen by inspection of Figure 1, decidedly enlarged in the directions normal to the Cu–Cl bond which is in agreement with the general acceptance of smaller force constants for bending than for stretching vibrations. The same statement holds for the bridging ligands, where the maximum extension of the vibration ellipsoid nearly coincides with the normal to the plane defined by the copper and the two bridging chlorines (see Figure 2).

The molecular structure of the $(C_6H_5)_4P^+$ ion is in close agreement with published structures containing the same or a similar cation. The phenyl rings are arranged tetrahedrally around the phosphorus (see Figure 3). The mean P–C bond length of 1.775 Å is somewhat shorter compared to the values 1.796 Å (corrected for libration of the phenyl rings) found by Goldstein[9] in the tetraphenylphosphonium and 1.799 Å (uncorrected) found by Fritchie[10] in the triphenylmethylphosphonium ion. The standard deviation from the mean, calculated from the equation

$$\sigma^2 = \sum_{i=1}^{i=N} (\chi_i - \bar{\chi})^2/(N-1)$$

where χ_i is the ith bond length and $\bar{\chi}$ is the mean of the N equivalent bond lengths, amounts to 0.007 Å and is comparable to the esd's for the individual bonds, so that all four P–C bonds may have equal length within the error limit.

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(5) D. Schwarzenbach, Institut fur Kristallographie und Petrographie, Eidgenossische Technische Hochschule, Zurich, 1972, unpublished work.

(6) W. R. Busing, Report ORABS 2, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1966.

(7) See paragraph at end of paper regarding supplementary material.

(8) J. M. Stewart, F. A. Kundell, and J. C. Baldwin, Program System XRAY 67, Computer Science Center, University of Maryland, July 1970.

(9) P. Goldstein, K. Seff, and K. N. Trueblood, *Acta Crystallogr., Sect. B*, 24, 778 (1968).

(10) C. J. Fritchie, *Acta Crystallogr.*, 20, 107 (1966).

Table I. Atomic Positional Parameters in $(C_6H_5)_4PCuCl_3$ with the Estimated Standard Deviations of the Last Digit in Parentheses

Atom	x	y	z	Atom	x	y	z
Cu	0.1197 (1)	0.0476 (1)	0.0978 (1)	C(25)	0.3180 (10)	0.8805 (5)	0.1409 (6)
Cl(1)	0.2064 (3)	0.0288 (1)	0.2660 (2)	C(26)	0.2863 (9)	0.8148 (4)	0.0972 (6)
Cl(2)	0.2331 (3)	0.1457 (1)	0.0918 (2)	C(31)	0.2824 (10)	0.6499 (4)	0.0729 (6)
Cl(3)	0.8815 (2)	0.9960 (1)	0.0587 (2)	C(32)	0.1365 (10)	0.6200 (4)	0.0479 (6)
P	0.6741 (3)	0.2946 (1)	0.0147 (2)	C(33)	0.1037 (10)	0.5789 (5)	0.1196 (7)
C(11)	0.5235 (8)	0.3311 (4)	0.0500 (5)	C(34)	0.2198 (12)	0.5682 (5)	0.2169 (7)
C(12)	0.4548 (10)	0.3944 (4)	0.0112 (6)	C(35)	0.3653 (11)	0.5983 (5)	0.2421 (6)
C(13)	0.3397 (10)	0.4220 (4)	0.0442 (7)	C(36)	0.3964 (10)	0.6396 (4)	0.1699 (6)
C(14)	0.2921 (10)	0.3864 (5)	0.1134 (6)	C(41)	0.8382 (9)	0.2839 (4)	0.1299 (5)
C(15)	0.3582 (10)	0.3228 (5)	0.1525 (6)	C(42)	0.9092 (9)	0.2198 (4)	0.1595 (6)
C(16)	0.4780 (9)	0.2963 (4)	0.1239 (5)	C(43)	0.9662 (10)	0.7120 (5)	0.2473 (7)
C(21)	0.3795 (9)	0.7878 (4)	0.0462 (5)	C(44)	0.9137 (10)	0.7674 (5)	0.1819 (6)
C(22)	0.5018 (9)	0.8274 (4)	0.0382 (5)	C(45)	0.9802 (10)	0.8328 (5)	0.2104 (6)
C(23)	0.5297 (9)	0.8933 (4)	0.0813 (6)	C(46)	0.8953 (9)	0.3410 (4)	0.1954 (6)
C(24)	0.4386 (10)	0.9194 (4)	0.1326 (6)				
H(12)	0.504 (11)	0.577 (5)	0.045 (7)	H(32)	0.954 (11)	0.361 (5)	0.027 (7)
H(13)	0.299 (11)	0.468 (5)	0.021 (7)	H(33)	0.000 (11)	0.549 (5)	0.099 (7)
H(14)	0.209 (11)	0.404 (5)	0.141 (7)	H(34)	0.804 (11)	0.042 (5)	0.231 (7)
H(15)	0.323 (11)	0.293 (5)	0.213 (7)	H(35)	0.531 (11)	0.094 (5)	0.184 (7)
H(16)	0.541 (11)	0.249 (5)	0.158 (7)	H(36)	0.505 (11)	0.671 (5)	0.197 (7)
H(22)	0.427 (11)	0.197 (5)	0.003 (7)	H(42)	0.856 (11)	0.182 (5)	0.109 (7)
H(23)	0.614 (11)	0.916 (5)	0.064 (7)	H(43)	0.916 (11)	0.665 (5)	0.227 (7)
H(24)	0.455 (11)	0.969 (5)	0.160 (7)	H(44)	0.820 (11)	0.756 (5)	0.108 (7)
H(25)	0.248 (11)	0.895 (5)	0.185 (7)	H(45)	0.934 (11)	0.877 (5)	0.164 (7)
H(26)	0.200 (11)	0.781 (5)	0.112 (7)	H(46)	0.829 (11)	0.386 (5)	0.165 (7)

Table II. Mean-Square Amplitudes of Vibrations[a] ($\text{Å}^2 \times 10^{-3}$)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	42.8 (0.6)	44.9 (0.6)	41.5 (0.6)	−6.7 (0.6)	16.7 (0.5)	−2.0 (0.5)
Cl(1)	69 (1)	55 (1)	40 (1)	3 (1)	13 (1)	−6 (1)
Cl(2)	85 (2)	67 (2)	76 (2)	−35 (1)	44 (1)	−12 (1)
Cl(3)	45 (1)	67 (1)	45 (1)	−14 (1)	22 (1)	−7 (1)
P	33 (1)	37 (1)	40 (1)	−0.4 (1)	16 (1)	0.2 (1)
C(11)	38 (5)	36 (5)	42 (5)	−6 (4)	12 (4)	−9 (4)
C(12)	52 (7)	57 (6)	60 (6)	10 (5)	27 (5)	9 (5)
C(13)	59 (7)	66 (7)	90 (7)	29 (5)	34 (6)	4 (5)
C(14)	40 (6)	100 (8)	63 (6)	5 (6)	21 (5)	−4 (6)
C(15)	44 (6)	71 (7)	53 (6)	−5 (5)	21 (5)	−5 (5)
C(16)	47 (6)	53 (6)	47 (5)	−9 (5)	22 (4)	−6 (4)
C(21)	32 (6)	35 (5)	41 (5)	3 (4)	10 (4)	2 (4)
C(22)	34 (5)	47 (5)	43 (5)	0.3 (5)	12 (5)	−3 (4)
C(23)	47 (6)	46 (5)	65 (6)	−12 (5)	21 (5)	−7 (5)
C(24)	63 (7)	40 (6)	52 (6)	6 (5)	11 (5)	−5 (4)
C(25)	56 (6)	53 (6)	66 (6)	0.7 (5)	35 (5)	5 (5)
C(26)	55 (6)	28 (5)	60 (6)	−2 (5)	24 (5)	−6 (4)
C(31)	40 (6)	43 (5)	52 (5)	3 (5)	19 (5)	−3 (5)
C(32)	61 (6)	63 (6)	58 (6)	3 (5)	34 (5)	24 (5)
C(33)	64 (7)	76 (7)	81 (7)	−19 (6)	29 (6)	11 (6)
C(34)	107 (8)	59 (7)	80 (7)	16 (7)	70 (6)	21 (6)
C(35)	63 (7)	65 (6)	65 (6)	15 (6)	23 (6)	5 (5)
C(36)	64 (7)	38 (5)	51 (6)	0.0 (5)	32 (5)	7 (4)
C(41)	40 (5)	33 (5)	41 (5)	0.1 (5)	22 (4)	−1 (4)
C(42)	43 (6)	63 (6)	39 (5)	−1 (5)	3 (5)	−7 (5)
C(43)	54 (7)	65 (7)	55 (6)	−17 (5)	7 (5)	6 (5)
C(44)	43 (7)	91 (8)	46 (6)	−6 (6)	12 (5)	4 (5)
C(45)	52 (7)	63 (7)	64 (6)	17 (5)	24 (5)	24 (5)
C(46)	36 (6)	53 (6)	46 (5)	1 (5)	13 (5)	−6 (5)

[a] The temperature factors were calculated using the expression $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

The average of the 24 C–C bond distances is 1.391 Å in agreement with the distances of 1.390 Å (corrected for libration) in the tetraphenylphosphonium ion,[9] 1.389 Å (corrected) found in the tetraphenylarsonium ion by Palenik,[11] and 1.381 Å in the triphenylmethylphosphonium ion.[10] The standard deviation of the C–C bonds from their mean (defined as above) is 0.01 Å, almost as large as the esd's of individual C–C bonds. No systematic deviation of the phenyl rings from a regular hexagon can therefore be recognized. The C–H distances after refinement of the hydrogen positional parameters range from 0.96 to 1.15 Å with a mean value of 1.06 Å. The esd's for the individual C–H bonds are calculated to be about 0.1 Å.

Least-squares planes were calculated for the four phenyl rings to test the degree of planarity. As can be seen from Table V, where equations for the planes and deviations of the individual carbon atoms are listed, all rings are planar within the uncertainty in the positional parameters. The root-mean-square deviations of the constituent atoms are 0.016, 0.005, 0.005, and 0.016 Å for phenyl rings 1, 2, 3, and 4, respectively.

Figure 4 shows the packing of the $(C_6H_5)_4P^+$ and $[Cu_2Cl_6]^{2-}$ within the unit cell viewed down *a*. The centers

(11) G. J. Palenik, *Acta Crystallogr.*, 20, 471 (1966).

Table III. Interatomic Distances[a]

Atoms	Dist, Å	Atoms	Dist, Å
(I) Distances within the $[Cu_2Cl_6]^{2-}$ Ion			
Cu-Cl(1)	2.200 (2)	Cu-Cl(3)	2.321 (2)
Cu-Cl(2)	2.179 (3)	Cu-Cu	3.355 (1)
Cu-Cl(3)	2.292 (2)		
(II) Distances within the $(C_6H_5)_4P^+$ Ion			
P-C(11)	1.777 (9)	P-C(31)	1.770 (9)
P-C(21)	1.783 (7)	P-C(41)	1.768 (6)
Av P-C	1.775 (7)[b]		
C(11)-C(12)	1.392 (11)	C(31)-C(32)	1.388 (12)
C(12)-C(13)	1.405 (15)	C(32)-C(33)	1.386 (14)
C(13)-C(14)	1.373 (15)	C(33)-C(34)	1.399 (11)
C(14)-C(15)	1.390 (13)	C(34)-C(35)	1.386 (14)
C(15)-C(16)	1.399 (14)	C(35)-C(36)	1.388 (13)
C(16)-C(11)	1.409 (12)	C(36)-C(31)	1.387 (10)
C(21)-C(22)	1.400 (12)	C(41)-C(42)	1.390 (11)
C(22)-C(23)	1.388 (11)	C(42)-C(43)	1.390 (10)
C(23)-C(24)	1.378 (14)	C(43)-C(44)	1.371 (12)
C(24)-C(25)	1.381 (14)	C(44)-C(45)	1.396 (13)
C(25)-C(26)	1.390 (11)	C(45)-C(46)	1.399 (10)
C(26)-C(21)	1.396 (13)	C(46)-C(41)	1.404 (11)
Av C-C	1.391 (11)[b]		
Av C-H	1.06 (6)[b]		

[a] Estimated standard deviations shown in parentheses are right adjusted to the last significant digit of the previous number. [b] Esd's of average bond lengths were calculated from the equation $\sigma^2 = \Sigma_{i=1}{}^{i=N}(\chi_i - \bar{\chi})^2/(N-1)$ where χ_i is the *i*th bond length and $\bar{\chi}$ is the mean of the *N* equivalent bond lengths.

Table IV. Interatomic Angles[a]

Atoms	Angle, deg	Atoms	Angle, deg
(I) Angles within the $[Cu_2Cl_6]^{2-}$ Ion			
Cl(1)-Cu-Cl(2)	100.9 (1)	Cl(2)-Cu-Cl(3)	96.8 (1)
Cl(1)-Cu-Cl(3)	97.4 (1)	Cl(3)-Cu-Cl(2)	143.3 (1)
Cl(3)-Cu-Cl(1)	143.6 (1)	Cl(3)-Cu-Cl(3)	86.7 (1)
Cu-Cl(3)-Cu	93.3 (1)		
(II) Angles within the $(C_6H_5)_4P^+$ Ion			
C(11)-P-C(21)	111.9 (4)	C(21)-P-C(31)	108.0 (4)
C(11)-P-C(31)	110.0 (4)	C(21)-P-C(41)	108.8 (4)
C(11)-P-C(41)	107.3 (4)	C(31)-P-C(41)	110.8 (4)
		Av C-P-C	109.5
C(11)-C(12)-C(13)	120.0 (9)	C(31)-C(32)-C(33)	120.2 (7)
C(12)-C(13)-C(14)	120.5 (8)	C(32)-C(33)-C(34)	118.9 (9)
C(13)-C(14)-C(15)	120.6 (9)	C(33)-C(34)-C(35)	120.9 (9)
C(14)-C(15)-C(16)	119.5 (9)	C(34)-C(35)-C(36)	119.6 (7)
C(15)-C(16)-C(11)	120.4 (7)	C(35)-C(36)-C(31)	119.8 (8)
C(16)-C(11)-C(12)	119.0 (8)	C(36)-C(31)-C(32)	120.6 (8)
C(21)-C(22)-C(23)	119.6 (8)	C(41)-C(42)-C(43)	120.9 (7)
C(22)-C(23)-C(24)	120.3 (8)	C(42)-C(43)-C(44)	120.2 (8)
C(23)-C(24)-C(25)	120.3 (8)	C(43)-C(44)-C(45)	120.4 (7)
C(24)-C(25)-C(26)	120.6 (9)	C(44)-C(45)-C(46)	119.6 (7)
C(25)-C(26)-C(21)	119.3 (8)	C(45)-C(46)-C(41)	120.2 (7)
C(26)-C(21)-C(22)	119.9 (7)	C(46)-C(41)-C(42)	118.8 (6)
		Av C-C-C	120.0
		Av C-C-H	119.9

[a] See footnote *a* of Table III.

of the $[Cu_2Cl_6]^{2-}$ dimers (being centers of inversion) lie at the eight edges of the unit cell (000, 100, 010, 001, 110, 101, 011, 111) and are generated by the twofold screw axis at $0, {}^1/_2, {}^1/_2$ and $1, {}^1/_2, {}^1/_2$. The shortest distance between adjacent dimers is the identity period along $a = 9.28$ Å, thus excluding any important bonding interaction. The $(C_6H_5)_4P^+$ cations are located in the space between the dimers; individual cations and anions are separated by normal van der Waals distances (shortest Cl-C distance 3.54 Å).

Discussion of the Structure

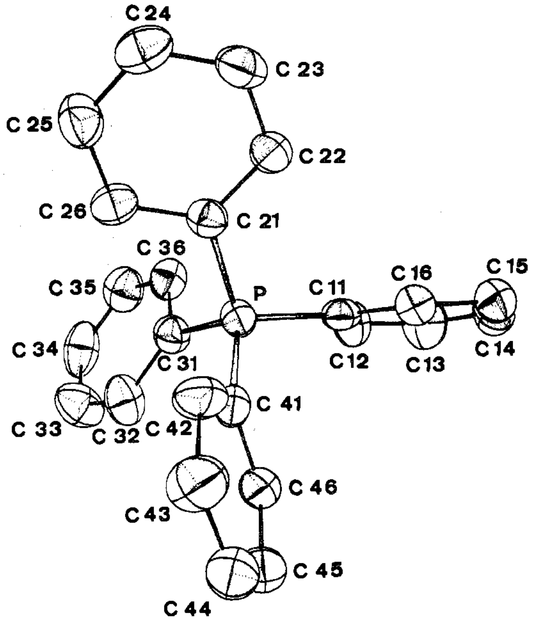

Figure 3. The $(C_6H_5)_4P^+$ ion.

Table V. Least-Squares Planes[a] for Phenyl Rings and Deviations of the Constituent Atoms in Å × 10^{-3}

Atom	Dev	Atom	Dev
Ring I: C(11)-C(16)			
$0.4563I + 0.4780J + 0.7505K = 5.632$			
C(11)	9	C(14)	5
C(12)	8	C(15)	21
C(13)	10	C(16)	23
Ring II: C(21)-C(26)			
$0.3403I - 0.3862J + 0.8574K = -4.245$			
C(21)	3	C(24)	6
C(22)	5	C(25)	4
C(23)	6	C(26)	3
Ring III: C(31)-C(36)			
$-0.4848I + 0.8036J + 0.3451K = 9.327$			
C(31)	3	C(34)	5
C(32)	5	C(35)	3
C(33)	5	C(36)	3
Ring IV: C(41)-C(46)			
$-0.8639I - 0.2130J + 0.4565K = -6.531$			
C(41)	9	C(44)	25
C(42)	2	C(45)	14
C(43)	19	C(46)	2

[a] Planes are defined as $PI + QJ + RK = S$ in orthogonal angstrom space. *I, J, K* are 1.0 Å in magnitude with *I* parallel to the crystallographic axis *a*, *K* perpendicular to *a* in the plane of *a* and *c*, and *J* perpendicular to the plane of *a* and *c*.

The most predominant feature of the structure is the presence of nonplanar $[Cu_2Cl_6]^{2-}$ ions in marked contrast to the published structures for $KCuCl_3{}^{2-}$, NH_4CuCl_3,[2] and $(CH_3)_2NH_2CuCl_3$,[3] which contain essentially planar dimers. The absence of any further long-range coordination around the copper atom in $(C_6H_5)_4PCuCl_3$ can be explained as a consequence of the much more space-consuming tetraphenylphosphonium cation which prevents a close approach of different dimers, so that the commonly found distorted octahedron with four short and two longer bonds around copper does not form. Otherwise, an unfavorable electrostatic charge distribution would arise. The fact that the fifth and sixth ligand positions in the coordination sphere of the copper atom remain unoccupied leads to a displacement of the chloride ligands out from the planar configuration, a matter of fact very often observed in four-coordinate copper

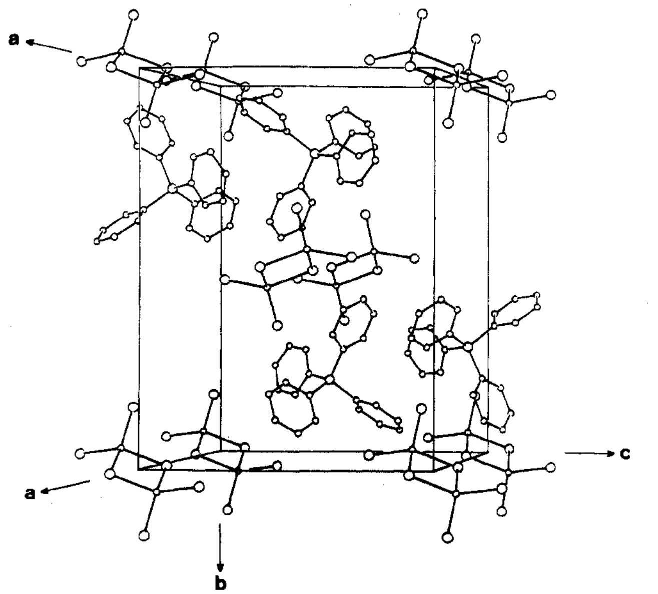

Figure 4. The packing of $[Cu_2Cl_6]^{2-}$ and $(C_6H_5)_4P^+$ ions within the unit cell. View is perpendicular to the plane *bc*.

complexes which are in some way prevented from completing the coordination by additional long bonds. This can in principle be understood as a consequence of the d^9 system of copper(II) being normally energetically not very sensitive to stereochemical changes, so that different arrangements of the ligands do not differ much in energy. The actual stereochemistry reflects a rather subtle balance of overlap effects (between central atom and ligand orbitals), antibonding ligand-ligand interactions, and packing effects in the crystal. The ligand-ligand repulsion may be the reason for the distortion of the dimers under study, although, from a purely electrostatic point of view, the Madelung potential alone favors a tetrahedral arrangement over a planar one.

The mean Cu-Cl distance in $(C_6H_5)_4PCuCl_3$ (2.248 Å) is somewhat smaller than the mean of the four in-plane bonds in $KCuCl_3$ (2.288 Å). This is very often observed when going from a higher to a lower coordination and can be attributed to reduced ligand-ligand interactions. As a consequence the Cu-Cu distance (3.355 (1) Å) is also shortened compared to $KCuCl_3$ (3.443 (3) Å) and $(CH_3)_2NH_2CuCl_3$ (3.444 (6) Å).

The other compounds with bulky cations mentioned in the Introduction seem to have an analogous structure. Tetraphenylarsonium trichlorocuprate(II), $(C_6H_5)_4AsCuCl_3$, is isomorphous with unit cell parameters refined from powder diffraction data: $a = 9.298$ (8) Å, $b = 19.596$ (11) Å, $c = 13.743$ (9) Å, and $\beta = 111.60$ (5)°. The bromo complexes tetraphenylphosphonium tribromocuprate(II), $(C_6H_5)_4PCuBr_3$, and tetrabutylammonium tribromocuprate(II), $(C_4H_9)_4NCuBr_3$, are both not isomorphous indeed. However, their electronic reflection spectra[1] are rather similar to those of the chloro complexes apart from the expected bathochromic shift of the electron-transfer bands as a consequence of the lower optical electronegativity of bromine. It is therefore plausible to assume that in the bromo compounds, too, nonplanar dimers $[Cu_2Br_6]^{2-}$ are present.

Spectral and Magnetic Properties

Recently the study of the spectral and magnetic properties of dimeric copper(II) halides has received considerable attention. Compounds containing the $[Cu_2Cl_6]^{2-}$ ion show always a pronounced yellow-red or green-red pleochroism when examined with polarized light.[3,12] The red color seems to arise always from an electron-transfer band of the type Cl → Cu at about 19 kK in the planar dimers;[4] this transition is strongly polarized with the maximum absorption in the Cu-Cu direction and is absent in monomeric complexes as in the yellow $(C_2H_5NH_3)_2CuCl_4$. A green-red pleochroism is also observed in the nonplanar dimers under study. The red color here arises from a band at some 21-22 kK.[1] It would be interesting to compare the electronic spectra of monomeric planar and tetrahedral halide complexes with those of dimeric compounds of different symmetries. A thorough study of the electronic absorption spectra of such compounds is under way in this laboratory.

Great interest in compounds containing dimeric $[Cu_2Cl_6]^{2-}$ or $[Cu_2Br_6]^{2-}$ ions has also been aroused by magnetic studies.[13,14] One difficulty lies in the fact that the magnetic susceptibility, especially at low temperatures, is governed by two effects, namely, the spin-spin interaction between two copper ions in the same dimer (leading to a singlet state some 38 cm^{-1} below a triplet in $KCuCl_3$[14]) and a magnetic interaction between adjacent dimers which is a cooperative effect over the whole lattice and results in the formation of ferromagnetic or antiferromagnetic spin arrays. Because of the large separation of adjacent dimers in $(C_6H_5)_4PCuCl_3$, investigation of its magnetic properties should be specially suited for a study of the undisturbed exchange interaction between copper ions within the dimer.

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Registry No. $(C_6H_5)_4PCuCl_3$, 50860-38-3; $(C_6H_5)_4AsCuCl_3$, 50807-65-3.

Supplementary Material Available. Table VI, a listing of structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-1361.

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