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Molecules with an M_4X_4 Core. II.[1]
X-Ray Crystallographic Determination of the Molecular Structure of Tetrameric Triphenylphosphinecopper(I) Bromide in Crystalline $[PPh_3CuBr]_4 \cdot 2CHCl_3$

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Tetrameric triphenylphosphinecopper(I) bromide crystallizes from chloroform as the solvated species $[PPh_3CuBr]_4 \cdot xCHCl_3$ ($x = 2.0$ for the idealized structure and ~1.5 for the actual crystal examined). The crystals belong to the centrosymmetric monoclinic space group $C2/c$ [C_{2h}^6; No. 15], unit cell parameters being $a = 28.461$ (9) Å, $b = 15.983$ (4) Å, $c = 18.044$ (5) Å, and $\beta = 112.59$ (1)°. The observed density of 1.56 (2) g cm^{-3} is consistent with the value of 1.58 g cm^{-3} calculated from $V = 7578$ Å^3, mol wt 1802, and $Z = 4$. X-Ray diffraction data complete to $2\theta = 40°$ (Mo Kα radiation) were collected with a Picker FACS-1 automated diffractometer, and the structure was solved *via* a combination of Patterson, Fourier, and least-squares refinement techniques. Using anisotropic thermal parameters for all nonhydrogen atoms, and with hydrogen atoms included in calculated positions, the final discrepancy indices are $R_F = 6.44\%$ and $R_{wF} = 7.19\%$ for the 2412 independent reflections. The molecule has precise (*i.e.*, crystallographically dictated) C_i symmetry with the Cu_4Br_4 core defining a "step-like" configuration—in sharp constrast to the "cubane" configuration of the Cu_4Cl_4 core in $[PPh_3CuCl]_4$. Two copper atoms, Cu(1) and Cu(1′), have a tetrahedral coordination geometry, while the other two (Cu(2) and Cu(2′)) are in trigonal-planar coordination sites. Copper-bromine distances range from 2.377 (2) to 2.664 (2) Å, while intramolecular copper· · ·copper distances are Cu(1)· · ·Cu(2′) = 2.991 (2), Cu(1′)· · ·Cu(2) = 2.991 (2), and Cu(1)· · ·Cu(1′) = 3.448 (3) Å.

Introduction

Our recent involvement with the polynuclear hydridocopper complex $(PPh_3CuH)_6$,[2,3] in which the copper–copper distances ranged from 2.494 (6) to 2.674 (5) Å, has led us to investigate a number of tetrameric phosphine (and arsine) copper(I) halides. Prior to this series of studies, only one structural investigation of such a species had been reported, Wells (in 1936) having found a copper· · ·copper distance of 2.60 Å in $(AsEt_3CuI)_4$.[4,5] Since Mason and Mingos[6] have demonstrated that the intermetallic bond order is greater (*i.e.*, the metal· · ·metal distance should be shorter) in hydrido-bridged *vis a vis* the analogous halogeno-bridged species, it seems clear that our investigations are warranted.

Following a single-crystal X-ray diffraction study of $(PPh_3CuCl)_4$ (in which Cu· · ·Cu distances were found to range from 3.118 (1) to 3.430 (1) Å),[1] we embarked on an analysis of the bromo analog, $(PPh_3CuBr)_4$. We expected to be able to follow variations in copper· · ·copper distance within cubane-like $(PPh_3CuX)_4$ species as a function of X; instead, serendipitously, we found that the Cu_4Br_4 core in $(Ph_3PCuBr)_4$ *did not* define a cube but, rather, formed a new framework, which we term a "step" structure. Preliminary results of this study have appeared previously;[7] a full account appears below.

Experimental Section

Collection and Reduction of the X-Ray Diffraction Data. The complex was prepared *via* the procedure of Jardine, Rule, and Vohra.[8] Crystals were obtained by the slow evaporation of a saturated solution of $(PPh_3CuBr)_4$ in chloroform. The crystals are initially white but become yellow following prolonged exposure to X-irradiation; significant decomposition of the crystals occurs in an X-ray beam (*vide infra*).

The crystal chosen for the single-crystal X-ray diffraction study was a regular parallelepiped bounded by well-formed $\{011\}$ and $\{100\}$ faces. Dimensions were $(100)\rightarrow(\bar{1}00)$ = 0.6 mm, $(011)\rightarrow(0\bar{1}\bar{1})$ = 0.3 mm, and $(0\bar{1}1)\rightarrow(01\bar{1})$ = 0.3 mm.

A preliminary photographic study, using $h(0\text{–}3)l$ and $hk(0\text{–}3)$ precession photographs along with b and c cone-axis photographs, revealed C_{2h} $(2/m)$ Laue symmetry for the diffraction pattern, provided approximate unit-cell parameters, and showed the following systematic absences: hkl for $h + k = 2n + 1$ and $h0l$ for $l = 2n + 1$. These extinctions are consistent either with the noncentrosymmetric monoclinic space group Cc (C_s^4; No. 9)[9] or with the centrosymmetric monoclinic space group $C2/c$ (C_{2h}^6; No. 15).[9] The successful solution of the structure proves the latter, centrosymmetric, case to be the true space group.

The crystal was aligned and centered on a Picker FACS-1 diffractometer with a^* coincident with the instrumental ϕ axis. Under "high-resolution" conditions,[10] the 2θ, ω, and χ settings were determined for the resolved Mo Kα_1 peaks (λ 0.70930 Å[11]) of 12 high-angle ($2\theta \approx 40°$) reflections which were well-dispersed in reciprocal space. These values were used in a least-squares refinement of the cell and orientation parameters. The resulting unit cell parameters (at 25 ± 1°) are $a = 28.4606$ (87) Å, $b = 15.9831$ (37) Å, $c =$

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[1] Part I: M. R. Churchill and K. L. Kalra, *Inorg. Chem.*, 13, 1065 (1974). This article describes an X-ray diffraction study of $(PPh_3CuCl)_4$. This species has also been investigated by two other research groups: W. R. Clayton and S. G. Shore, *Cryst. Struct. Commun.*, 2, 605 (1973); M. R. Truter, personal communication.

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[3] M. R. Churchill, S. A. Bezman, J. A. Osborn, and J. Wormald, *Inorg. Chem.*, 11, 1818 (1972).

[4] A. F. Wells, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, 94, 447 (1936).

[5] F. G. Mann, D. Purdie, and A. F. Wells, *J. Chem. Soc.*, 1503 (1936).

[6] R. Mason and D. M. P. Mingos, *J. Organometal. Chem.*, 50, 53 (1973).

[7] M. R. Churchill and K. L. Kalra, *J. Amer. Chem. Soc.*, 95, 5772 (1973).

[8] F. H. Jardine, L. Rule, and A. G. Vohra, *J. Chem. Soc. A*, 238 (1970).

[9] "International Tables for X-Ray Crystallography," Vol. 1, 2nd ed, Kynoch Press, Birmingham, England, 1965, pp 89, 101.

[10] M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, 12, 525 (1973).

[11] J. A. Bearden, *Rev. Mod. Phys.*, 39, 78 (1967).

18.0438 (54) Å, and $\cos\beta = -0.38406$ (30) (corresponding to $\beta =$ 112.59 (1)°). The unit cell volume is 7578.4 Å^3.

The observed density ($\rho_{obsd} = 1.56$ (2) g cm^{-3}, by flotation) is not in good agreement with the value of 1.422 g cm^{-3} calculated for $Z = 4$ and mol wt 1622.98 (for unsolvated $(PPh_3CuBr)_4$) or with the value of 1.632 g cm^{-3} calculated for $Z = 4$ and mol wt 1861.74 (corresponding to the *stoichiometric* solvated species $(PPh_3CuBr)_4 \cdot 2CHCl_3$). However, as outlined below, the refinement of occupancy factors for chloroform of solvation yields an occupancy of ~75%, suggesting a stoichiometry $(PPh_3CuBr)_4 \cdot {\sim}1.5CHCl_3$, for which the calculated density with $Z = 4$ is 1.579 g cm^{-3}. [N.B. The density *of the actual crystal used in the analysis* was not measured. It is probable that there is a range of densities corresponding to a range in the stoichiometry of the crystals.]

For $Z = 4$ there is no symmetry imposed upon the $(PPh_3CuBr)_4$ molecule in space group Cc; for space group $C2/c$ (in the absence of disorder) the $(PPh_3CuBr)_4$ molecule is required to possess C_2 or C_i symmetry. The successful elucidation of the crystal structure (*vide infra*) shows the molecule to crystallize in the centrosymmetric space group $C2/c$ with crystallographically imposed C_i ($\bar{1}$) symmetry. No crystallographic symmetry is imposed upon the $CHCl_3$ molecule.

Intensity data were measured by executing a coupled θ(crystal)-2θ(counter) scan using the procedure described previously.[10] The following details are pertinent to the present study. (1) Nb-filtered Mo radiation was used. (2) Scan speed = 2.0°/min. (3) The scan was from 0.87° below the Mo Kα_1 peak to 0.87° above the Mo Kα_2 peak. (4) Background counts, of 20-sec duration each, were measured at the low- and high-2θ limits of the scan. (5) The takeoff angle was 3.0°. (6) The detector was 330 mm from the crystal, with a 6 mm × 6 mm aperture.

Reflections of the type $h + k = 2n$ in the octants hkl and $\bar{h}kl$ and in the angular range $0° < 2\theta \leqslant 40°$ were measured. [Very few reflections were observable above $2\theta = 40°$ on long-exposure precession photographs.] Three strong check reflections (14,0,0, $\bar{2}$06, 130) were measured after each batch of 48 reflections in order to monitor crystal decomposition, possible changes in crystal orientation, etc. No misorientation of the crystal occurred (the alignment being checked at the termination of data collection), but some anisotropic reduction in intensity of the check reflections was observed (14,0,0 by 11%, $\bar{2}$06 by 19%, 130 by 9.2%). Application of an *anisotropic* linear decay correction[12] to the entire data set reduced the root-mean-square deviations in the standard reflections to 0.86, 1.36, and 1.94% (respectively). The raw intensity data were assigned estimated standard deviations (assuming an "ignorance factor" of $p = 0.03$) and reduced to values of $|F_o|$ and $\sigma(|F_o|)$ precisely as has been described previously.[10,13] Any reflection having a net negative count was reset to zero. All data were retained, none being rejected as "not significantly above background."

A total of 122 reflections having $(\sin\theta)/\lambda < 0.154$ were corrected empirically for the falsely low values of their low-angle background counts. [A description of the method of correction has been given in a previous publication.[10]]

At the termination of data collection, a strong axial reflection (14,0,0) was measured by a θ-2θ scan, at $\chi = 90°$ and at 10° intervals from $\phi = 0°$ to $\phi = 350°$. The variation in intensity [defined by (maximum − minimum)/mean] was 20%, thereby indicating the necessity for an absorption correction. These data, along with the entire data set, were corrected for absorption.[14] The resulting ϕ dependence of the intensity of this reflection was less than 2%, thus providing an independent confirmation of the validity of the absorption correction. Maximum and minimum transmission factors for the primary data set were 0.457 and 0.267 ($\mu = 37.2$ cm^{-1}).

Finally, equivalent pairs of $hk0$ and $\bar{h}k0$ reflections were averaged and their intensities replaced by the σ^{-2}-weighted average, with appropriately modified standard deviations. The final data set consisted of 2412 symmetry-independent reflections and represented a unique data set complete to $2\theta = 40°$.

Solution and Refinement of the Structure. Scattering factors for neutral copper, bromine, phosphorus, and carbon were taken from the compilation of Cromer and Waber;[15] both the real and the imaginary components of anomalous dispersion[16] were included specifically in the calculation of structure factor amplitudes. For hydrogen, the scattering factors of Mason and Robertson[17] were used.

The function minimized during least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$, where $w(hkl) = \sigma^{-2}(hkl)$. The discrepancy indices used in the text are defined as

$$R_F = \frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|} \times 100\ (\%)$$

$$R_{wF} = \left[\frac{\Sigma w(|F_o| - |F_c|)}{\Sigma w|F_o|^2}\right]^{1/2} \times 100\ (\%)$$

Computer programs used during the structural analysis were FORDAP (Fourier synthesis, by A. Zalkin), LSHF (a locally modified version of SFLS5, by C. T. Prewitt), STAN1 (calculation of distances, angles, and their esd's, by B. G. DeBoer), PLOD (least-squares planes etc., by B. G. DeBoer), and ORTEP (thermal ellipsoid drawings, by C. K. Johnson). All calculations were performed on an IBM 370/155 computer.

A three-dimensional Patterson synthesis suggested that the true space group was $C2/c$ with the $(PPh_3CuBr)_4$ molecule lying on a crystallographic inversion center and provided the coordinates for the two copper and two bromine atoms of the crystallographic asymmetric unit.

A series of three-dimensional electron density maps, with each successive map being phased by an increasing number of atoms, led to the location of all nonhydrogen atoms of the $(PPh_3CuBr)_4$ molecule.

Full-matrix least-squares refinement of positional and isotropic thermal parameters for 42 nonhydrogen atoms (which define the asymmetric unit of the $(PPh_3CuBr)_4$ molecule) led to convergence at $R_F = 13.5\%$ and $R_{wF} = 15.5\%$. A difference-Fourier synthesis at this stage revealed three major diffuse peaks (of height 4.34, 3.53, and 2.83 e Å^{-3}), which were attributed to the three chlorine atoms of a chloroform molecule of solvation. Refinement was continued, using anisotropic thermal parameters for all nonhydrogen atoms of the $(PPh_3CuBr)_4$ molecule and isotropic thermal parameters for the atoms of the $CHCl_3$ molecule; individual occupancy factors for the chlorine atoms were also varied at this stage. Convergence occurred with $R_F = 8.3\%$ and $R_{wF} = 9.6\%$. A difference-Fourier synthesis at this point indicated marked anisotropy about many of the atomic positions but did not yield the positions of the 30 independent hydrogen atoms of the $(PPh_3CuBr)_4$ molecule. Hydrogen atoms were therefore included in calculated positions (based upon a regular trigonal geometry about carbon and a C–H distance of 0.95 Å[18]) and each was assigned an isotropic thermal parameter 1.2 times that of the carbon atom to which it was attached.

Atoms of the chloroform molecule were assigned an occupancy factor of 0.75 (the mean of the three independent values obtained *via* refinement and consistent with the observed density, *vide supra*). Continued refinement of positional and anisotropic thermal parameters for all nonhydrogen atoms, with fixed contribution from hydrogen atoms, led to final convergence with $R_F = 6.44\%$ and $R_{wF} = 7.19\%$.

Data were inspected for evidence of secondary extinction; none was found. The principal features of a final difference-Fourier synthesis were peaks of height 1.38 e Å^{-3} (at 0.096, 0.168, 0.360),

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(12) The formula used for the anisotropic decay correction is

$$I(\text{cor}) = \frac{I(\text{obsd})}{\sqrt{(P_1^{\,2} + P_2^{\,2} + P_3^{\,2})/\left(\dfrac{P_1^{\,2}}{k_1^{\,2}} + \dfrac{P_2^{\,2}}{k_2^{\,2}} + \dfrac{P_3^{\,2}}{k_3^{\,2}}\right)}}$$

where k_i is the fraction remaining of the ith standard at this time (time being determined *via* the serial number of the reflection) and P_i is the cosine of the angle between the reciprocal lattice vector of the reflections under consideration and that of the ith standard. This method was programmed by Dr. B. G. DeBoer and is quite similar to a method described previously [K. O. Hodgson and K. N. Raymond, *Inorg. Chem.*, 11, 171 (1972)—see, especially, left-hand column, p 172] *except* that it is less sensitive to nonorthogonality of the standards (since Hodgson and Raymond used P_i, while DeBoer's method uses P_i^2).

(13) Data reduction was performed using the FORTRAN IV program REDUCE, by B. G. DeBoer.

(14) Absorption corrections were calculated using the FORTRAN IV program DRAB, by B. G. DeBoer.

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(18) M. R. Churchill, *Inorg. Chem.*, 12, 1213 (1973).

Table I. Final Positional and Isotropic Thermal Parameters[a] for Atoms in the Asymmetric Unit of $(PPh_3CuBr)_4 \cdot 2CHCl_3$

Atom	x	y	z	B, Å^2
(A) Atoms in the $(PPh_3CuBr)_4$ Molecule[b]				
Cu(1)	0.264452 (55)	0.354237 (89)	0.021443 (86)	5.18
Cu(2)	0.143017 (59)	0.215233 (97)	−0.003181 (89)	5.48
Br(1)	0.354901 (47)	0.362236 (81)	0.114298 (72)	5.48
Br(2)	0.228629 (47)	0.248790 (74)	0.089964 (69)	4.60
P(1)	0.22293 (12)	0.47173 (18)	−0.02547 (17)	3.98
P(2)	0.07922 (12)	0.23360 (20)	0.03494 (19)	4.76
C(1)	0.24110 (42)	0.52891 (60)	−0.09755 (60)	4.09
C(2)	0.20653 (42)	0.57379 (67)	−0.16229 (63)	4.62
C(3)	0.22133 (48)	0.61675 (76)	−0.21431 (70)	5.83
C(4)	0.27044 (65)	0.61591 (74)	−0.20619 (75)	7.12
C(5)	0.30691 (49)	0.57228 (85)	−0.14326 (88)	7.10
C(6)	0.29258 (42)	0.52745 (72)	−0.08782 (68)	5.32
C(7)	0.15331 (39)	0.45879 (61)	−0.07562 (57)	3.77
C(8)	0.11704 (47)	0.51643 (65)	−0.07306 (65)	5.24
C(9)	0.06504 (39)	0.49585 (94)	−0.11134 (68)	6.42
C(10)	0.04890 (47)	0.42195 (86)	−0.14675 (72)	6.54
C(11)	0.08338 (42)	0.36795 (76)	−0.15014 (66)	5.38
C(12)	0.13440 (45)	0.38395 (67)	−0.11593 (65)	4.99
C(13)	0.22885 (39)	0.54856 (65)	0.05045 (59)	3.84
C(14)	0.22935 (48)	0.52269 (71)	0.12176 (75)	6.05
C(15)	0.23277 (51)	0.57934 (83)	0.18468 (65)	6.45
C(16)	0.23464 (56)	0.66093 (76)	0.17453 (80)	7.41
C(17)	0.23259 (75)	0.68752 (87)	0.09940 (92)	11.00
C(18)	0.23058 (65)	0.63214 (84)	0.03937 (73)	8.63
C(19)	0.01602 (46)	0.23946 (71)	−0.04301 (64)	5.21
C(20)	−0.02493 (51)	0.28253 (87)	−0.03650 (78)	7.17
C(21)	−0.07090 (55)	0.28236 (98)	−0.09786 (96)	9.31
C(22)	−0.07519 (60)	0.24050 (96)	−0.16812 (89)	9.39
C(23)	−0.03404 (64)	0.20062 (89)	−0.17384 (95)	8.42
C(24)	0.00951 (43)	0.20096 (81)	−0.11304 (69)	6.21
C(25)	0.07802 (45)	0.14763 (71)	0.09639 (68)	5.15
C(26)	0.03775 (58)	0.09538 (90)	0.08025 (75)	8.27
C(27)	0.03824 (63)	0.02609 (98)	0.12794 (99)	10.79
C(28)	0.08242 (73)	0.01539 (86)	0.19763 (97)	9.36
C(29)	0.12388 (56)	0.06567 (99)	0.21501 (85)	8.25
C(30)	0.12066 (48)	0.13148 (77)	0.16406 (77)	6.44
C(31)	0.08108 (39)	0.32351 (67)	0.09655 (64)	4.44
C(32)	0.06450 (45)	0.32319 (81)	0.15985 (76)	6.24
C(33)	0.06565 (48)	0.39946 (97)	0.19982 (72)	7.03
C(34)	0.08466 (50)	0.46968 (78)	0.17832 (96)	8.01
C(35)	0.10182 (56)	0.46617 (92)	0.11818 (83)	8.11
C(36)	0.10176 (51)	0.39399 (74)	0.07987 (69)	6.06
H(2)	0.1717	0.5747	−0.1696	5.54
H(3)	0.1972	0.6472	−0.2573	7.08
H(4)	0.2801	0.6459	−0.2436	8.52
H(5)	0.3415	0.5722	−0.1373	8.04
H(6)	0.3168	0.4971	−0.0448	6.30
H(8)	0.1285	0.5682	−0.0463	6.12
H(9)	0.0400	0.5350	−0.1108	7.70
H(10)	0.0137	0.4090	−0.1705	7.85
H(11)	0.0714	0.3165	−0.1771	6.45
H(12)	0.1584	0.3439	−0.1185	6.00
H(14)	0.2279	0.4640	0.1289	7.26
H(15)	0.2337	0.5614	0.2354	7.74
H(16)	0.2367	0.6982	0.2166	8.88
H(17)	0.2335	0.7460	0.0907	13.20
H(18)	0.2300	0.6509	−0.0109	10.35
H(20)	−0.0215	0.3113	0.0114	8.60
H(21)	−0.0989	0.3105	−0.0927	11.17
H(22)	−0.1071	0.2401	−0.2123	11.27
H(23)	−0.0369	0.1723	−0.2217	10.10
H(24)	0.0374	0.1726	−0.1184	7.45
H(26)	0.0081	0.1059	0.0337	9.92
H(27)	0.0099	−0.0105	0.1151	12.95
H(28)	0.0840	−0.0296	0.2329	12.23
H(29)	0.1537	0.0557	0.2615	9.90
H(30)	0.1492	0.1675	0.1762	7.73
H(32)	0.0517	0.2735	0.1742	7.49
H(33)	0.0535	0.4018	0.2420	8.44
H(34)	0.0856	0.5208	0.2058	9.61
H(35)	0.1149	0.5155	0.1037	9.73
H(36)	0.1147	0.3926	0.0386	7.27
(B) Atoms of the $CHCl_3$ Molecule				
Cl(1)	0.09865 (32)	0.08505 (62)	0.41297 (62)	
Cl(2)	0.04932 (40)	0.21778 (94)	0.33418 (77)	
Cl(3)	0.13898 (77)	0.20942 (140)	0.37649 (131)	

[a] "Equivalent isotropic thermal parameters" provided for nonhydrogen atoms correspond to the average mean-square displacement along the three principal axes of the vibration ellipsoid. [b] Atoms in the "other half" of the $(PPh_3CuBr)_4$ molecule are labeled with a prime and are related to those in the basic asymmetric unit by the transformation $[x', y', z'] = [^1/_2 - x, ^1/_2 - y, -z]$.

0.86 e Å^{-3} (at 0.064, 0.264, 0.372), 0.78 e Å^{-3} (at 0.160, 0.168, 0.396), 0.74 e Å^{-3} (at 0.120, 0.156, 0.456), and 0.73 e Å^{-3} (at 0.152, 0.242, 0.360). These peaks are all in the immediate vicinity of the chloroform molecule and presumably reflect inadequate treatment of thermal motion and/or disorder of the $CHCl_3$ molecule, and/or loss of $CHCl_3$ from the crystal during the collection of diffraction data.(19) No other peaks were greater than 0.6 e Å^{-3}.

The standard deviation in an observation of unit weight, defined by $[\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, was 1.79. The number of reflections (m) was 2412, and the total number of refined parameters (n) was 406, yielding an m:n ratio of 5.9:1. The function $\Sigma w(|F_o| - |F_c|)^2$ was not significantly dependent either upon θ or upon $|F_o|$—thereby indicating a correctly assigned weighting scheme.

A table of observed and calculated structure factor amplitudes is available.(20) Final positional and isotropic thermal parameters are collected in Table I. Anisotropic thermal parameters are listed in Table II.

The Molecular Structure

Interatomic distances and their estimated standard deviations (esd's) are shown in Table III; interatomic angles and their esd's are collected in Table IV. The crystal consists of discrete molecular units of $(PPh_3CuBr)_4$ and $CHCl_3$; the idealized stoichiometry, assuming occupancy factors of unity for $CHCl_3$, is $(PPh_3CuBr)_4 \cdot 2CHCl_3$. However, the stoichiometry of the crystal examined approximates to $(PPh_3CuBr)_4 \cdot {\sim}1.5CHCl_3$ (*i.e.*, 0.75 occupancy for $CHCl_3$).

The individual species are mutually separated by normal van der Waals distances. There are no abnormally short intermolecular contacts.

The overall geometry of the $(PPh_3CuBr)_4$ molecule and the numbering of atoms are shown in Figure 1. [Hydrogen atoms, omitted from this diagram for clarity's sake, are numbered similarly to their attached carbon atoms.] The molecule possesses precise (*i.e.*, crystallographically dictated) C_i ($\bar{1}$) symmetry and is centered on the special position $^1/_4$, $^1/_4$, 0. Atoms of the basic asymmetric unit are labeled normally; those of the "other half" of the molecule, which is related to the basic asymmetric unit by the transformation ($^1/_2 - x$, $^1/_2 - y$, $-z$), are labeled with a prime.

The stereochemistry of the $P_4Cu_4Br_4$ "core" of the molecule is illustrated in Figure 2. In contradistinction to most other species with an M_4X_4 core[21-23] (and, in particular,

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(19) We note here that the carbon atom of the chloroform molecule was ill behaved during attempted refinement and was not included in the final calculations.

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

(21) R. S. Nyholm, M. R. Truter, and C. W. Bradford, *Nature (London)*, 228, 648 (1970).

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Table II. Anisotropic Thermal Parameters[a] for $(PPh_3CuBr)_4 \cdot 2CHCl_3$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	$\langle U \rangle$[b]
			(A) Atoms of the $(PPh_3CuBr)_4$ Molecule				
Cu(1)	5.75 (9)	3.92 (9)	5.30 (9)	0.91 (7)	1.49 (7)	0.49 (7)	0.21, 0.26, 0.29
Cu(2)	6.28 (10)	5.49 (9)	5.05 (9)	0.34 (7)	2.61 (8)	−0.19 (7)	0.23, 0.27, 0.29
Br(1)	5.40 (8)	5.58 (8)	4.48 (8)	0.63 (6)	0.79 (6)	−1.17 (6)	0.22, 0.25, 0.32
Br(2)	6.03 (8)	4.26 (7)	3.88 (7)	−0.18 (6)	2.30 (6)	−0.42 (5)	0.21, 0.24, 0.28
P(1)	4.95 (17)	3.13 (17)	3.44 (16)	0.03 (13)	1.18 (14)	−0.27 (14)	0.19, 0.21, 0.26
P(2)	5.34 (21)	4.94 (21)	4.04 (19)	−0.22 (16)	1.85 (17)	−0.14 (17)	0.22, 0.25, 0.26
C(1)	6.2 (9)	2.6 (6)	3.7 (8)	−0.3 (6)	2.2 (7)	−0.6 (6)	0.17, 0.22, 0.28
C(2)	6.8 (9)	3.7 (7)	4.1 (8)	−0.6 (7)	2.9 (8)	0.1 (6)	0.20, 0.22, 0.30
C(3)	6.4 (10)	5.9 (9)	5.5 (9)	0.1 (8)	2.6 (8)	0.1 (7)	0.26, 0.27, 0.28
C(4)	13.6 (16)	3.4 (8)	4.5 (9)	−0.8 (10)	3.7 (10)	−0.3 (7)	0.21, 0.23, 0.42
C(5)	7.8 (11)	6.9 (10)	10.0 (12)	−3.1 (9)	7.2 (11)	−2.9 (9)	0.19, 0.26, 0.42
C(6)	4.6 (9)	5.8 (8)	6.1 (8)	0.6 (6)	2.5 (7)	−0.2 (7)	0.22, 0.27, 0.30
C(7)	5.2 (8)	2.9 (7)	3.1 (6)	0.7 (7)	1.5 (6)	0.5 (6)	0.18, 0.20, 0.26
C(8)	8.1 (11)	2.9 (7)	5.4 (8)	1.1 (8)	3.4 (8)	0.4 (6)	0.18, 0.24, 0.33
C(9)	2.0 (8)	11.4 (14)	5.5 (8)	2.3 (8)	1.1 (6)	3.4 (9)	0.14, 0.25, 0.41
C(10)	5.4 (11)	6.9 (10)	5.7 (9)	−3.7 (10)	0.4 (7)	−1.6 (8)	0.16, 0.31, 0.36
C(11)	3.5 (9)	6.4 (4)	5.1 (8)	−0.7 (8)	0.3 (7)	0.3 (7)	0.19, 0.27, 0.31
C(12)	7.0 (10)	3.4 (8)	4.8 (7)	0.8 (7)	2.5 (7)	−0.1 (6)	0.20, 0.24, 0.30
C(13)	5.0 (7)	3.2 (9)	3.4 (8)	0.3 (5)	1.7 (5)	0.8 (6)	0.18, 0.23, 0.25
C(14)	8.8 (9)	3.7 (8)	6.7 (9)	0.3 (6)	4.2 (8)	1.2 (9)	0.20, 0.27, 0.34
C(15)	10.1 (10)	6.3 (11)	3.3 (8)	0.6 (8)	2.9 (7)	−0.5 (8)	0.18, 0.28, 0.36
C(16)	12.8 (12)	3.0 (9)	6.9 (11)	−0.6 (7)	4.3 (9)	−0.2 (7)	0.19, 0.28, 0.40
C(17)	22.7 (20)	4.1 (9)	8.3 (12)	−3.1 (10)	8.3 (13)	0.2 (11)	0.19, 0.29, 0.54
C(18)	17.3 (15)	5.3 (11)	4.0 (8)	−3.5 (9)	4.9 (9)	−2.7 (9)	0.15, 0.27, 0.48
C(19)	7.0 (10)	4.9 (8)	2.9 (9)	−1.5 (8)	1.0 (8)	0.3 (7)	0.19, 0.23, 0.33
C(20)	6.2 (10)	7.9 (10)	6.4 (11)	0.3 (8)	1.2 (10)	−1.4 (8)	0.26, 0.29, 0.35
C(21)	7.0 (13)	11.2 (13)	7.3 (12)	1.0 (9)	−0.0 (11)	−0.9 (11)	0.26, 0.35, 0.41
C(22)	9.5 (15)	9.1 (12)	5.6 (12)	−5.1 (12)	−1.6 (10)	2.2 (10)	0.22, 0.25, 0.40
C(23)	10.7 (15)	7.4 (11)	10.1 (16)	0.3 (11)	7.2 (15)	−0.7 (10)	0.25, 0.31, 0.40
C(24)	4.7 (9)	8.0 (10)	3.2 (9)	−0.8 (7)	−1.6 (7)	1.3 (8)	0.14, 0.29, 0.36
C(25)	6.0 (9)	4.4 (8)	4.6 (9)	0.7 (8)	1.7 (8)	0.3 (7)	0.23, 0.25, 0.29
C(26)	11.3 (14)	6.8 (11)	5.2 (9)	−0.7 (10)	1.5 (9)	2.3 (9)	0.21, 0.32, 0.41
C(27)	10.5 (13)	9.2 (4)	9.3 (12)	−1.6 (10)	0.1 (11)	2.6 (12)	0.29, 0.32, 0.47
C(28)	15.7 (18)	5.9 (10)	10.0 (15)	−0.1 (12)	7.9 (15)	1.1 (10)	0.24, 0.31, 0.45
C(29)	8.9 (12)	7.7 (11)	8.9 (12)	2.6 (10)	4.1 (10)	2.1 (11)	0.27, 0.31, 0.38
C(30)	7.3 (11)	5.3 (10)	6.8 (10)	0.9 (7)	2.8 (10)	1.4 (8)	0.24, 0.30, 0.32
C(31)	4.4 (7)	3.9 (4)	4.3 (8)	0.2 (6)	0.8 (6)	0.2 (7)	0.21, 0.23, 0.27
C(32)	6.4 (8)	7.0 (11)	6.6 (9)	−0.1 (7)	3.8 (8)	−0.8 (9)	0.23, 0.29, 0.32
C(33)	6.9 (9)	9.5 (12)	5.2 (8)	1.6 (9)	2.8 (7)	−2.1 (10)	0.20, 0.29, 0.38
C(34)	6.4 (9)	4.0 (10)	11.5 (15)	−0.9 (7)	1.1 (9)	−0.7 (10)	0.22, 0.29, 0.42
C(35)	10.8 (12)	8.1 (15)	7.9 (11)	−0.5 (9)	6.4 (10)	1.5 (10)	0.21, 0.34, 0.39
C(36)	10.5 (10)	3.3 (8)	4.8 (8)	−0.1 (8)	3.5 (7)	−1.7 (7)	0.16, 0.27, 0.37
			(B) Atoms of the $CHCl_3$ Molecule				
Cl(1)	15.1 (7)	16.3 (7)	26.8 (10)	1.3 (5)	0.5 (6)	2.9 (7)	
Cl(2)	21.1 (9)	48.7 (19)	30.5 (12)	18.8 (11)	18.4 (9)	27.1 (13)	
Cl(3)	37.9 (21)	42.4 (26)	41.9 (24)	−0.5 (18)	3.6 (18)	−24.6 (22)	

[a] These anisotropic thermal parameters have units of Å² and are analogous to the normal isotropic thermal parameters, entering the expression for the structure factor in the form $\exp[-0.25(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)]$. [b] These values correspond to the root-mean-square amplitudes of vibration (in Å) of the atom along the three principal axes of its vibration ellipsoid. For orientations, see figures.

with $(PPh_3CuCl)_4$[1,7]), the present molecule does not possess a "cubane" skeleton but has a different structure, which we term a "step" configuration. We note here that atoms in the $(PPh_3CuBr)_4$ structure have variable coordination numbers (CN's). Thus, Cu(1) and Cu(1′) are in approximately tetrahedral coordination environments (CN = 4), while Cu(2) and Cu(2′) each have a trigonal stereochemistry (CN = 3). Similarly, Br(2) and Br(2′) have a pyramidal geometry (CN = 3) while Br(1) and Br(1′) have an angular coordination geometry (CN = 2).

The ten edges of the Cu_4Br_4 "step" are each defined by a Cu-Br bond. While these bond lengths show considerable variations, there is a predominating systematic pattern; *i.e.*, the higher the coordination numbers of the atoms involved in the bond, then the longer is the bond. Thus (in order of increasing bond distance) we have Cu(2)-Br(1′) = Cu(2′)-

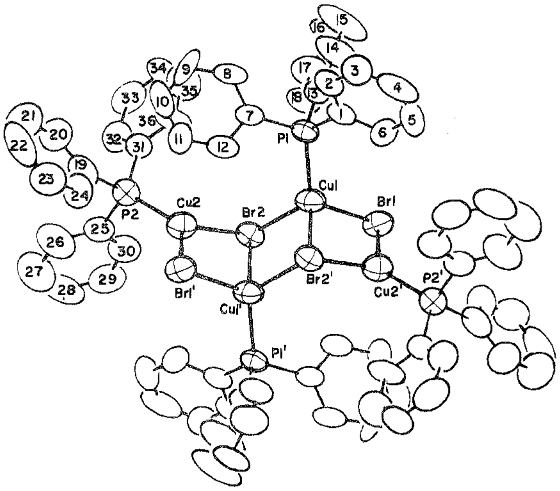

Figure 1. Geometry and numbering of atoms in the $(PPh_3CuBr)_4$ molecule. (Carbon atoms are labeled with numbers only.)

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(23) B. A. Averill, T. Hershkovitz, R. H. Holm, and J. A. Ibers, *J. Amer. Chem. Soc.*, **95**, 3523 (1973)–see, especially, Table IX, p 3532.

Table III. Interatomic Distances (in Å) with Esd's for $(PPh_3CuBr)_4$[a,b]

Atoms	Dist	Atoms	Dist
A. Copper···Copper Distances			
Cu(1)···Cu(2')	2.9905 (22)	Cu(1)···Cu(2)	3.9873 (23)
Cu(2)···Cu(1')	2.9905 (22)	Cu(1')···Cu(2')	3.9873 (23)
Cu(1)···Cu(1')	3.4481 (29)		
B. Copper–Bromine Distances			
Cu(1)–Br(1)	2.4773 (21)	Cu(2)–Br(1')	2.3765 (20)
Cu(1)–Br(2)	2.5253 (19)	Cu(2)–Br(2)	2.4297 (21)
Cu(1)–Br(2')	2.6637 (19)		
C. Bromine···Bromine Distances			
Br(1)···Br(2)	3.8966 (20)	Br(2)···Br(1')	3.9565 (20)
Br(1)···Br(2')	3.9565 (20)	Br(1')···Br(2')	3.8966 (20)
Br(2)···Br(2')	3.8801 (25)		
D. Copper–Phosphorus Distances			
Cu(1)–P(1)	2.2070 (33)	Cu(2)–P(2)	2.1943 (36)
E. Phosphorus–Carbon Distances			
P(1)–C(1)	1.819 (10)	P(2)–C(19)	1.811 (12)
P(1)–C(7)	1.847 (11)	P(2)–C(25)	1.774 (12)
P(1)–C(13)	1.799 (11)	P(2)–C(31)	1.805 (11)
F. Distances within Phenyl Rings			
C(1)–C(2)	1.401 (13)	C(19)–C(20)	1.397 (16)
C(2)–C(3)	1.354 (14)	C(20)–C(21)	1.351 (16)
C(3)–C(4)	1.348 (17)	C(21)–C(22)	1.397 (20)
C(4)–C(5)	1.396 (17)	C(22)–C(23)	1.372 (20)
C(5)–C(6)	1.412 (15)	C(23)–C(24)	1.302 (17)
C(6)–C(1)	1.407 (14)	C(24)–C(19)	1.353 (15)
C(7)–C(8)	1.398 (13)	C(25)–C(26)	1.356 (16)
C(8)–C(9)	1.411 (15)	C(26)–C(27)	1.399 (18)
C(9)–C(10)	1.338 (16)	C(27)–C(28)	1.406 (19)
C(10)–C(11)	1.326 (15)	C(28)–C(29)	1.361 (19)
C(11)–C(12)	1.366 (14)	C(29)–C(30)	1.377 (16)
C(12)–C(7)	1.396 (13)	C(30)–C(25)	1.375 (15)
C(13)–C(14)	1.346 (13)	C(31)–C(32)	1.393 (14)
C(14)–C(15)	1.426 (15)	C(32)–C(33)	1.410 (16)
C(15)–C(16)	1.321 (15)	C(33)–C(34)	1.365 (17)
C(16)–C(17)	1.400 (17)	C(34)–C(35)	1.351 (18)
C(17)–C(18)	1.383 (17)	C(35)–C(36)	1.345 (16)
C(18)–C(13)	1.355 (15)	C(36)–C(31)	1.357 (14)

[a] Esd's were calculated by considering those elements of the positional correlation matrix whose magnitudes were greater than 0.05. The calculation was performed using the FORTRAN IV program STAN1 by B. G. DeBoer. Contributions from errors in the unit cell dimensions are included. [b] Bond lengths are not corrected for the effects of thermal motion.

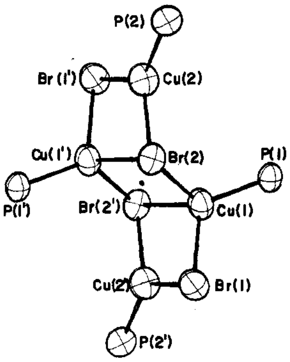


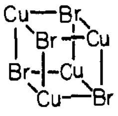
Figure 2. Stereochemistry of the $P_4Cu_4Br_4$ "core" of the $(PPh_3CuBr)_4$ molecule.

Br(1) = 2.3765 (20) Å [CN's 3 and 2]; Cu(2)-Br(2) = Cu(2')-Br(2') = 2.4297 (21) Å [CN's 3 and 3]; Cu(1)-Br(1) = Cu(1')-Br(1') = 2.4773 (21) Å [CN's 4 and 2]; Cu(1)-Br(2) = Cu(1')-Br(2') = 2.5253 (19) Å [CN's 4 and 3]; and Cu(1)-Br(2') = Cu(1')-Br(2) = 2.6637 (19) Å [CN's 4 and 3].

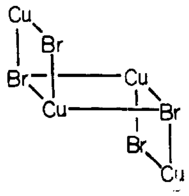
The four copper atoms are *precisely* coplanar. Copper-copper distances, in order of increasing length, are Cu(1)···Cu(2') = Cu(1')···Cu(2) = 2.9905 (22) Å and Cu(1)···Cu(1') = 3.4481 (29) Å. The "through-space" contacts, Cu(1)···Cu(2) and Cu(1')···Cu(2'), are considerably longer, at 3.9873 (23) Å. These distances are all sufficiently long as to preclude any significant Cu···Cu interactions. For the purpose of comparison, we may note that Cu···Cu distances within the "cubane" skeleton of $[PPh_3CuCl]_4$ range from 3.1179 (13) to 3.4298 (18) Å.

Bromine···bromine distances within the $(PPh_3CuBr)_4$ molecule show little variation: individual values within the "step" skeleton are Br(2)···Br(2') = 3.8801 (25) Å and Br(1)···Br(2') = Br(1')···Br(2) = 3.9565 (20) Å, while the "through-space" contacts are Br(1)···Br(2) = Br(1')···Br(2') = 3.8966 (20) Å. It may well be, therefore, that the stabilization of the "step" (relative to the "cubane") structure owes its origin principally to the minimization of bromine···bromine interactions. (However, see "Discussion.")

Note that the van der Waals radius for bromine is ~1.95 Å[24] and that the hypothetical "cubane" structure (I) contains *six* next-to-nearest neighbor Br···Br interactions as opposed to only *five* for the "step" structure (II). We emphasize that the four bromine atoms are *precisely* coplanar and that their relative positions are (approximately) defined by two coplanar fused equilateral triangles.



I



II

Within each of the three Cu-Br-Cu-Br rings, individual bond angles vary significantly from 90°. Thus, within the strictly planar central ring, Br(2)-Cu(1)-Br(2') = Br(2')-Cu(1')-Br(2) = 96.76 (6)°, while Cu(1')-Br(2)-Cu(1) = Cu(1)-Br(2')-Cu(1') = 83.24 (6)°. Within one of the two symmetry-related outer rings [which is only approximately planar, the root-mean-square deviation from planarity being 0.073 Å—see Table V], angles about copper are, again, greater than 90° [Br(2')-Cu(1)-Br(1) = 100.57 (7)° and Br(1)-Cu(2')-Br(2') = 110.81 (8)°] while angles about bromine are less than 90° [*i.e.*, Cu(1)-Br(1)-Cu(2') = 76.04 (6)° and Cu(2')-Br(2')-Cu(1) = 71.74 (6)°]. The dihedral angle between the planes Br(1')-Cu(2)-Br(2) and Br(2)-Cu(1')-Br(1') is 168.7°.

Interatomic angles *between* the various four-membered rings are not so strikingly dependent upon the identity of the central atom. Thus, Br(1)-Cu(1)-Br(2) = Br(1')-Cu(1')-Br(2') = 102.32 (7)° and Cu(1)-Br(2)-Cu(2) = Cu(1')-Br(2')-Cu(2') = 107.15 (7)°.

The gross geometry of the Cu_4Br_4 core of the $(PPh_3CuBr)_4$ molecule is best described in terms of the dihedral angle of 107.8° between the strictly planar system Br(2)-Cu(1)-Br(2')-Cu(1') and the approximately planar system Br(2)-Cu(2)-Br(1')-Cu(1').

Atoms Cu(1) and Cu(1') each have a distorted tetrahedral coordination environment. The distortion is in the direction of local C_{3v} symmetry about copper; the Br-Cu(1)-Br angles (*vide supra*) range from 96.76 (6) to 102.32 (7)° (average 99.88°), while the P(1)-Cu(1)-Br angles are significantly greater, individual values being P(1)-Cu(1)-Br(2) = 119.89 (10)°, P(1)-Cu(1)-Br(1) = 118.66 (10)°, and P(1)-Cu(1)-

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(24) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960—see, especially, Table 7-20, p 260.

Table IV. Interatomic Angles (in Degrees) for $(PPh_3CuBr)_4$, with Esd's[a]

Atoms	Angle	Atoms	Angle
(A) Angles within the Cu_4Br_4 Systems			
Br(2)-Cu(1)-Br(2′)	96.76 (6)	Br(2)-Cu(1′)-Br(1′)	100.57 (7)
Cu(1′)-Br(2)-Cu(1)	83.24 (6)	Cu(1′)-Br(1′)-Cu(2)	76.04 (6)
Br(2′)-Cu(1′)-Br(2)	96.76 (6)	Br(1′)-Cu(2)-Br(2)	110.81 (8)
Cu(1)-Br(2′)-Cu(1′)	83.24 (6)	Cu(2)-Br(2)-Cu(1′)	71.74 (6)
Br(2′)-Cu(1)-Br(1)	100.57 (7)	Br(1)-Cu(1)-Br(2)	102.32 (7)
Cu(1)-Br(1)-Cu(2′)	76.04 (6)	Cu(1)-Br(2)-Cu(2)	107.15 (7)
Br(1)-Cu(2′)-Br(2′)	110.81 (8)	Br(1′)-Cu(1′)-Br(2′)	102.32 (7)
Cu(2′)-Br(2′)-Cu(1)	71.74 (6)	Cu(1′)-Br(2′)-Cu(2′)	107.15 (7)
(B) Phosphorus-Copper-Bromine Angles			
P(1)-Cu(1)-Br(1)	118.66 (10)	P(2)-Cu(2)-Br(1′)	128.75 (11)
P(1)-Cu(1)-Br(2)	119.89 (10)	P(2)-Cu(2)-Br(2)	118.97 (11)
P(1)-Cu(1)-Br(2′)	114.86 (10)		
(C) Copper-Phosphorus-Carbon Angles			
Cu(1)-P(1)-C(1)	116.38 (36)	Cu(2)-P(2)-C(19)	117.25 (39)
Cu(1)-P(1)-C(7)	114.09 (34)	Cu(2)-P(2)-C(25)	108.01 (41)
Cu(1)-P(1)-C(13)	114.14 (35)	Cu(2)-P(2)-C(31)	117.87 (37)
(D) Carbon-Phosphorus-Carbon Angles			
C(1)-P(1)-C(7)	104.60 (48)	C(19)-P(2)-C(25)	105.88 (54)
C(1)-P(1)-C(13)	103.44 (46)	C(19)-P(2)-C(31)	102.86 (53)
C(7)-P(1)-C(13)	102.62 (47)	C(25)-P(2)-C(31)	103.57 (54)
(E) Internal Angles of the Phenyl Rings			
C(6)-C(1)-C(2)	118.4 (10)	C(24)-C(19)-C(20)	118.9 (11)
C(1)-C(2)-C(3)	122.2 (11)	C(19)-C(20)-C(21)	120.5 (13)
C(2)-C(3)-C(4)	120.3 (12)	C(20)-C(21)-C(22)	117.7 (15)
C(3)-C(4)-C(5)	120.6 (12)	C(21)-C(22)-C(23)	120.8 (13)
C(4)-C(5)-C(6)	120.2 (12)	C(22)-C(23)-C(24)	119.9 (14)
C(5)-C(6)-C(1)	118.3 (11)	C(23)-C(24)-C(19)	122.2 (13)
C(12)-C(7)-C(8)	116.1 (10)	C(30)-C(25)-C(26)	117.4 (12)
C(7)-C(8)-C(9)	118.6 (10)	C(25)-C(26)-C(27)	123.2 (13)
C(8)-C(9)-C(10)	122.9 (12)	C(26)-C(27)-C(28)	116.1 (15)
C(9)-C(10)-C(11)	118.2 (11)	C(27)-C(28)-C(29)	122.2 (14)
C(10)-C(11)-C(12)	122.3 (11)	C(28)-C(29)-C(30)	117.9 (14)
C(11)-C(12)-C(7)	121.7 (10)	C(29)-C(30)-C(25)	123.1 (13)
C(18)-C(13)-C(14)	117.1 (10)	C(36)-C(31)-C(32)	119.8 (11)
C(13)-C(14)-C(15)	122.6 (11)	C(31)-C(32)-C(33)	117.9 (12)
C(14)-C(15)-C(16)	120.7 (11)	C(32)-C(33)-C(34)	119.9 (12)
C(15)-C(16)-C(17)	116.4 (12)	C(33)-C(34)-C(35)	119.9 (13)
C(16)-C(17)-C(18)	122.5 (12)	C(34)-C(35)-C(36)	121.3 (13)
C(17)-C(18)-C(13)	120.6 (12)	C(35)-C(36)-C(31)	120.9 (12)
(F) External Angles of the Phenyl Rings[b]			
P(1)-C(1)-C(2)	123.5 (9)	P(2)-C(19)-C(20)	124.9 (10)
P(1)-C(1)-C(6)	118.1 (8)	P(2)-C(19)-C(24)	116.2 (10)
P(1)-C(7)-C(8)	125.3 (8)	P(2)-C(25)-C(26)	124.1 (10)
P(1)-C(7)-C(12)	118.5 (8)	P(2)-C(25)-C(30)	118.6 (10)
P(1)-C(13)-C(14)	118.8 (9)	P(2)-C(31)-C(32)	124.3 (9)
P(1)-C(13)-C(18)	124.0 (9)	P(2)-C(31)-C(36)	115.9 (9)

[a] See footnotes to Table III. [b] Hydrogen Atoms are in calculated positions (see text).

Br(2′) = 114.86 (10)°. The atom Cu(1) lies 1.192 Å above the plane defined by Br(1), Br(2), and Br(2′).

Atoms Cu(2) and Cu(2′) each have an approximately trigonal-planar coordination geometry, individual angles being P(2)-Cu(2)-Br(1′) = 128.75 (11)°, P(2)-Cu(2)-Br(2) = 118.97 (11)°, and Br(2)-Cu(2)-Br(1′) = 110.81 (8)°. The copper atom lies 0.162 Å above the plane defined by P(2), Br(2), and Br(1′)—see Table V.

The Cu(tetrahedral)-P distances [Cu(1)-P(1) = Cu(1′)-P(1′) = 2.2070 (33) Å] are slightly longer than the Cu(trigonal)-P distances [Cu(2)-P(2) = Cu(2′)-P(2′) = 2.1943 (36) Å]; however, the difference of 0.0127 (49) Å is significant only at the 2.5σ level.

The Triphenylphosphine Ligand

Phosphorus-carbon distances show considerable variations; those involving P(1) range from 1.799 (11) to 1.847 (11) Å (average 1.822 Å), while those involving P(2) range from 1.774 (12) to 1.811 (12) Å (average 1.797 Å).

As is general for metal-phosphine complexes,[25] angles about the phosphorus atoms show systematic deviations from the ideal tetrahedral value of 109.47°. About P(1), the Cu-P-C angles range from 114.09 (34) to 116.38 (36)° (average 114.87°), while C-P-C angles are 102.62 (47)-104.60 (48)° (average 103.55°). For P(2), the Cu-P-C and C-P-C angles are respectively 108.01 (41)-117.87 (37)° (average 114.38°) and 102.86 (53)-105.88 (54)° (average 104.10°).

The 36 carbon-carbon bond distances within the six phenyl rings range from 1.302 (17) to 1.426 (15) Å, the mean value being 1.373 Å—identical with the average value of 1.373 Å found for $(PPh_3CuCl)_4$[1] but lower than the accepted C-C(aromatic) distance of 1.394 ± 0.005 Å.[26] Presumably, the lower value observed for $(PPh_3CuBr)_4$ and $(PPh_3CuCl)_4$ is an artifact of librational motion.

(25) M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A*, 2970 (1968)—see, especially, Table 7, p 2976.

(26) L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, No. 18, S16s (1965).

Table V. Least-Squares Planes (and Deviations Therefrom) within the $(PPh_3CuBr)_4$ Molecule[a-c] and Dihedral Angles

Atom	Dev, Å	Atom	Dev, Å
Plane I: $0.2775X + 0.8167Y - 0.5059Z = 4.0518$			
Br(1′)*	0.076	Cu(1′)*	−0.066
Cu(2)*	−0.080	P(2)	−0.739
Br(2)*	0.071	P(1′)	−1.758
Plane Ia: $0.1720X + 0.8527Y - 0.4932Z = 3.6635$			
Br(1′)*	0.000	Br(2)*	0.000
Cu(2)*	0.000		
Plane Ib: $0.3561X + 0.7835Y - 0.5092Z = 4.4475$			
Br(2)*	0.000	Br(1′)*	0.000
Cu(1′)*	0.000		
Plane II: $0.7497X - 0.2496Y + 0.6129Z = 4.3366$			
Br(2)*	0.000	Cu(1′)*	0.000
Cu(1)*	0.000	P(1)	−1.590
Br(2′)*	0.000	P(1′)	1.590
Plane III: $0.2775X + 0.8167Y - 0.5059Z = 6.4244$			
Br(1)*	−0.076	Cu(2′)*	0.080
Cu(1)*	0.066	P(2′)	0.739
Br(2′)*	−0.071	P(1)	1.758
Plane IV: $0.0572X + 0.8785Y - 0.4743Z = 3.1189$			
Br(2)*	0.000	P(2)*	0.000
Br(1′)*	0.000	Cu(2)	0.162
Plane V: $-0.4115X + 0.8506Y - 0.3273Z = 0.4708$			
Br(1)*	0.000	Cu(1)	1.192
Br(2)*	0.000	P(1)	3.398
Br(2′)*	0.000		
Plane VI: $-0.0575X + 0.8133Y + 0.5790Z = 5.4968$			
C(1)*	0.004	C(5)*	0.002
C(2)*	−0.006	C(6)*	−0.002
C(3)*	0.006	P(1)	0.015
C(4)*	−0.004		
Plane VII: $0.3200X + 0.4022Y - 0.8578Z = 5.5991$			
C(7)*	0.006	C(11)*	−0.005
C(8)*	0.007	C(12)*	−0.007
C(9)*	−0.019	P(1)	0.116
C(10)*	0.018		
Plane VIII: $0.9357X - 0.0396Y + 0.3505Z = 5.7097$			
C(13)*	0.006	C(17)*	−0.013
C(14)*	−0.011	C(18)*	0.007
C(15)*	0.004	P(1)	−0.054
C(16)*	0.008		
Plane IX: $0.4222X + 0.8373Y - 0.3473Z = 3.7856$			
C(19)*	−0.014	C(23)*	0.006
C(20)*	0.015	C(24)	0.003
C(21)*	−0.007	P(2)	−0.012
C(22)*	−0.004		
Plane X: $-0.6137X + 0.5842Y + 0.5311Z = 1.2749$			
C(25)*	−0.004	C(29)*	0.006
C(26)*	−0.010	C(30)*	0.007
C(27)*	0.022	P(2)	0.020
C(28)*	−0.021		
Plane XI: $0.7132X - 0.2330Y + 0.6611Z = 1.0571$			
C(31)*	−0.032	C(35)*	−0.010
C(32)*	0.018	C(36)*	0.028
C(33)*	0.000	P(2)	−0.107
C(34)*	−0.004		

Dihedral Angles

Planes	Angle, deg	Planes	Angle, deg
I–II	107.8	Ia–Ib	168.7
I–III	0.0	II–III	107.8

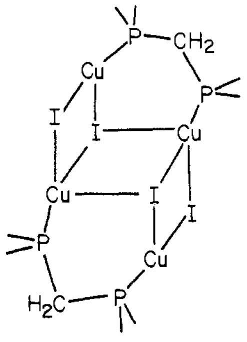
[a] All calculations performed using the FORTRAN IV program PLOD, by B. G. DeBoer. [b] Equations to planes are given in cartesian coordinates, such that $[X, Y, Z] = [xa + zc \cos\beta, yb, zc \sin\beta]$. [c] Atoms marked with an asterisk were assigned unit weight; all other atoms were given zero weight.

Carbon–carbon–carbon angles within the six independent phenyl groups range from C(12)-C(7)-C(8) = 116.1 (10)° to C(25)-C(26)-C(27) = 123.2 (13)°, averaging 120.0°, as expected for planar hexagons. It is interesting to note that internal angles at the P-bonded carbon atoms are all less than the ideal trigonal value, individual values being as follows: C(6)-C(1)-C(2) = 118.4 (10)°, C(12)-C(7)-C(8) = 116.1 (10)°, C(18)-C(13)-C(14) = 117.1 (10)°, C(24)-C(19)-C(20) = 118.9 (11)°, C(30)-C(25)-C(26) = 117.4 (12)°, and C(36)-C(31)-C(32) = 119.8 (11)°. This pattern of small angles at the P-bonded carbons has been noted previously for the phenyl groups in $(PPh_3CuCl)_4$,[1] $(PPh_2Me)_2Ni(\sigma\text{-}C_6F_5)Br$,[27] and $(PPh_2Me)_2Ni(\sigma\text{-}C_6F_5)_2$[28] and will probably prove to be a general phenomenon.

As shown in Table V, the six phenyl groups are each planar within the limits of experimental error, maximum deviations from planarity being 0.006 Å for the ring defined by atoms C(1)-C(6), 0.019 Å for C(7)-C(12), 0.013 Å for C(13)-C(18), 0.015 Å for C(19)-C(24), 0.022 Å for C(25)-C(30), and 0.032 Å for C(31)-C(36).

Discussion

To our knowledge, the only other complex that has been shown to possess a structure analogous to that of the present $(PPh_3CuBr)_4$ molecule is the tetranuclear species $(Ph_2PCH_2PPh_2)_2Cu_4I_4$ (III) reported recently by Marsich, Nardin, and Randaccio.[29] The two crystallographically independent copper· · ·copper distances within the planar Cu_4 parallelogram in this molecule are 2.682 (7) Å [between copper atoms bridged by the bis(diphenylphosphino)methane ligands] and 3.108 (7) Å.



III

A point that becomes clear from a consideration of the structures of $(PPh_3CuCl)_4$,[1] $(PPh_3CuBr)_4$, and $(Ph_2PCH_2PPh_2)_2Cu_4I_4$,[29] is the extreme variability of the (presumably nonbonding) copper· · ·copper distances. This point is brought home even more clearly *via* a comparison of the crystal structures of $(PPh_3)_3Cu_2Cl_2$ (in which the Cu· · ·Cu distance is 2.909 (2) Å)[30] and $(PPh_3)_3Cu_2Cl_2 \cdot C_6H_6$ (in which Cu· · ·Cu = 3.14 Å[31]). Here, the presence of solvent of crystallization causes an increase of ~0.23 Å in the copper· · ·copper distance—thereby clearly indicating the nonbonding nature of the copper· · ·copper vector in the binuclear copper complex.

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[27] M. R. Churchill, K. L. Kalra, and M. V. Veidis, *Inorg. Chem.*, 12, 1656 (1973).

[28] M. R. Churchill and M. V. Veidis, *J. Chem. Soc., Dalton Trans.*, 670 (1972).

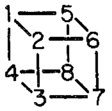
[29] M. Marsich, G. Nardin, and L. Randaccio, *J. Amer. Chem. Soc.*, 95, 4053 (1973).

[30] V. G. Albano, P. L. Bellon, G. Ciani, and M. Manassero, *J. Chem. Soc., Dalton Trans.*, 171 (1972).

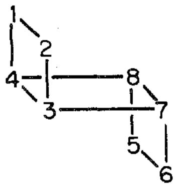
[31] D. F. Lewis, S. J. Lippard, and P. S. Welker, *J. Amer. Chem. Soc.*, 92, 3805 (1970).

The factors which determine whether a Cu_4X_4 (X = halogen) core will take up a "cubane" or a "step" configuration are clearly complex. We know that, in the solid state, $(PPh_3CuCl)_4$[1] and $(Et_3AsCuI)_4$[4,5] have a "cubane" structure, whereas $(PPh_3CuBr)_4$ and $(Ph_2PCH_2PPh_2)_2Cu_4I_4$ have the "step" structure. The stabilization of one form rather than the other must involve a combination of the following factors: (i) minimization of nonbonding X· · ·X contacts within the molecule [this has been discussed above for the $(PPh_3CuBr)_4$ molecule]; (ii) relative stability of trigonally *vs.* tetrahedrally coordinated Cu(I); (iii) relative stability of two, as opposed to three, coordinated halogen atoms; (iv) steric and electronic properties of the substituents on copper (*e.g.*, phosphine or arsine ligand); (v) any restrictions imposed by chelating or bridging substituents on copper; (vi) crystal forces (molecular packing).

One interesting thought which emerges is that it might be possible to prepare both the "cubane" and the "step" isomers of some species. Indeed, it is not impossible that the two forms could interconvert (perhaps reversibly) in solution. The transformation from the "cubane" structure (IV) to the "step" structure (V) requires only a *net* breaking of two bonds (1-5 and 2-6) and the rotation of one face (5-6-7-8) through 180° about the 7-8 axis.



IV



V

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Registry No. $(PPh_3CuBr)_4 \cdot 1.5CHCl_3$, 51153-47-0.

Supplementary Material Available. 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 Street, 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-74-1427.

Contribution from the Department of Chemistry,
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Determination of the Stability Constants for Equilibria Involving Copper(II) and Fluoride Ions in Aqueous Solutions[1]

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A fluoride specific ion electrode in conjunction with a reference electrode and millivolt meter has been used to determine equilibrium constants for the formation of complex ions between copper(II) ions and fluoride ions in aqueous solutions at 25°. Measurements were made at ionic strengths of 0.080 and 0.050. It was found that two equilibria are important, one involving the formation of CuF^+ and the other involving the formation of CuF_2. The values of the stability constants for CuF^+ and CuF_2 at 0.080 ionic strength are 7.4 ± 0.4 and 1 ± 1, respectively, and at 0.050 ionic strength these same values are 8.6 ± 0.9 and 7 ± 2.

Introduction

A number of ion-specific electrodes (sensitive to the activity of a certain ion) have been recently developed. These electrodes in conjunction with a suitable reference electrode and a voltmeter can be used to study equilibria involving complex ions. In this study, a fluoride specific ion electrode was utilized to examine the complex ion equilibria involving copper(II) ions and fluoride ions in aqueous solutions.

Three groups have previously looked at the equilibria between copper(II) ions and fluoride ions and in each case only one equilibrium was found to be important, that being

$$Cu^{2+}(aq) + F^-(aq) \rightleftarrows CuF^+(aq) \qquad (1)$$

Ahrland and Rosengren[4] used a potentiometric method and obtained a value of 9 ± 1 working at an ionic strength of 1 *M* and 20°. A potentiometric method was also used by Connick and Paul[5] and they obtained a value of 5 ± 1 at an ionic strength of 0.5 *M* and at 25°. A value of 6.8 ± 0.5 was determined at 1.0 *M* ionic strength and 25° by Mesaric and Hume[6] using polarography.

The purpose of this research was to see if the fluoride specific ion electrode might be sensitive enough under the proper experimental conditions to detect the occurrence of further equilibria between copper(II) and fluoride ions beyond the one involving the formation of CuF^+ and, if so, to determine the equilibrium constants for those equilibria.

Experimental Section

The potential measurements were made with an Orion Model 94-09 fluoride specific ion electrode, an Orion Model 90-01 single-junction reference electrode, and an Orion Model 801 pH-millivolt meter. The temperature of the solutions was maintained at 25.0 ± 0.1° in a constant-temperature bath. The pH-millivolt meter was standardized with a standard fluoride solution each day that measurements were

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[1] Presented in part at the Missouri Academy of Science Meeting, Cape Girardeau, Mo., April 1972.

[2] From the Masters thesis of S. G., Southeast Missouri State University, Jan 1972.

[3] To whom correspondence should be addressed.

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[6] S. S. Mesaric and D. N. Hume, *Inorg. Chem.*, **2**, 1063 (1963).