Crystal and Molecular Structure of Methyltriphenylphosphonium Hexaiodotetracuprate(I)

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The crystal structure of the title compound has been determined from single-crystal *X*-ray diffraction data by conventional methods. The yellow complex crystallises in rhombohedral space group $R\bar{3}c$, with $Z = 2$ in unit cell of dimensions $a = b = c = 15.603(2)$ Å, $\alpha = \beta = \gamma = 53.133(2)°$. Full-matrix least-squares refinement returned a final *R* factor of 0.038 for 1 206 reflections. The complex has overall C_{3v} symmetry, with the $[Ph_3MeP]^+$ ion adopting a ' propeller-like ' conformation and the $[Cu_4I_6]^{2-}$ ion forming a tetrahedron of copper atoms with iodine atoms displaced from the centre of each edge. Thus each copper atom has approximately trigonal planar co-ordination and is bridged by three iodine atoms. Within the crystal alternate anions have an inverted core of copper atoms whilst still accommodating the same iodine atoms on tetrahedron edges. Cu–I bond distances range from 2.539(5) to 2.638(5) Å, and Cu–I–Cu bond angles are 63.9(2) and 65.2(2)°. The non-bonded Cu · · · Cu separations of the Cu_4 tetrahedron are 2.742(7) and 2.757(7) Å. The observed structure is consistent with that previously suggested on the basis of i.r., Raman, and n.q.r. studies.

HALOGENOCUPRATE(I) complexes exhibit a wide variety of stoicheiometries, with structures mainly based upon a tetrahedral copper co-ordination; *e.g.*, $[CuCl(PPh_3)_3]$ and $[CuCl(dmt)_3]$ (dmt = dimethylthiourea) are mononuclear,[1,2] $[(CuCl)_2(PPh_3)_3]$ and $[(CuCl)_2(cot)_3]$ (cot = *trans*-cyclo-octene) are dinuclear,[3,4] $K_2[CuCl_3]$, $[NH_4]_2[CuCl_3]$, and $[NH_4]_2[CuBr_3]$ have CuX_4 groups sharing two corners to form infinite $[CuX_3]_n^{2n-}$ polymers,[5,6] and $Cs[Cu_2Cl_3]$ and $[PhN_2]Cu_2Br_3$ form double chains of $[Cu_2X_3]_n^{n-}$ ions.[7,8]

Recently *X*-ray crystal structure determinations have established some unusual geometries, *e.g.* the complex $[Co(NH_3)_6]_4[Cu_5Cl_{17}]$ contains the $[Cu_5Cl_{16}]^{11-}$ ion in which four $CuCl_4$ tetrahedra share a chlorine atom with a central tetrahedral Cu^+ ion.[9] Of particular interest are the complexes of general formula $[(CuX)_nL_m]$, where L is a neutral ligand, which have been found to adopt the ' cubane ' (copper atoms all four-co-ordinate tetrahedral) [10-12] or ' step ' (two copper atoms four-co-ordinate tetrahedral, two three-co-ordinate trigonal) [13-16] structures.

Bowmaker *et al.* have recently synthesised compounds containing the anion $[CuX_2]^-$ (X = Cl or Br) [17] but when attempting to prepare $[CuI_2]^-$ they obtained a bright

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[10] M. R. Churchill and K. L. Kalra, *Inorg. Chem.*, 1974, **13**, 1065.
[11] M. R. Churchill, B. G. DeBoer, and S. J. Mendak, *Inorg. Chem.*, 1975, **14**, 2041.
[12] M. R. Churchill and K. L. Kalra, *Inorg. Chem.*, 1974, **13**, 1899.
[13] M. R. Churchill and K. L. Kalra, *Inorg. Chem.*, 1974, **13**, 1427.
[14] M. R. Churchill, B. G. DeBoer, and D. J. Donovan, *Inorg. Chem.*, 1975, **14**, 617.
[15] A. Camus, G. Nardin, and L. Randaccio, *Inorg. Chim. Acta*, 1975, **12**, 23.
[16] G. Nardin and L. Randaccio, *Acta Cryst.*, 1974, **B30**, 1377.
[17] G. A. Bowmaker, L. D. Brockliss, and R. Whiting, *Austral. J. Chem.*, 1973, **26**, 29.

yellow crystalline ionic solid which analysed as $(Ph_3MeP)Cu_2I_3$. The colour suggested a multinuclear anion; i.r., Raman, and n.q.r. spectra were consistent with the presence of the hexaiodotetracuprate(I) ion $[Cu_4I_6]^{2-}$, and a structure was suggested in which the copper atoms lie on the corners of a tetrahedron with iodine atoms bridging along the edges, to give each copper atom a trigonal co-ordination.[18] We have investigated the crystal structure in an attempt to confirm the existence of the $[Cu_4I_6]^{2-}$ ion and to provide further data relative to trigonal copper co-ordination.

EXPERIMENTAL

The crystals are thick yellow needles with hexagonal cross-section. Initial *X*-ray photography showed the crystals to be rhombohedral, the (111) direction coinciding with the needle elongation. Unit-cell constants were determined from a least-squares refinement of the setting angles of twelve high-angle reflections (θ range 16.3—20.5°) by use of a Hilger and Watts four-circle automatic diffractometer.[19]

Crystal Data.—$C_{38}H_{36}Cu_4I_6P_2$, $M = 1\,570.2$, Rhombohedral, $a = b = c = 15.603(2)$ Å, $\alpha = \beta = \gamma = 53.133(2)°$ (standard deviations from the least-squares fitting to the setting angles), $U = 2\,253.7$ Å^3, $D_m = 2.33$ g cm^{-3}, $Z = 2$, $D_c = 2.31$ g cm^{-3}, $F(000) = 1\,456$. Mo-K_α radiation, $\lambda = 0.710\,7$ Å, Zr filter; μ(Mo-K_α) = 54.3 cm^{-1}. Space group $R\bar{3}c$ (No. 167). Crystal size 0.23 × 0.17 × 0.17 mm, crystal faces {111}, {011}; mosaic spread 0.12°.

Intensity data within a Bragg limit of 27° ($sin\theta/\lambda$ 0.64) were collected by an asymmetric 2θ—ω scan of 65 steps from 0.50° in 2θ below, to 0.80° in 2θ above the calculated $K_{\bar{\alpha}}$ peak position. Each step was counted for 2 s, with 30 s stationary-background counts at each end of the scan range. Reflections examined were $\pm h$, $\pm k$, $\pm l$ with the restriction $l \geqslant k \geqslant h$ giving two independent measurements for each equivalent reflection. These were averaged to give 1 206 unique reflections with $I > 3\sigma(I)$ [where $\sigma(I) = \{T + t^2B + (pI)^2\}^{\frac{1}{2}}$, T = integrated peak count, B = average background count, t = ratio of scan to background times, p was assigned a value of 0.04].[20a] Data were corrected for Lorentz and polarisation factors and for absorption.[20b]

Structure Determination and Refinement.—The entire unit cell contains 12I, 8Cu, 4P, 4 methyl, and 12 phenyl groups. The general multiplicity of space group $R\bar{3}c$ is 12 and therefore most of the atoms are required to occupy special positions.[21] The P atoms must occupy (*a*) and (*b*), or (*c*); the methyl group must occupy (*a*) and (*b*), or (*c*): the Cu atoms could occupy (*a*) and (*d*), or (*a*) and (*e*), or (*b*) and (*d*), or (*b*) and (*e*), or (*a*) and (*b*) and (*c*), or else two sets of 4 in positions (*c*); the I and phenyl groups could be in general positions (*f*) or some combinations of the special positions. As the heaviest atoms, iodine, were in fact the least-rigidly constrained, a Patterson function was computed and the iodine atoms were located and found to occupy general positions. It was expected that the copper-atom positions would be readily deduced by examination of the Patterson function for I · · · Cu vectors, but surprisingly, no copper atom positions could be found which were fully consistent with their restricted positions and the expected peak heights in the Patterson synthesis. An electron-density synthesis phased by the I atom alone was therefore computed. This revealed two large peaks in positions (*c*) with $x = 0.04$ and 0.17, and another solitary peak of nearly similar height in a completely general position. These 12 'atoms' corresponding to the peak in the general position occurred in pairs separated by only 1.8 Å, and it was evident that the emerging structure did not match the expected molecular geometry nor even the atomic composition analysis. Nevertheless, the two larger peaks were assigned scattering factors appropriate to copper and the other peak those appropriate to phosphorus. A structure-factor calculation was then computed. This lowered the residual R from 0.54 (I only) to 0.20. Trial least-squares cycles were computed, including refinement of occupancy factors and isotropic temperature factors. In this way R was reduced to 0.169. The results of these refinements are listed in Table 1.

TABLE 1

Attempted refinement of trial model

Atoms	Initial B	Refined B	Initial occupancy	Refined occupancy
I	3.6	3.5	1.00	1.00 *
Cu(1)	4.5	6.6	0.33	0.18
Cu(2)	4.5	6.8	0.33	0.10
P	4.5	1.4	1.00	1.12

* Not refined.

The atoms labelled Cu(1) and Cu(2) should clearly be lighter atoms than Cu, that labelled P should actually be heavier than P. The refined occupancy factor of the atom labelled Cu(1) is approximately one half of its initial value. Once the possibility of half-weighting or 'systematic disorder' was conceived the true atomic arrangement quickly became apparent: I occupied 12 general positions, Cu two independent copper atoms, four half-weighted Cu atoms on (*c*) *i.e.* x,x,x, at $x = 0.04$, and twelve half-weighted Cu atoms in general positions. Thus total Cu atoms in cell = $4 \times \frac{1}{2} + 12 \times \frac{1}{2} = 8$; P — 4 P atoms on (*c*) at $x = 0.17$.

This is consistent with the analysis figures, the n.q.r. results which indicated two kinds of copper atoms present in a 1 : 3 ratio, the likely molecular geometry, the Patterson peak-heights and distribution, and the attempted refinement results.

The existence of the half-weighted Cu atoms can be rationalised in the following way. The Cu atoms form a tetrahedral pattern in which one Cu atom lies on the three-fold axis and three Cu atoms are positioned symmetrically about the axis. The iodine atoms occupy the edges of the tetrahedron, giving a basic anionic unit $[Cu_4I_6]^{2-}$. Every alternate $[Cu_4I_6]^{2-}$ ion has its Cu_4 tetrahedron inverted, but still accommodates the same I atoms on its tetrahedron edges. Any individual tetrahedron has its full complement of atoms, but time-averaging causes the copper atoms to appear half-weighted. The close approach (1.8 Å) referred to earlier does not in reality occur, as the atoms involved alternate from one unit to the next.

The appropriate changes were made to the atom labels, form-factor identifiers, and occupancies, and a structure-factor calculation then returned a reliability index R of

[18] G. A. Bowmaker, L. D. Brockliss, C. D. Earp, and R. Whiting, *Austral. J. Chem.*, 1973, **26**, 2593.

[19] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1967, **22**, 457.

[20] (*a*) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 197; (*b*) the absorption program used was DABS, a modification of DATAPH; P. Coppens, paper G1, International Summer School on Crystallographic Computing, Ottawa, 1969.

[21] 'International Tables for *X*-Ray Crystallography,' vol. I, Kynoch Press, Birmingham, 1962, p. 274.

0.166. A difference-Fourier now clearly revealed the methyl carbon atom and all carbon positions of the benzene ring.

Full-matrix least-squares refinement was then commenced.[22] Atomic scattering factors were from ref. 23,

TABLE 2

Atomic co-ordinates and standard deviations

Atom	x/a	y/b	z/c
I	−0.156 24(5)	0.192 77(5)	0.103 58(5)
Cu(1)	0.040 9(2)	0.040 9	0.040 9
Cu(2)	−0.142 9(2)	0.075 7(2)	0.022 8(2)
P	0.172 4(2)	0.172 4	0.172 4
C(1)	0.323 7(6)	0.145 6(6)	0.092 4(6)
C(2)	0.396 6(7)	0.085 4(8)	0.149 7(8)
C(3)	0.514 7(8)	0.074 1(10)	0.082 6(10)
C(4)	0.553 7(8)	0.119 7(9)	−0.032 1(9)
C(5)	0.480 9(9)	0.180 6(11)	−0.092 5(9)
C(6)	0.363 7(9)	0.191 9(10)	−0.027 0(8)
C(Me)	0.127 2(9)	0.127 2	0.127 2

with those for iodine and copper corrected for real dispersion effects.[24] The function minimised was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 4|F_o|^2/\sigma^2(F_o^2)$. For atoms on special positions only one third of the calculated parameter shifts were applied. After two cycles with all atoms isotropic, R 0.096 and R' 0.113 $\{R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{\frac{1}{2}}\}$. All atoms were then assigned anisotropic thermal parameters, with those for atoms on the special positions x,x,x being constrained such that $\beta_{11} = \beta_{22} = \beta_{33}$ and $\beta_{12} = \beta_{13} = \beta_{23}$.[25] As before, the appropriate fractional shifts were applied to these variables and the affected parameters were reset after each cycle. After 4 cycles, refinement converged with R 0.038 and R' 0.048. During the latter stages of refinement the weighting scheme was checked by analysis of $\langle \Sigma w \Delta^2 \rangle$ throughout the data and found to be satisfactory. Final atomic co-ordinates and thermal parameters are given in Tables 2 and 3 respectively, together with their estimated standard deviations. Tables of observed and calculated structure factors are deposited with Supplementary Publication No. SUP 21787 (6 pp., 1 microfiche).*

TABLE 3

Anisotropic thermal parameters ($\times 10^4$, for I $\times 10^5$) * and standard deviations

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
I	75(5)	779(5)	986(6)	−209(4)	−266(4)	−514(4)
Cu(1)	75(5)	75	75	−31(3)	−31	−31
Cu(2)	64(2)	75(2)	81(2)	−23(1)	−28(1)	−35(1)
P	60(4)	60	60	−25(2)	−25	−25
C(1)	74(6)	70(6)	59(6)	−29(5)	−26(5)	−26(5)
C(2)	63(7)	126(10)	89(8)	−24(7)	−31(6)	−50(7)
C(3)	77(8)	164(13)	111(11)	−36(9)	−26(8)	−70(9)
C(4)	68(7)	129(11)	126(11)	−29(7)	−9(7)	−86(10)
C(5)	87(9)	191(16)	110(10)	−59(10)	−2(9)	−83(11)
C(6)	97(9)	160(13)	64(8)	−63(9)	−17(7)	−34(8)
C(Me)	120(27)	120	120	−55(15)	−55	−55

* The scattering factor is of the form $f = f_0 \exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$.

DISCUSSION

Description of the Structure.—The crystal structure consists of discrete $[Ph_3MeP]^+$ and $[Cu_4I_6]^{2-}$ ions. Their packing into the unit cell is displayed in Figure 1. To avoid confusion only one anion (in only one of the two possible configurations) and its encompassing array of phosphine cations has been drawn. The omitted anions are located about each corner of the rhombohedron. Observed bond distances and angles are listed in Tables 4 and 5 respectively.

The Methyltriphenylphosphonium Cation.—The $[Ph_3MeP]^+$ ion has an overall geometry which resembles a propeller, similar to those observed in other complexes containing this ion.[26-30] In the present compound, crystallographic symmetry demands a regular twist of the propeller ' blades ', the angle of twist, as defined by the C(Me)–P–C(1)–C(6) torsion angle, being −54°. This geometry, together with the numbering scheme and bond lengths and angles, is depicted in Figure 2.

The phosphorus atom is tetrahedral [C(Me)–P–C(1) 109.3(8), C(1)–P–C(1′) 109.5(6)°]. The P–C(Me) distance [1.81(2) Å] is longer than P–C(1) [1.79(1.5) Å] as would be expected, although the difference here is not significant. The phenyl C–C bond distances range from 1.33(3) to 1.43(3) Å, mean 1.39 Å; the C–C–C angles range from 118(2) to 122(2)°, mean 120.0°. A least-squares plane

TABLE 4

Interatomic distances (Å), with standard deviations in parentheses

P–C(Me)	1.81(2)	P–C(1)	1.79(2)
C(1)–C(2)	1.38(2)	C(4)–C(5)	1.41(3)
C(2)–C(3)	1.43(3)	C(5)–C(6)	1.42(3)
C(3)–C(4)	1.33(3)	C(6)–C(1)	1.38(3)
Cu(1)–I(1)	2.541(5)	Cu(22)–I(4)	2.578(5)
Cu(22)–I(2)	2.638(5)	Cu(22)–I(6)	2.539(5)
Cu(1) · · · Cu(21)	2.742(7)	Cu(21) · · · Cu(22)	2.757(7)
I(1) · · · I(2)	4.38(2)	I(1) · · · I(6)	4.52(2)

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue. (Items less than 10 pp. are supplied as full-size copoes.)

[22] All computing was carried out on the University of Auckland Burroughs B6700 computer. Major programs used were XRC/HILGOUT, XRC/FOURIER, XRC/CUCLS, written by R. J. Dellaca of the University of Canterbury, Christchurch.

[23] Ref. 21, vol. III, 1962, pp. 202, 210.

[24] Ref. 23, p. 215.

[25] W. J. A. M. Peterse and J. H. Palm, *Acta Cryst.*, 1966, **20**, 147.

[26] A. T. McPhail, G. M. Semeniuk, and D. B. Chesnut, *J. Chem. Soc.* (*A*), 1971, 2174.

[27] F. J. Hollander, D. H. Templeton, and A. Zalkin, *Inorg. Chem.*, 1973, **12**, 2262.

[28] R. M. Wing, *J. Amer. Chem. Soc.*, 1968, **90**, 4828.

[29] N. N. Greenwood, J. A. McGinnety, and J. D. Owen, *J. Chem. Soc.* (*A*), 1971, 809.

[30] C. J. Fritchie, *Acta Cryst.*, 1966, **20**, 107.

calculation shows each phenyl ring to be planar with a maximum deviation of 0.011 Å.

The Hexaiodotetracuprate(I) *Anion*.—The structure of the $[Cu_4I_6]^{2-}$ anion has been partially described in the section on structure determination. The observed pattern of half-weighted copper atoms is a time-averaged superimposition of two Cu_4 tetrahedra, one of which is inverted with respect to the other. Figure 3 gives a view of the two superimposed Cu_4 tetrahedra with their attached octahedral array of iodine atoms. Each individual $[Cu_4I_6]^{2-}$ cluster consists, then, of a non-bonded tetrahedron of copper atoms with each pair of

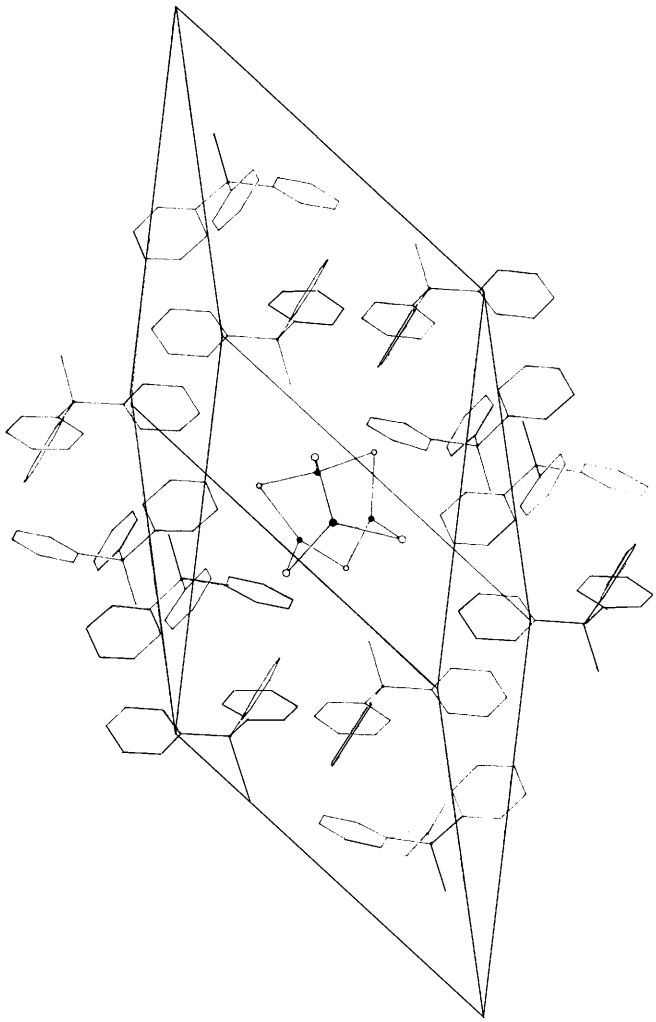

FIGURE 1 A portion of the unit-cell contents. For clarity, anions located around each corner of the rhombohedron have been omitted. Alternate anions would have an inverted core of copper atoms. Large open circles are iodine, large closed circles copper, and small closed circles phosphorus

TABLE 5

Bond angles (°), with standard deviations in parentheses

C(Me)–P–C(1)	109.3(8)	C(1)–P–C(1)	109.5(6)
C(6)–C(1)–C(2)	121(2)	C(3)–C(4)–C(5)	122(2)
C(1)–C(2)–C(3)	119(2)	C(4)–C(5)–C(6)	118(2)
C(2)–C(3)–C(4)	121(2)	C(5)–C(6)–C(1)	120(2)
I(2)–Cu(1)–I(3)	119.2(2)	I(4)–Cu(22)–I(6)	117.9(2)
I(2)–Cu(22)–I(4)	120.1(2)	I(6)–Cu(22)–I(2)	121.6(2)
Cu(1)–I(3)–Cu(23)	63.9(2)	Cu(21)–I(5)–Cu(23)	65.2(2)
Cu(23) · · · Cu(1) · · · Cu(22)	60.4(2)		
Cu(1) · · · Cu(23) · · · Cu(22)	59.8(2)		
Cu(22) · · · Cu(23) · · · Cu(21)	60.0(2)		

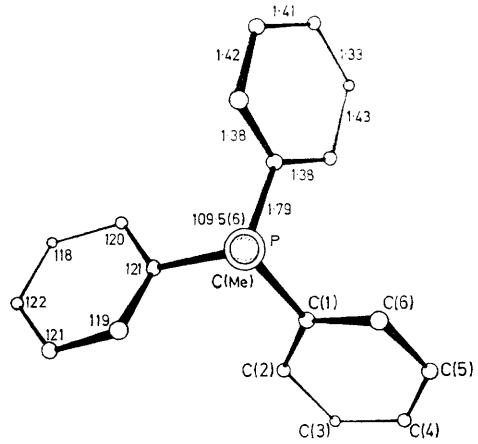

FIGURE 2 The $[Ph_3MeP]^+$ cation viewed along the C(Me)-P axis. Standard deviations for bonds and angles involving C atoms are 0.03 Å and 2° respectively; P–C(Me) is 1.81(2), C(Me)–P–C(1) 109.3(8)

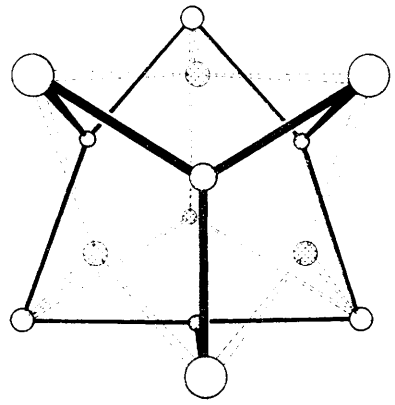

FIGURE 3 A view of the superimposed Cu_4 tetrahedra. Hatched circles represent one set of copper atoms, cross-hatched circles represent the other

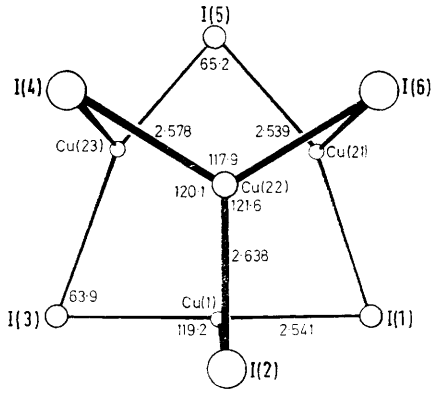

FIGURE 4 The geometry of the $[Cu_4I_6]^{2-}$ ion. Standard deviations in bonds and angles are 0.005 Å and 0.2° respectively

copper atoms being bridged by an iodine atom lying out from the tetrahedron edge. The geometry of one such ion is illustrated in Figure 4. Although each $[Cu_4I_6]^{2-}$ ion has potential T_d symmetry, the particular arrangement of the individual atoms causes one three-fold axis of the T_d point-group to be unique and therefore the overall anionic symmetry reduces to C_{3v}. Thus, Cu(1) which lies on the unique three-fold axis is crystallographically different from Cu(21), Cu(22), and Cu(23).

The non-equivalence of the copper atoms confirms the explanation given previously [18] for the observed splitting patterns for the copper and iodine n.q.r. signals. The ^{63}Cu n.q.r. frequencies at 26.8 and 26.15 MHz (77 K) can be assigned on the basis of their relative intensities to Cu(1) and the set Cu(21), Cu(22), Cu(23) respectively. The presence of two closely spaced ^{127}I n.q.r. signals of approximately equal intensity can likewise be explained by the presence of two inequivalent sets of iodine atoms, I(1)–(3) and I(4)–(6).

The co-ordination geometry of all four copper atoms is approximately trigonal planar. Cu(1) is symmetrically bonded to I(1), I(2), and I(3) (Figure 4) with I–Cu(1)–I angles of 119.2(2)° and is displaced 0.240 Å from the plane of the three iodine atoms towards the centre of the Cu_4 tetrahedron. The I–Cu–I angles about the remaining three copper atoms are 120.1, 121.6, and 117.9(2)°. These copper atoms are displaced towards the centre of the ion by only 0.100 Å from the planes of their respective iodine atoms. The Cu–I bond distances are 2.539, 2.541, 2.578, and 2.638(5) Å (Figure 4). These values compare with Cu–I distances in other recently reported three-co-ordinate complexes. The most directly comparable are for those atoms in the $(CuI)_4$ 'step' structures where the co-ordination numbers of copper and iodine are 3 and 2 respectively. In $[\{(PPh_3)CuI\}_4]$ the Cu–I distance is 2.527(2) Å; [14] in $[(CuI)_4(dpm)_2]$[dpm = bis(diphenylphosphino)methane] it is 2.510(4) Å.[15] When the copper and iodine co-ordination numbers are both 3 the distances increase to 2.592(2) and 2.718(4) Å.[14,15] The Cu–I–Cu angles in $[Cu_4I_6]^{2-}$ [63.9(2) and 65.2(2)°] are close to those described for two-co-ordinate iodine in the $(CuI)_4$ step structures. In $[\{(PPh_3)CuI\}_4]$ and $[(CuI)_4(dpm)_2]$ the appropriate Cu–I–Cu angles are 66.80(7) and 62.9(4)°.[14,15] A similar value [63.9(2)°] has been found in the four-co-ordinate copper complex $[\{CuI(nas)\}_2]$ [nas = (*o*-dimethylaminophenyl)dimethylarsine].[31]

Non-bonded Approach Distances.—The tetrahedron formed by the four copper atoms has relatively short Cu · · · Cu distances: Cu(1) · · · Cu(21) 2.742(7) and Cu(21) · · · Cu(22) 2.757(7) Å. These compare with the corresponding distances in $[(PEt_3CuI)_4]$ [2.927(2) Å] [10] and $[(AsEt_3CuI)_4]$ [2.783(2) Å].[12] In the related bromide and chloride complexes the Cu · · · Cu distances are all longer (3.0—3.4 Å).[11]

The octahedron of iodine atoms is slightly distorted by a small elongation along the $\bar{3}$ axis, giving I · · · I separations of 4.38 and 4.52 Å.

The most likely explanation for the observed distortions of the copper and iodine polyhedra are the interionic approaches. The two shortest I · · · C(Ph) distances are only 3.85(2) for I · · · C(5) and 3.92(2) Å for I · · · C(6). Perhaps of more significance is the close approach of 3.46(2) Å between Cu(1) and C(Me). The van der Waals radius of copper is not known accurately but it is possible to estimate its likely value as being of the order of 2.2 Å by comparison with published values for other elements.[32] The van der Waals radius for a methyl group has been listed as 2.0 Å,[33] giving a total Cu · · · C(Me) van der Waals contact distance of 4.2 Å. Thus the observed separation of 3.46 Å is very short indeed.

The relative orientation of the anions and cations in the crystal explains the unusually large low-frequency shift of the methyl rocking band in the i.r. spectrum.[18] The short Cu(1) · · · C(Me) distance (3.46 Å), and the fact that Cu(1) experiences a greater displacement (0.240 Å) from the plane of its co-ordinated iodine atoms than Cu(21), Cu(22), and Cu(23) (0.100 Å) suggests the presence of a repulsive interaction between the methyl group and Cu(1). If this repulsion is greatest for the equilibrium configuration, and is less for displacements of the methyl group along the rocking co-ordinate, then this interaction would result in a 'flattening' of the potential well for the rocking mode, with a concomitant decrease in the frequency of this vibration. The unusual increase in intensity of the methyl symmetric bending mode in the i.r.[18] might also be the result of a repulsive interaction of the type described, although it is not so easy to postulate a specific mechanism in this case.

The co-ordination geometry in the present compound can be compared with that in $[(Et_2NCS_2)Cu]_4$,[34] $[(Pr_2NCOS)Cu]_6$,[35] $[(Pr_2NCS_2)Ag]_6$,[36] and $[PhMe_3P]_4[Cu_8\{S_2C_2(CN)_2\}_6]$.[37] In each of these compounds the metal atoms exhibit trigonal, almost planar, co-ordination to ligands which bridge pairs of metal atoms to form a polyhedral cluster. As in the present case, the deviation from planar co-ordination involves a slight displacement of the metal atom towards the centre of the polyhedron. Trigonal co-ordination of copper(I), while still quite rare in comparison with tetrahedral co-ordination, is also known in a number of mononuclear complexes (see ref. 38, and refs. therein). The ^{63}Cu n.q.r. frequencies for $[Ph_3MeP]_2[Cu_4I_6]$ (26.15 and 26.8 MHz at 77 K),[18] $[(Et_2NCS_2)Cu]_4$ (26.96 MHz at 293 K),[39] and $[(Me_3PS)_3Cu][ClO_4]$ (26.35 MHz at 77 K, 25.07 at *ca.* 290 K),[38]

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all of which involve trigonal co-ordination of copper(I), are similar in magnitude, and comments which have been made concerning the origin of the electric-field gradient at the copper nucleus and the nature of the bonding in the latter compound[38] could also apply to the other two.

The question of the possible existence of metal–metal bonding in polynuclear copper complexes, and the relationship of the metal–metal distance to bond order has been the subject of some discussion recently.[31,37,40-48] Cu · · · Cu bond orders of 1, $\frac{3}{4}$, and $\frac{2}{3}$ have been deduced for the compounds $[(Ph_3P)CuH]_6$ [d(Cu · · · Cu) 2.494—2.674 Å],[47] $[Ph_3PIr]_2[Cu_4(C{:}CPh)_8]$ (2.665—2.823 Å),[48] and $[PhMe_3P]_4[Cu_8\{S_2C_2(CN)_2\}_6]$ (2.783—2.871 Å).[37] These bond orders were deduced by use of the 'inert gas' or eighteen-electron rule, which accounts very well for the structures of a large number of transition-metal carbonyl clusters. The second of the aforementioned three compounds involves copper with a formal oxidation state of zero,[48] with no bridging ligands, so the postulated existence of copper–copper bonding in this compound seems reasonable. In the other two compounds, however, the copper atoms have formal oxidation states of unity, and are directly bonded to bridging ligands. As there are several mononuclear copper(I) complexes which do not obey the eighteen-electron rule (*e.g.* the trigonal mononuclear complexes referred to), the use of this rule to determine the presence or otherwise of metal–metal bonding in these polynuclear complexes must be open to question. For example, it was not considered necessary to invoke metal–metal bonding to account for the structure of tetrameric (4-methyl-2-cupriobenzyl)dimethylamine, in spite of the presence of the very short copper–copper distances of 2.377 and 2.389 Å, the shortest yet reported for a polynuclear copper complex.[41]

It seems likely that copper–copper distances in cluster compounds involving bridging ligands are determined at least partly by the bonding requirements of the bridging ligand, so that this distance in itself is not likely to be a very reliable measure of the extent of copper–copper bonding. Clearly the measurement of some other property more directly related to metal–metal bond strengths would be required. It might therefore be useful to note that the main features of the vibrational spectrum of the $[Cu_4I_6]^{2-}$ ion (with the geometry determined here) can be accounted for by means of a very simple valence force-field which does not include a force constant corresponding to a direct Cu · · · Cu interaction (Figure 5 of ref. 18, $\beta \approx 65°$).

As the present work yields the first definitive structure for an anion of the formal type $[M_2X_3]_n^{n-}$ (M = group IB metal, X = halogen), it is interesting to compare this with the structures of other ions of this stoicheiometry which have been previously suggested.

The existence of an anion $[Ag_4I_6]^{2-}$, with a structure similar to that found here for $[Cu_4I_6]^{2-}$, has been postulated on the basis of molecular weight and *X*-ray diffraction studies of KI/AgI solutions in acetone.[49] The structure which fits the *X*-ray diffraction data best has Ag–I 2.85 Å, I–Ag–I 111°, and Ag–I–Ag 106°. These results imply tetrahedral co-ordination of the silver, with the fourth co-ordination position possibly being occupied by a solvent molecule.

A number of salts of composition $M[Cu_2Cl_3]$ {M = $[Et_3PH]^+$, $[Et_3NH]^+$, $[Bu_3NH]^+$, and $[EtPipH]^+$} which are liquids at room temperature have been reported recently.[50] The i.r. and Raman bands assigned to the anions in these compounds are very broad, and it is likely that a number of anionic complexes are present in equilibrium. A hypothetical $[Cu_2Cl_3]^-$ ion with a C_{2v} structure involving two terminal and one bridging chloride was considered in a discussion of the vibrational spectra, but the spectral data are not good enough to allow distinction between this and alternative structures.

The possible existence of an anion of the type $[Cu_8X_{12}]^{4-}$ (X = Br or I), with a structure similar to that found for the anion in $[PhMe_3P]_4[Cu_8\{S_2C_2(CN)_2\}_6]$, has been postulated on the basis of the similarity in co-ordination properties of the sulphur atoms in the $[S_2C_2(CN)_2]^{2-}$ ligand and the heavy halide ions.[37] Similar arguments can be applied to the copper 1,1-diethoxycarbonyl-2,2-ethylenedithiolato- and dithiosquaratocomplexes.[44] Such an ion would consist of a cube of eight copper atoms, with halide ions bridging pairs of copper atoms along the 12 edges of the cube. It is now clear, however, that essentially the same co-ordination geometry about the copper atoms can be achieved in an ion of the type $[Cu_4X_6]^{2-}$, the structure being based on tetrahedron rather than on a cube. It is not yet clear what factors determine the number of metal atoms incorporated in bridged clusters of this type. In this connection, a recently reported compound formulated as $[Ph_4P]_4[Cu_8(SPh)_{12}]$[51] might, in view of the present results, have the formula $[Ph_4P]_2[Cu_4(SPh)_6]$.

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