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Crystal Structures of Tetraphenylarsonium Dichlorocuprate(I), Tetraphenylphosphonium Dichlorocuprate(I) and Tetraphenylphosphonium Dibromocuprate(I)

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The crystal structures of the title compounds have been determined from single-crystal X-ray diffraction data. $[As(C_6H_5)_4][CuCl_2]$ crystallizes in space group $I\bar{4}$, with a=17.470(12), c=14.522(7) Å and Z=8. $[P(C_6H_5)_4][CuCl_2]$ and $[P(C_6H_5)_4][CuBr_2]$ are isostructural and crystallize in space group $P2_1/c$, with a=9.266(3), b=18.027(4), c=13.482(4) Å, β=102.77(2)°, Z=4, and a=9.337(4), b=18.292(6) Å, c=13.573(4) Å, β=102.25(3)°, Z=4, respectively. All three compounds contain monomeric anions. In $[As(C_6H_5)_4][CuCl_2]$, Cu–Cl=2.069(3) and 2.072(3) Å and Cl–Cu–Cl=176.36(11)°; in $[P(C_6H_5)_4][CuCl_2]$, Cu–Cl=2.088(2) and 2.090(2) Å and Cl–Cu–Cl=174.66(9)°; in $[P(C_6H_5)_4][CuBr_2]$, Cu–Br=2.211(2) and 2.216(2) Å and Br–Cu–Br=173.62(7)°.

Tetrabutylammonium dichlorocuprate(I) and tetrabutylammonium dibromocuprate(I) both contain linear, monomeric anions.[1,2] In crystalline tetrabutylammonium diiodocuprate(I), on the other hand, the anion is a planar $[Cu_2I_4]^{2-}$ dimer, containing trigonal-planar coordinated copper(I).[3] With the smaller tetrapropylammonium cation a $[Cu_4Br_6]^{2-}$ aggregate containing three-coordinated copper(I),[4] a planar $[Cu_2I_4]^{2-}$ dimer,[5] a $[Cu_3I_4]^{-}$ chain containing both three- and four-coordinated copper(I),[6] and a discrete $[Cu_5I_7]^{2-}$ ion containing four-coordinated copper(I)[7] have been obtained. Tetraphenylarsonium, which is similar in size and shape to tetrabutylammonium but which would be expected to differ with respect to the delocalisation of the positive charge, crystallizes with a non-planar $[Cu_2I_4]^{2-}$ anion.[8] Infrared and Raman spectra and nuclear quadrupole resonance frequencies indicate that tetraphenylarsonium dichlorocuprate(I) contains a linear, monomeric $[CuCl_2]^{-}$ ion.[1] Similarly, the slightly smaller tetraphenylphosphonium cation would appear to crystallize with a monomeric $[CuBr_2]^{-}$ anion,[1] but with both a planar and a folded $[Cu_2I_4]^{2-}$ anion.[9]

Whereas the geometry of the $[CuCl_2]^{-}$ monomer is well-established from a number of crystal structure determinations,[2,10–18] that of the $[CuBr_2]^{-}$ monomer has been determined only in tetrabutylammonium dibromocuprate(I),[2] in $[\{[CH_3C(CH_2P(C_6H_5)_2)_3]IrP_3\}_3Cu_5Br_4][CuBr_2]$[19] and in the cation radical salt of tetraselenotetracene, TSeT, with dibromocuprate(I).[20] The last compound contains a bent $[CuBr_2]^{-}$ ion with Br–Cu–Br=153.8(1)° and a Cu···Br contact of 2.829(2) Å to an adjacent anion. A

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Table 1. Crystal and experimental data for tetraphenylarsonium dichlorocuprate(I), tetraphenylphosphonium dichlorocuprate(I) and tetraphenylphosphonium dibromocuprate(I).

	$[As(C_6H_5)_4][CuCl_2]$	$[P(C_6H_5)_4][CuCl_2]$	$[P(C_6H_5)_4][CuBr_2]$
M_r	517.8	473.8	562.7
Unit-cell dimensions	a=17.470(12), c=14.522(7) Å	a=9.266(3), b=18.027(4), c=13.482(4) Å, β=102.77(2)°	a=9.337(4), b=18.292(6), c=13.573(4) Å, β=102.25(3)°
Space group[27a]	$I\bar{4}$ (No. 82)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
Z	8	4	4
D_c	1.55 gcm^{-3}	1.43 gcm^{-3}	1.65 gcm^{-3}
μ(Mo$K\alpha$)	2.83 mm^{-1}	1.35 mm^{-1}	4.81 mm^{-1}
Habit	Colourless tetragonal sphenoids	Colourless prisms	Colourless prisms
Crystal size	0.20×0.21×0.24 mm	0.23×0.21×0.22 mm	0.19×0.15×0.18 mm
Temperature	290 K	290 K	290 K
$2\theta_{max}$	50°	50°	50°
Scan mode	ω-2θ	ω-2θ	ω-2θ
2θ scan rate	2.5–15 °min^{-1}	2.5–15 °min^{-1}	2.5–15 °min^{-1}
No. of independent reflections measured	2046	3884	4007
No. of observed independent reflections [$I>3.0\ \sigma(I)$]	1439	1700	1766
Method used to solve structure	Patterson; successive electron-density calculations	Coordinates of $[P(C_6H_5)_4]$ $[CuBr_2]$ as starting point for refinement	Patterson, successive electron-density calculations
No. of parameters refined	252	253	253
Reflections weighted according to	$w=[\sigma(F_o)^2+0.0004(F_o)^2]^{-1}$	$w=[\sigma(F_o)^2+0.0003(F_o)^2]^{-1}$	$w=[\sigma(F_o)^2+0.0005(F_o)^2]^{-1}$
Final R	0.031	0.046	0.043
Maximum residual electron density	0.29 eÅ^{-3}	0.31 eÅ^{-3}	0.35 eÅ^{-3}

Table 2. Fractional coordinates and equivalent isotropic thermal parameters (Å^2) for the non-hydrogen atoms in $[As(C_6H_5)_4][CuCl_2]$. B_{eq} is defined as $8\pi^2/3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$. Estimated standard deviations are given in parentheses.

Atom	x	y	z	B_{eq}
Cu	0.30002(6)	0.20551(5)	0.01839(7)	4.68(3)
Cl(1)	0.2538(2)	0.1649(1)	0.1404(2)	6.60(8)
Cl(2)	0.3408(1)	0.2423(1)	−0.1079(2)	6.33(8)
As(1)	0.0000	0.0000	0.0000	3.26(3)
C(11)	−0.0873(4)	−0.0071(4)	−0.0784(5)	3.5(2)
C(12)	−0.1365(5)	−0.0686(4)	−0.0749(6)	4.5(2)
C(13)	−0.1982(5)	−0.0730(5)	−0.1361(7)	5.3(3)
C(14)	−0.2088(5)	−0.0142(5)	−0.1971(6)	4.7(2)
C(15)	−0.1607(5)	0.0474(5)	−0.1998(6)	5.3(3)
C(16)	−0.1000(5)	0.0508(5)	−0.1416(6)	5.2(3)
As(2)	0.0000	0.0000	0.5000	2.82(3)
C(21)	0.0878(4)	−0.0083(4)	0.4220(5)	3.3(2)
C(22)	0.1290(4)	0.0571(4)	0.4006(6)	3.8(2)
C(23)	0.1887(5)	0.0526(5)	0.3415(6)	5.1(2)
C(24)	0.2078(5)	−0.0149(5)	0.3022(6)	5.2(3)
C(25)	0.1678(6)	−0.0802(6)	0.3239(6)	6.0(3)
C(26)	0.1059(5)	−0.0770(4)	0.3826(5)	4.4(2)
As(3)	0.0000	0.5000	0.2500	3.00(2)
C(31)	0.0782(4)	0.4563(4)	0.1740(5)	3.8(2)
C(32)	0.1112(4)	0.3879(4)	0.2003(6)	3.9(2)
C(33)	0.1707(4)	0.3591(5)	0.1471(7)	4.7(2)
C(34)	0.1988(5)	0.3992(5)	0.0727(6)	5.0(2)
C(35)	0.1666(5)	0.4698(5)	0.0505(6)	5.0(2)
C(36)	0.1060(5)	0.4975(5)	0.0990(6)	4.6(2)
As(4)	0.5000	0.0000	0.2500	3.02(3)
C(41)	0.4648(4)	0.0818(4)	0.3269(5)	3.7(2)
C(42)	0.3959(5)	0.1172(5)	0.3084(6)	4.2(2)
C(43)	0.3718(5)	0.1777(5)	0.3646(7)	5.2(3)
C(44)	0.4180(6)	0.2006(5)	0.4354(7)	5.7(3)
C(45)	0.4878(5)	0.1655(5)	0.4515(6)	5.2(3)
C(46)	0.5094(5)	0.1053(5)	0.3979(6)	4.8(2)

monomeric $[CuBr_2]^-$ ion has been inferred in $[Au(S_2CN(C_4H_9)_2)_2][CuBr_2]$ from isomorphism with the dibromoaurate(I).[21,22] The structure of $[Au(S_2CN(C_4H_9)_2)_2][CuBr_2]$ was not, however, refined. In order to confirm the monomeric nature of the dichlorocuprate(I) and dibromocuprate(I) ions in the tetraphenylarsonium and tetraphenylphosphonium compounds and to investigate possible deviations from linearity in the presence of these cations, the crystal structures of $[As(C_6H_5)_4][CuCl_2]$ and $[P(C_6H_5)_4][CuBr_2]$ and also that of $[P(C_6H_5)_4][CuCl_2]$ have been determined.

EXPERIMENTAL

Tetraphenylarsonium dichlorocuprate(I) and tetraphenylphosphonium dibromocuprate(I) were prepared according to the method of Bowmaker, Brockliss and Whiting,[1] except that the solutions of the compounds were allowed to cool slowly to room temperature. Tetraphenylphosphonium dichlorocuprate(I) was prepared in an analogous manner from tetraphenylphosphonium chloride and copper(I) chloride (molar ratio 1:1) in ethanol, the

solution being refluxed and allowed to cool to room temperature under nitrogen. In all three cases, crystals were deposited from the solutions after a few days.

Approximate unit-cell dimensions and space groups were determined from rotation and Weissenberg photographs. For $[As(C_6H_5)_4][CuCl_2]$ the space groups $I4$, $I\bar{4}$ and $I4/m$ are consistent with the Laue symmetry and systematic absences. Space group $I\bar{4}$ was considered to be that most likely to be correct, which was later confirmed by the determination of the structure. $[P(C_6H_5)_4][CuCl_2]$ and $[P(C_6H_5)_4][CuBr_2]$ are isostructural and crystallize in space group $P2_1/c$.

Diffracted intensities were measured with a Syntex $P2_1$ diffractometer using graphite-monochromated Mo$K\alpha$ radiation. A 96-step profile was recorded for each reflection and the Lehmann and Larsen profile-analysis method[23] was used to calculate the intensities.[24] Data was corrected for Lorentz and polarisation effects. Empirical corrections[25] for the effects of absorption were made after solution of the structures. The unit-cell parameters were determined from diffractometer setting angles for 15 reflections. Crystal data and further details concerning the collection of intensity data are given in Table 1.

STRUCTURE DETERMINATION AND REFINEMENT

The structures of $[As(C_6H_5)_4][CuCl_2]$ and $[P(C_6H_5)_4][CuBr_2]$ were solved from Patterson and successive electron-density maps.[26] The atomic coordinates of $[P(C_6H_5)_4][CuBr_2]$ were

Table 3. Fractional coordinates and equivalent isotropic thermal parameters (Å^2) for the non-hydrogen atoms in $[P(C_6H_5)_4][CuCl_2]$. B_{eq} is defined as $8\pi^2/3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$. Estimated standard deviations are given in parentheses.

Atom	x	y	z	B_{eq}
Cu	0.34793(10)	0.19945(5)	0.08615(7)	5.81(3)
Cl(1)	0.2527(2)	0.0973(1)	0.0357(2)	7.35(7)
Cl(2)	0.4458(2)	0.2977(1)	0.1504(2)	7.12(7)
P	0.8654(2)	0.16826(8)	0.4735(1)	3.51(5)
C(11)	0.7319(6)	0.1064(3)	0.4032(5)	3.4(2)
C(12)	0.6798(7)	0.1184(3)	0.2982(5)	4.6(2)
C(13)	0.5804(7)	0.0694(4)	0.2422(5)	5.5(2)
C(14)	0.5345(7)	0.0074(4)	0.2877(7)	5.7(3)
C(15)	0.5864(8)	−0.0052(4)	0.3896(6)	5.5(3)
C(16)	0.6840(6)	0.0442(4)	0.4477(5)	4.3(2)
C(21)	1.0161(6)	0.1696(3)	0.4106(4)	3.5(2)
C(22)	1.0855(7)	0.2340(3)	0.3935(5)	4.5(2)
C(23)	1.2025(7)	0.2321(4)	0.3437(5)	5.4(2)
C(24)	1.2507(7)	0.1651(4)	0.3144(5)	5.6(2)
C(25)	1.1815(8)	0.0999(4)	0.3313(5)	5.8(3)
C(26)	1.0638(7)	0.1018(3)	0.3791(5)	5.4(2)
C(31)	0.7923(6)	0.2585(3)	0.4808(5)	3.8(2)
C(32)	0.8782(7)	0.3109(4)	0.5432(5)	5.4(2)
C(33)	0.8246(10)	0.3829(4)	0.5498(6)	6.7(3)
C(34)	0.6858(11)	0.4011(4)	0.4957(7)	6.5(3)
C(35)	0.5997(8)	0.3498(4)	0.4343(6)	5.9(3)
C(36)	0.6517(7)	0.2779(3)	0.4273(5)	4.7(2)
C(41)	0.9247(6)	0.1350(3)	0.6006(4)	3.5(2)
C(42)	0.8226(6)	0.1366(3)	0.6631(5)	4.5(2)
C(43)	0.8606(8)	0.1083(4)	0.7600(5)	5.1(2)
C(44)	0.9996(9)	0.0797(4)	0.7968(5)	5.5(2)
C(45)	1.1018(7)	0.0801(4)	0.7364(6)	5.5(2)
C(46)	1.0666(6)	0.1072(3)	0.6376(5)	4.3(2)

Table 4. Fractional coordinates and equivalent isotropic thermal parameters (Å^2) for the non-hydrogen atoms in $[P(C_6H_5)_4][CuBr_2]$. B_{eq} is defined as $8\pi^2/3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$. Estimated standard deviations are given in parentheses.

Atom	x	y	z	B_{eq}
Cu	0.33576(12)	0.19444(6)	0.08622(8)	5.98(4)
Br(1)	0.23833(11)	0.08579(5)	0.04154(8)	7.59(3)
Br(2)	0.43579(10)	0.29872(5)	0.14837(8)	6.97(3)
P	0.8644(2)	0.1675(1)	0.4767(1)	3.62(5)
C(11)	0.7331(7)	0.1062(4)	0.4040(6)	3.6(2)
C(12)	0.6834(8)	0.1191(4)	0.3018(6)	4.8(3)
C(13)	0.5857(9)	0.0725(5)	0.2451(6)	5.6(3)
C(14)	0.5369(8)	0.0126(5)	0.2879(8)	6.1(3)
C(15)	0.5858(9)	−0.0021(4)	0.3903(7)	5.5(3)
C(16)	0.6836(8)	0.0462(4)	0.4478(5)	4.3(2)
C(21)	1.0139(7)	0.1712(4)	0.4144(5)	3.8(2)
C(22)	1.0784(8)	0.2362(4)	0.3950(6)	4.7(3)
C(23)	1.1957(9)	0.2337(5)	0.3470(6)	5.6(3)
C(24)	1.2474(9)	0.1696(5)	0.3192(6)	5.8(3)
C(25)	1.1861(10)	0.1054(5)	0.3385(7)	6.2(3)
C(26)	1.0658(9)	0.1051(4)	0.3852(6)	5.5(3)
C(31)	0.7877(8)	0.2559(4)	0.4830(5)	4.1(2)
C(32)	0.8710(9)	0.3071(5)	0.5459(7)	6.2(3)
C(33)	0.8129(13)	0.3778(5)	0.5529(8)	7.4(4)
C(34)	0.6738(14)	0.3939(5)	0.4973(9)	6.9(4)
C(35)	0.5954(11)	0.3447(5)	0.4382(8)	6.6(4)
C(36)	0.6493(9)	0.2752(4)	0.4296(6)	5.0(3)
C(41)	0.9214(7)	0.1335(4)	0.6008(5)	3.5(2)
C(42)	0.8180(8)	0.1346(4)	0.6623(6)	4.7(3)
C(43)	0.8534(9)	0.1048(5)	0.7586(6)	5.4(3)
C(44)	0.9878(9)	0.0745(5)	0.7937(6)	5.8(3)
C(45)	1.0909(9)	0.0753(5)	0.7349(7)	5.9(3)
C(46)	1.0588(8)	0.1039(4)	0.6375(6)	4.7(2)

used as starting points also for the refinement of $[P(C_6H_5)_4][CuCl_2]$. Full-matrix least-squares refinement[26] of positional and isotropic thermal parameters gave R=0.055, R=0.099 and R=0.125 for $[As(C_6H_5)_4][CuCl_2]$, $[P(C_6H_5)_4][CuCl_2]$ and $[P(C_6H_5)_4][CuBr_2]$, respectively. After empirical corrections[25] for the effects of absorption, R=0.053, R=0.085 and R=0.105. Inclusion of anisotropic thermal parameters gave R=0.036, R=0.061 and R=0.053, respectively. Finally, hydrogen atoms were included as fixed contributions [C−H=1.0 Å, $B=B_{eq}$ of carrying carbon atom (see Tables 2−4)], R values of 0.031, 0.046 and 0.043 being obtained. Further details concerning the refinements are summarized in Table 1. Atomic scattering factors were taken from the *International Tables for X-Ray Crystallography*.[27b] Atomic coordinates and equivalent isotropic thermal parameters are given in Tables 2−4. Structure factors, hydrogen-atom coordinates, and distances and angles within the cations may be obtained from the authors.

DISCUSSION

The geometries of the monomeric anions determined in the three structures are illustrated in Fig. 1. Bond distances and angles within the $[CuCl_2]^-$ ions agree well with the values

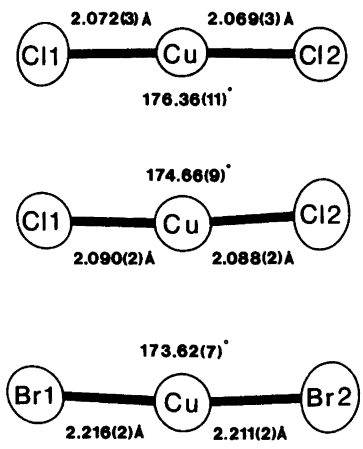

Fig. 1. The $[CuCl_2]^-$ and $[CuBr_2]^-$ anions in $[As(C_6H_5)_4][CuCl_2]$, $[P(C_6H_5)_4][CuCl_2]$ and $[P(C_6H_5)_4][CuBr_2]$, respectively. Thermal ellipsoids enclose 50 % probability.[28]

determined previously for monomeric anions,[2,10–18] *viz.* Cu–Cl between 1.96(1) and 2.11(1) Å and Cl–Cu–Cl between 169.5(8) and 180°. The $[CuBr_2]^-$ ion in $[P(C_6H_5)_4][CuBr_2]$ is nearly linear and the Cu–Br distances, 2.211(2) and 2.216(2) Å, are closely similar to those in the linear $[CuBr_2]^-$ monomers determined hitherto, *i.e.* 2.226(1) Å in $[N(C_4H_9)_4][CuBr_2]$[2] and 2.221(10) Å in $[\{[CH_3C(CH_2P(C_6H_5)_2)_3]IrP_3\}_3Cu_5Br_4][CuBr_2]$[19] but somewhat shorter than Cu–Br in the bent $[CuBr_2]^-$ ion in $TSeT[CuBr_2]$, *viz.* 2.267(2) and 2.282(3) Å.[20]

The As–C bond lengths in the four crystallographically independent tetraphenylarsonium cations in $[As(C_6H_5)_4][CuCl_2]$ are 1.907(7), 1.912(7), 1.914(7) and 1.915(8) Å, respectively. Within the tetraphenylphosphonium cation in $[P(C_6H_5)_4][CuCl_2]$ P–C=1.776(6), 1.787(6), 1.773(6) and 1.784(6) Å, the corresponding distances in $[P(C_6H_5)_4][CuBr_2]$ being 1.794(7), 1.780(7), 1.779(7) and 1.768(7) Å. The cations show no anomalous geometrical features.

Systematics of crystalline tetraphenylarsonium and tetraphenylphosphonium compounds with a cation: anion stoichiometry of 1:1 show that in such compounds the cations invariably stack in parallel columns within which the repeat distance varies between 7 and 8 Å.[29] The anions occupy holes between the columns, the symmetry of the resulting structure being largely dependent on the symmetry of the anion.[29] In view of this, it is somewhat surprising that the structures of tetraphenylarsonium dichlorocuprate(I) and tetraphenylphosphonium dichlorocuprate(I) and dibromocuprate(I) differ so radically. Moreover, $[As(C_6H_5)_4][CuCl_2]$ might perhaps have been expected to crystallize in a space group of lower symmetry in analogy with compounds containing anions with similar geometry.[29] Stereoscopic projections of the unit cells of $[As(C_6H_5)_4][CuCl_2]$ and $[P(C_6H_5)_4][CuBr_2]$ are shown in Figs. 2–3. In $[As(C_6H_5)_4][CuCl_2]$ the cations are arranged in two different types of column along *c*, both with a repeat distance of $\frac{1}{2}c$. As(1) and As(2) stack with nearly eclipsed phenyl rings, the dihedral angle between the least-squares plane through the ring C(11)–C(16) and that through $C(21^i)$–$C(26^i)$ being 18° [symmetry code (i):$\bar{x}$, $\bar{y}$, z]. As(3) and As(4) stack, however, with staggered phenyl rings, these cations being related to one another by an approximate *c* glide plane perpendicular to *a*(or *b*) [see Fig. 2]. No such column formation is observed in $[P(C_6H_5)_4][CuCl_2]$ and $[P(C_6H_5)_4][CuBr_2]$ (Fig. 3).

The shortest contacts between copper(I) and carbon and between chlorine and carbon in $[As(C_6H_5)_4][CuCl_2]$ are $Cu\cdots C(13^i)$=3.681(9) Å, $Cl(1)\cdots C(42)$=3.578(9) Å and $Cl(2)\cdots C(22^{ii})$=3.547(8) Å. In both $[P(C_6H_5)_4][CuCl_2]$ and $[P(C_6H_5)_4][CuBr_2]$ there is one

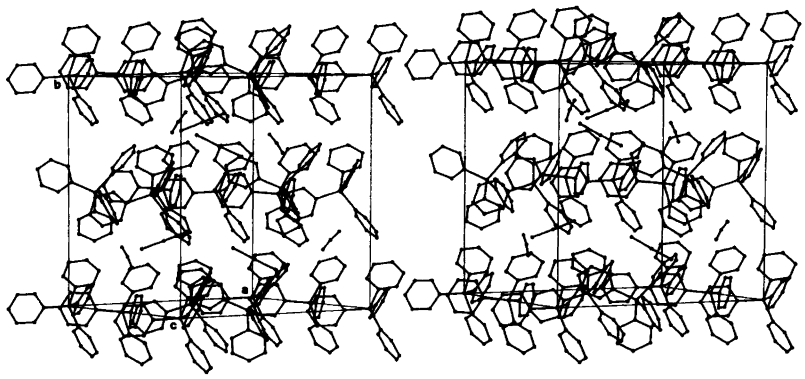

Fig. 2. Stereoscopic view[28] of the unit cell of $[As(C_6H_5)_4][CuCl_2]$. All atoms are represented as spheres of radius 0.05 Å.

very short Cu···C contact: Cu···C(22^{iii})=3.363(6) and 3.387(8) Å, respectively, and four other Cu···C distances less than 3.6 Å. The shortest chlorine-carbon distances are C(1)···C(44^{iv})=3.555(7), Cl(1)···C(34^{v})=3.622(7) and Cl(2)···C(15^{vi})=3.597(7) Å, the corresponding distances in $[P(C_6H_5)_4][CuBr_2]$ being 3.673(9), 3.668(10) and 3.681(8) Å, respectively. All these contacts are shorter than the shortest such distances in tetrabutylammonium dichlorocuprate(I) and dibromocuprate(I), *i.e.* Cu···C=3.720(4) Å, Cl···C=3.846(4) and Cu···C=3.757(5) Å, Br···C=3.876(5) Å, respectively. [Symmetry code: (*i*):$\bar{x}$, $\bar{y}$, z; (*ii*): $\frac{1}{2}-x$, $\frac{1}{2}-y$, $z-\frac{1}{2}$; (*iii*): $x-1$, $\frac{1}{2}-y$, $z-\frac{1}{2}$; (*iv*): $x-1$, y, $z-1$; (*v*): $1-x$, $y-\frac{1}{2}$, $\frac{1}{2}-z$; (vi): $1-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$].

Like tetrabutylammonium both tetraphenylarsonium and tetraphenylphosphonium crystallize with monomeric $[CuX_2]^-$, X=Cl,Br. The structure of $[As(C_6H_5)_4][CuBr_2]$ has not yet been reported, but it seems likely that this compound will also prove to contain a monomeric $[CuBr_2]^-$ ion. All three cations crystallize with dimeric diiodocuprate(I) anions.[3,8,9] These findings are in accordance with the hypothesis that large cations with low, well-screened positive charge tend to stabilize the formation of discrete anions in the solid state, there being an increased tendency to polymerization of the iodocuprates(I) as

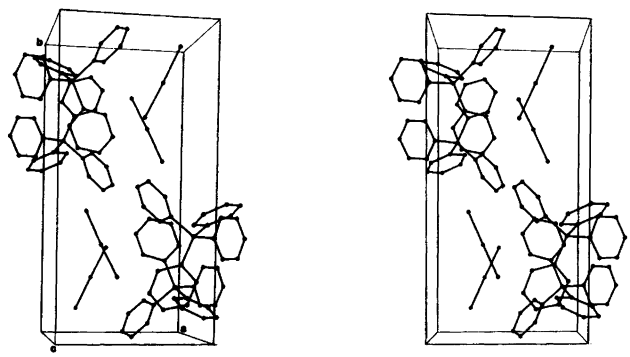

Fig. 3. Stereoscopic view[28] of the unit cell of $[P(C_6H_5)_4][CuBr_2]$. All atoms are represented as spheres of radius 0.05 Å.

compared with the bromo- and chlorocuprates(I). Smaller cations with similar geometry have been found to crystallize with larger anionic bromocuprate(I) and chlorocuprate(I) entities: A $[Cu_4Br_6]^{2-}$ aggregate containing three-coordinated copper(I) has been obtained with tetrapropylammonium,[4] and a planar $[Cu_2Br_4]^{2-}$ dimer containing three-coordinated copper(I)[30] and an infinite $[Cu_7Cl_{10}]^{3-}$ chain containing both two- and three-coordinated copper(I)[31] with tetraethylammonium as cation. With tetramethylammonium a $[Cu_2Br_5]^{3-}$ ion containing three-coordinated copper(I) has been obtained.[32] There would thus seem to be a tendency towards increased coordination number of copper(I), in these bromocuprates(I) and chlorocuprates(I), with decreasing size of and less well-screened positive charge on the cation.

Although tetraphenylarsonium crystallizes with a $[Cu_2I_4]^{2-}$ dimer which is folded about the bridging I···I contact such that the two ligand triangles are inclined at an angle of 147°, the $[CuCl_2]^-$ ion in $[As(C_6H_5)_4][CuCl_2]$ exhibits no exceptional deviation from linearity (Fig. 1). In the tetraphenylphosphonium compounds both the chlorocuprate(I) and the bromocuprate(I) ions are approximately linear, $[CuBr_2]^-$ deviating slightly more from linearity than $[CuCl_2]^-$, and the latter slightly more than $[CuCl_2]^-$ in $[As(C_6H_5)_4][CuCl_2]$ (see Fig. 1). Bis(tetraphenylphosphonium) di-μ-iodo-diiododicuprate(I) has been isolated both with a planar and with a folded $[Cu_2I_4]^{2-}$ anion.[9] The folding of the $[Cu_2I_4]^{2-}$ dimer would, however, seem to lack counterpart in the crystalline tetraphenylarsonium and tetraphenylphosphonium bromocuprate(I) and chlorocuprate(I) analogues.

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REFERENCES

1. Bowmaker, G.A., Brockliss, L.D. and Whiting, R. *Aust. J. Chem. 26* (1973) 29.
2. Asplund, M., Jagner, S. and Nilsson, M. *Acta Chem. Scand. A 37* (1983) 57.
3. Asplund, M., Jagner, S. and Nilsson, M. *Acta Chem. Scand. A 36* (1982) 751.
4. Asplund, M. and Jagner, S. *Acta Chem. Scand. A 38* (1984) 725.
5. Asplund, M. and Jagner, S. *Acta Chem. Scand. A 38* (1984) 411.
6. Hartl, H. and Mahdjour-Hassan-Abadi, F. *Z. Naturforsch. Teil B 39* (1984) 149.
7. Hartl, H. and Mahdjour-Hassan-Abadi, F. *Angew. Chem. 96* (1984) 359.
8. Asplund, M. and Jagner, S. *Acta Chem. Scand. A 38* (1984) 297.
9. Mahdjour-Hassan-Abadi, F. and Hartl, H. *In preparation.*
10. a. Newton, M.G., Caughman, H.D. and Taylor, R.C. *Chem. Commun.* (1970) 1227; b. *J. Chem. Soc. Dalton Trans.* (1974) 258.
11. Marsh, W.C. and Trotter, J. *J. Chem. Soc. A* (1971) 1482.
12. Kaiser, J., Brauer, G., Schröder, F.A., Taylor, I.F. and Rasmussen, S.E. *J. Chem. Soc. Dalton Trans.* (1974) 1490.
13. Siiman, O., Huber, C.P. and Post, M.L. *Inorg. Chim. Acta 25* (1977) L11.
14. Huber, C.P., Post, M.L. and Siimann, O. *Acta Crystallogr. B 34* (1978) 2629.
15. Francisco, R.H.P., de Almeida Santos, R.H., Lechat, J.R. and Massabni, A.C. *Acta Crystallogr. B 37* (1981) 232.
16. Sakurai, T., Kobayashi, K., Masuda, H., Tsuboyama, S. and Tsuboyama, K. *Acta Crystallogr. C 39* (1983) 334.
17. Clegg, W., Garner, C.D., Nicholson, J.R. and Raithby, P.R. *Acta Crystallogr. C 39* (1983) 1007.
18. Tsuboyama, S., Kobayashi, K., Sakurai, T. and Tsuboyama, K. *Acta Crystallogr. C 40* (1984) 1178.
19. Cecconi, F., Ghilardi, C.A., Midollini, S. and Orlandini, A. *Angew. Chem. Suppl.* (1983) 718.

20. Shibaeva, R.P., Kaminskii, V.F., Yagubskii, E.B. and Kushch, L.A. *Kristallografiya 28* (1983) 92.
21. Beurskens, P.T., Cras, J.A., Hummelink, T.W. and van der Linden, J.G.M. *Recl. Trav. Chim. Pays-Bas 89* (1970) 984.
22. Beurskens, P.T., Blaauw, H.J.A., Cras, J.A. and Steggerda, J.J. *Inorg. Chem 7* (1968) 805.
23. Lehmann, M.S. and Larsen, F.K. *Acta Crystallogr. A 30* (1974) 580.
24. Lindqvist, O. and Ljungström, E. *J. Appl. Crystallogr. 12* (1979) 134.
25. Walker, N. and Stuart, D. *Acta Crystallogr. A 39* (1983) 158.
26. Lindgren, O. *An Integrated Set of Crystallographic Programs.* In *On the Oxygen Coordination of Cerium in Some Sulfates and Chromates,* Thesis, Department of Inorganic Chemistry, Chalmers University of Technology and University of Göteborg, Göteborg 1977.
27. *International Tables for X-Ray Crystallography,* Kynoch Press, a. Birmingham 1952, Vol. 1; b. *Ibid.* 1974, Vol. 4, p. 72.
28. Johnson, C.K. *ORTEP* Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge 1965.
29. Müller, U. *Acta Crystallogr. B 36* (1980) 1075.
30. Asplund, M. and Jagner, S. *Acta Chem. Scand. A 38* (1984) 135.
31. Asplund, M. and Jagner, S. *Acta Chem. Scand. A 38* (1984) 807.
32. Asplund, M. and Jagner, S. *Acta Chem. Scand. A 39* (1985) 47.

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