Mixed-Metal (Cu/Ag) Halometallate(I) Clusters: Preparation and Crystal Structures of $[P(C_6H_5)_4]_4[Ag_2Cu_2I_8]$, $[P(C_6H_5)_4]_4[Ag_3CuI_8]$ and $[P(C_6H_5)_4]_2[AgCuBr_4]$

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Three heteronuclear copper–silver halometallates(I) have been prepared and their structures determined from single-crystal X-ray diffraction data, measured at 290 K. $[P(C_6H_5)_4]_4[Ag_2Cu_2I_8]$ and $[P(C_6H_5)_4]_4[Ag_3CuI_8]$ crystallize in space group $P\bar{1}$, with a = 13.434(5), b = 16.535(6), c = 11.050(5) Å, α = 103.28(3), β = 104.08(3), γ = 82.64(3)°, Z = 1, and a = 13.435(3), b = 16.550(4), c = 11.047(3) Å, α = 103.12(2), β = 104.14(2), γ = 82.88(2)°, Z = 1, respectively. Full-matrix least-squares refinement of 505 structural parameters gave R = 0.039 (6108 observed $[I > 3.0\sigma(I)]$ independent reflections) and R = 0.050 (6728 observed independent reflections) for $[P(C_6H_5)_4]_4[Ag_2Cu_2I_8]$ and $[P(C_6H_5)_4]_4[Ag_3CuI_8]$, respectively. $[P(C_6H_5)_4]_2[AgCuBr_4]$ crystallizes in space group $P2_1/n$ with a = 14.416(7), b = 7.951(5), c = 19.834(10) Å, β = 102.58(4)° and Z = 2. Full-matrix least-squares refinement of 313 structural parameters gave R = 0.047 for 2220 observed independent reflections. The tetranuclear $[Ag_2Cu_2I_8]^{4-}$ anion is centrosymmetric and can be described in terms of edge-sharing silver(I)-iodide tetrahedra, each linked via a common edge to an approximately planar copper(I)-iodide triangle. In the latter the copper(I) atom is displaced 0.050(1) Å from the plane through the three iodide ligands. The Cu–I distances associated with the three-coordinated centre are 2.577(1) (terminal), 2.599(1) and 2.601(2) Å (bridging), while the Ag–I distances involving the four-coordinated centre are 2.816(1), 2.824(1), 2.864(2) and 2.948(1) Å. The Ag···Ag and Ag···Cu contacts are 3.195(2) and 3.119(2) Å, respectively. In the analogous $[Ag_3CuI_8]^{4-}$ anion, the three-coordinated site (AgCu) is shared by a silver(I) atom and a copper(I) atom, the metal–ligand distances associated with this site being 2.638(1) (terminal), 2.670(1) and 2.678(1) Å (bridging), the metal atom being displaced 0.057(1) Å from the ligand plane. The Ag–I distances associated with the approximately tetrahedrally coordinated silver(I) centre are 2.834(1), 2.839(1), 2.880(1) and 2.968(1) Å. Metal–metal contacts are: Ag···Ag = 3.224(2) Å and Ag···AgCu = 3.147(1) Å. In the centrosymmetric dinuclear anion in $[P(C_6H_5)_4]_2[AgCuBr_4]$ the three-coordinated metal site is partially occupied by copper(I) and silver(I), with the metal atom displaced 0.057(1) Å from the plane through the bromide ligands. The metal–ligand distances are 2.401(2) (terminal) and 2.543(2) and 2.688(2) Å (bridging) and the metal–metal separation is 3.449(2) Å.

In halocuprates(I) crystallizing with symmetrically substituted quaternary ammonium and phosphonium cations, the coordination number of copper(I) in the anion and the concentration of halide ligand in the crystalline phase have been found to increase regularly with decreasing cation size (Refs. 1–3 and references therein). Ethanolic solutions of tetrapropylammonium bromide and copper(I) bromide, from which bis(tetrapropylammonium) hexa-μ-bromo-*tetrahedro*-tetracuprate(I), $[N(C_3H_7)_4]_2[Cu_4Br_6]$, a bromocuprate(I) cluster comprised of three-coordinated copper(I),[4] crystallizes have been shown to contain the centrosymmetric, monomeric $[CuBr_2]^-$ anion as the dominant, and probably the sole, bromocuprate(I) species.[3] The various results have been interpreted as suggesting cation–halide packing as a primary process at the solution–crystal interface during formation of a tetraalkylammonium or analogous halocuprate(I), copper(I) then diffusing into available interstices, with subsequent rearrangement resulting in the specific anion with appropriate copper(I) coordination number, such a mechanism implying a rapid ligand exchange rate for copper(I) in solution.

Analogous investigations on haloargentates(I) suggest a similar dependence of the coordination number of the metal on the size of the cation.[5–9] Those haloargentates(I) crystallizing with the smaller symmetrically substituted tetraalkylammonium cations, e.g. tetramethylammonium or tetraethylammonium, characterized hitherto by means of crystallographic studies, contain polymeric anions of stoichiometry $[AgX_2]^-$ (X = Cl or I),[5,10] $[Ag_2X_3]^-$ (X = Cl, Br or I)[6,7,11,12] and $[Ag_{13}X_{15}]^{2-}$ (X = I),[13] composed of silver(I)-halide tetrahedra. Tetrabutylammonium tetraiodotriargentate(I) contains a polymeric anion in which silver(I) is

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tetrahedrally coordinated,[14] whereas discrete, dinuclear $[Ag_2X_4]^{2-}$ species (X = Cl,Br), in which silver(I) exhibits distorted trigonal-planar coordination geometry have been isolated with the tetraphenylphosphonium cation,[8] and, more recently, also with tetraphenylarsonium.[9] In connection with an investigation of tetraphenylphosphonium iodoargentates(I), a discrete tetranuclear $[Ag_4I_8]^{4-}$ cluster, containing three- and four-coordinated silver(I), as well as a polymeric $[Ag_3I_4]^-$ anion in which silver(I) is tetrahedrally coordinated, have been prepared and characterised.[9]

If the tentative mechanism proposed[3] for the formation of tetraalkylammonium and analogous halocuprates(I) is valid also for haloargentates(I), it ought to be possible to prepare crystalline mixed-metal (Cu/Ag) halometallates(I) from solutions of RX, CuX and AgX, where R^+ is the appropriate tetraalkylammonium or analogous cation and X^- the appropriate halide ion. The tetraphenylphosphonium iodo- and bromometallate(I) systems were selected as being suitable for the investigation of this hypothesis. Since two dinuclear iodocuprate(I) species, $[Cu_2I_4]^{2-}$, both containing three-coordinated copper(I), can be isolated with the tetraphenylphosphonium cation,[15] whereas silver(I) is three- and four-coordinated in the anion in $[P(C_6H_5)_4]_4[Ag_4I_8]$,[9] it seemed that it might be possible to prepare an iodocuprate(I) species containing trigonal-planar coordinated copper(I) and tetrahedrally coordinated silver(I). In tetraphenylphosphonium di-μ-bromodibromodiargentate(I), the centrosymmetric dinuclear anion contains three-coordinated silver(I).[8] In the corresponding bromocuprate (I) the anion is a linear monomer,[16] although dinuclear $[Cu_2Br_4]^{2-}$ species are obtained with smaller cations, e.g. tetraethylphosphonium[1] and tetraethylammonium.[17] Here it was of interest to investigate whether or not a new type of anion containing, for example, two-coordinated copper(I) and three-coordinated silver(I) would be formed.

Experimental

Preparation of $[P(C_6H_5)_4]_4[Ag_2Cu_2I_8]$ and $[P(C_6H_5)_4]_4[Ag_3CuI_8]$. Tetraphenylphosphonium iodide (0.60 g; 1.3 mmol) (Fluka) was dissolved in 200 ml acetonitrile, and copper(I) iodide (0.082 g; 0.43 mmol) (Aldrich 99.999% Gold Label) was added. Following dissolution of CuI, silver(I) iodide (0.10 g; 0.43 mmol) (ICN Biomedicals, K & K) was added and dissolved by stirring and heating gently. The resulting solution was allowed to evaporate slowly, crystals of $[P(C_6H_5)_4]_4[Ag_2Cu_2I_8]$ (yellow prisms, m.p. 206–208 °C), $[P(C_6H_5)_4]_4[Ag_3CuI_8]$ (pale-yellow irregular-shaped prisms, m.p. 218–220 °C), $[P(C_6H_5)_4]_4[Ag_4CuI_8]$ (colourless, irregular-shaped prisms, m.p. 234–236 °C),[9] and $[P(C_6H_5)_4]_2[Cu_2I_4]$-*A* (colourless rectangular prisms, m.p. 210 °C)[15] being deposited after a few days. $[P(C_6H_5)_4]_2[Cu_2I_4]$-*A* was formed towards the end of the crystallization, its identity[15] being established from rotation and Weissenberg photographs. A fourfold increase of the total Cu:Ag molar ratio in the solution led to formation of a larger amount of $[P(C_6H_5)_4]_2[Cu_2I_4]$-*A*. Rotation and Weissenberg photographs for $[P(C_6H_5)_4]_4[Ag_2Cu_2I_8]$ and $[P(C_6H_5)_4]_4[Ag_3CuI_8]$ suggested isostructurality with each other and also with $[P(C_6H_5)_4]_4[Ag_4I_8]$.[9]

Preparation of $[P(C_6H_5)_4]_2[AgCuBr_4]$. Tetraphenylphosphonium bromide (0.21 g; 0.50 mmol) (Fluka), copper(I) bromide (0.036 g; 0.25 mmol) (Aldrich 99.999% Gold Label) and silver(I) bromide (0.047 g; 0.25 mmol) (ICN Biomedicals, K & K) were dissolved in 40 ml acetonitrile by heating under reflux for approximately 1 h. The solution was allowed to cool to ambient temperature and to evaporate slowly under a stream of nitrogen, pale-yellow needles of $[P(C_6H_5)_4]_2[AgCuBr_4]$, m.p. 190–191 °C, being deposited from the solution after a few days. Rotation and Weissenberg photographs for $[P(C_6H_5)_4]_2[AgCuBr_4]$ suggested isostructurality with $[P(C_6H_5)_4]_2[Ag_2Br_4]$.[8]

Mass spectrometric analyses. Several attempts were made to determine the Ag:Cu molar ratios in the three compounds by means of inductively coupled plasma mass spectrometry. For $[P(C_6H_5)_4]_4[Ag_2Cu_2I_8]$, an Ag:Cu molar ratio of 1.0 was obtained. For $[P(C_6H_5)_4]_4[Ag_3CuI_8]$ and $[P(C_6H_5)_4]_2[AgCuBr_4]$, the Ag:Cu ratios determined were in the ranges 2.5–2.6 and 0.8–1.2, respectively. It is thus evident that all three anions contain both silver and copper and that the Ag:Cu ratio in the anion in $[P(C_6H_5)_4]_4[Ag_2Cu_2I_8]$ is stoichiometric. Whether or not the values obtained for the other two compounds reflect real deviations from the ideal stoichiometry (3:1 and 1:1), respectively, is, however, uncertain; these deviations might be attributable to incomplete dissolution of the samples or difficulties in holding silver, in particular, in solution. That the compounds obtained melted with well-defined melting points, a large number of crystals from different batches being investigated, suggests constant rather than variable composition. For this reason, Ag:Cu molar ratios of 3:1 and 1:1 have been assumed in the refinement of $[P(C_6H_5)_4]_4[Ag_3CuI_8]$ and $[P(C_6H_5)_4]_2[AgCuBr_4]$ (see below).

Crystallography. Crystal and experimental data for $[P(C_6H_5)_4]_4[Ag_2Cu_2I_8]$, $[P(C_6H_5)_4]_4[Ag_3CuI_8]$ and $[P(C_6H_5)_4]_2[AgCuBr_4]$ are given in Table 1. Diffracted intensities were measured with a Syntex $P2_1$ diffractometer, using graphite-monochromated Mo$K\alpha$ radiation and the ω–2θ scan mode. A 96-step profile was recorded for each reflection, and the intensities were calculated[18] using the Lehmann and Larsen profile-analysis method.[19] Correction was made for Lorentz and polarisation effects; no corrections were made for absorption for $[P(C_6H_5)_4]_4[Ag_3CuI_8]$ and $[P(C_6H_5)_4]_2[AgCuBr_4]$, owing to difficulties in measuring and indexing crystal faces. For $[P(C_6H_5)_4]_4[Ag_2Cu_2I_8]$, a Gaussian correction was made using ABSORB,[20] the crystal dimensions (distance to faces from vertex) chosen as origin being: 0.000 (0−10, −100, −101), 0.256 (100), 0.345 (10−1), 0.433 (010) mm. Unit-cell dimensions were determined from diffractometer setting angles for 15 reflections.

Table 1. Crystal and experimental data for $[P(C_6H_5)_4]_4[Ag_2Cu_2I_8]$, $[P(C_6H_5)_4]_4[Ag_3CuI_8]$ and $[P(C_6H_5)_4]_2[AgCuBr_4]$.

	$[P(C_6H_5)_4]_4[Ag_2Cu_2I_8]$	$[P(C_6H_5)_4]_4[Ag_3CuI_8]$	$[P(C_6H_5)_4]_2[AgCuBr_4]$
M_r	2715.6	2759.9	1169.8
Unit cell dimensions/Å,°, Å^3	a = 13.434(5), b = 16.535(6) c = 11.050(5), α = 103.28(3) β = 104.08(3), γ = 82.64(3) V = 2310(1)	a = 13.435(3), b = 16.550(4) c = 11.047(3), α = 103.12(2) β = 104.14(2), γ = 82.88(2) V = 2314(1)	a = 14.416(7), b = 7.951(5) c = 19.834(10), β = 102.58(4) V = 2219(2)
Space group [a]	$P\bar{1}$	$P\bar{1}$	$P2_1/n$ (No. 14, non-standard setting)
Z	1	1	2
D_c/g cm^{-3}	1.95	1.98	1.75
Habit	Yellow prisms	Pake-yellow irregular-shaped prisms	Pale-yellow needles
M.p./°C	206–208	218–220	190–191
μ(Mo$K\alpha$)/mm^{-1}	3.70	3.66	4.85
Crystal size/mm	0.26×0.43×0.34	0.20×0.40×0.50	0.18×0.19×0.22
Temperature (data collection)/K	290	290	290
2θ range/°	$3.5 < 2\theta < 50.0$	$3.5 < 2\theta < 50.0$	$0.0 < 2\theta < 50.0$
2θ scan rate/°min^{-1}	2.0–20.0	2.0–20.0	3.0–20.0
No. of unique reflections measured	8157	7995	3905
No. of observed [$I > 3\sigma(I)$] reflections	6108	6728	2220
Correction for absorption	ABSORB[b] (max., min. transmission factors = 0.280, 0.487)	None	None
No. of parameters refined	505	505	313
Weights calculated according to	$w = [\sigma^2(F_o)+0.0008\ F_o^2]^{-1}$	$w = [\sigma^2(F_o)+0.0008\ F_o^2]^{-1}$	$w = [\sigma^2(F_o)+0.0008\ F_o^2]^{-1}$
R	0.039	0.050	0.047
R_w	0.048	0.066	0.054
Max residual electron density/e Å^{-3}	1.19	1.61	0.63

[a]Ref. 21*a*. [b]Ref. 20.

The atomic coordinates of $[P(C_6H_5)_4]_4[Ag_4I_8]$[9] were used as starting point for the refinement of $[P(C_6H_5)_4]_4[Ag_2Cu_2I_8]$ and $[P(C_6H_5)_4]_4[Ag_3CuI_8]$. In the former, copper(I) was assigned to the three-coordinated site in $[P(C_6H_5)_4]_4[Ag_4I_8]$.[9] Full-matrix least-squares refinement, including anisotropic thermal parameters for all non-hydrogen atoms, and with hydrogen atoms as a fixed contribution (C–H = 1.0 Å, B = 4.5 Å^2), yielded a final R value of 0.039 and R_w of 0.048 for 505 parameters and 6108 reflections. In the refinement of $[P(C_6H_5)_4]_4[Ag_3CuI_8]$, mean atomic scattering factors for silver and copper were employed for the atom in the three-coordinated site (AgCu), similar refinement with hydrogen atoms as a fixed contribution yielding R = 0.050 and R_w = 0.066 for 505 parameters and 6728 reflections. Identical refinement with silver and with copper in the AgCu site gave R = 0.058 and 0.065, respectively, combined with anomalous values for the thermal parameters.

Similarly, the atomic coordinates of $[P(C_6H_5)_4]_2[Ag_2Br_4]$[8] were used as starting point for the refinement of $[P(C_6H_5)_4]_2[AgCuBr_4]$, mean atomic scattering factors being used for the metal atom (AgCu). Full-matrix least-squares refinement, including anisotropic thermal parameters for all non-hydrogen atoms, and with isotropic thermal parameters for H set equal to the equivalent isotropic value of the carrying carbon and not refined, gave final values of R = 0.047 and R_w = 0.054 for 313 parameters and 2220 reflections. Analogous refinement with silver and copper in the metal site gave R = 0.066 and 0.074, respectively. Further details concerning the refinement of the three structures are given in Table 1. Atomic scattering factors were taken from Ref. 21b. Correction was made for anomalous dispersion[21b] in the refinement of $[P(C_6H_5)_4]_4[Ag_2Cu_2I_8]$, but not for $[P(C_6H_5)_4]_4[Ag_3CuI_8]$ and $[P(C_6H_5)_4]_2[AgCuBr_4]$. The computer programs employed are described in Refs. 22 and 23. Atomic coordinates and equivalent isotropic thermal parameters are given in Tables 2–4. Structure factors, anisotropic thermal parameters, hydrogen-atom coordinates for $[P(C_6H_5)_4]_2[AgCuBr_4]$, and connectivity relationships within the cations in $[P(C_6H_5)_4]_4[Ag_2Cu_2I_8]$, $[P(C_6H_5)_4]_4[Ag_3CuI_8]$ and $[P(C_6H_5)_4]_2[AgCuBr_4]$ may be obtained from the authors on request.

Discussion

The $[Ag_2Cu_2I_8]^{4-}$ anion is depicted in Fig. 1, and interatomic distances and angles within $[Ag_2Cu_2I_8]^{4-}$ and the structurally similar $[Ag_3CuI_8]^{4-}$ anion are given in Table 5. The Ag–I distances associated with the tetrahedrally coordinated silver(I) atom are similar in both anions, and are comparable with those determined for the four-coordinated silver(I) centre in $[P(C_6H_5)_4]_4[Ag_4I_8]$, viz. 2.842(2),

Table 2. Fractional coordinates and equivalent isotropic thermal parameters (Å^2) for the non-hydrogen atoms in $[P(C_6H_5)_4]_4[Ag_2Cu_2I_8]$. B_{eq} is defined as $\frac{8\pi^2}{3}\sum_i\sum_j U_{ij}\, a^*_i\, a^*_j\, a_i a_j$. Estimated standard deviations are given in parentheses.

Atom	x	y	z	B_{eq}
Ag	0.05667(6)	−0.05983(4)	−0.10251(6)	5.48(2)
Cu	0.15528(7)	−0.20352(5)	−0.28420(8)	3.52(3)
I(1)	0.03866(4)	0.11597(3)	−0.06026(5)	3.89(1)
I(2)	0.27508(4)	−0.11875(3)	−0.08712(5)	4.50(2)
I(3)	−0.02390(4)	−0.13065(3)	−0.36524(5)	4.33(2)
I(4)	0.21620(4)	−0.34818(3)	−0.40063(5)	4.62(2)
P(1)	0.5143(1)	0.8150(1)	0.4315(2)	2.73(5)
C(10)	0.5773(5)	0.8444(4)	0.5963(6)	2.8(2)
C(11)	0.5329(6)	0.9064(4)	0.6819(6)	3.6(2)
C(12)	0.5866(6)	0.9326(5)	0.8047(7)	4.3(2)
C(13)	0.6859(6)	0.8972(5)	0.8436(6)	4.1(2)
C(14)	0.7309(6)	0.8372(5)	0.7616(7)	4.2(2)
C(15)	0.6758(6)	0.8092(5)	0.6374(6)	3.8(2)
C(20)	0.3829(5)	0.8543(4)	0.4085(6)	2.9(2)
C(21)	0.3211(5)	0.8379(4)	0.4846(7)	3.6(2)
C(22)	0.2170(6)	0.8678(5)	0.4656(7)	4.4(2)
C(23)	0.1769(5)	0.9150(4)	0.3730(8)	3.9(2)
C(24)	0.2370(6)	0.9320(5)	0.2993(7)	4.1(2)
C(25)	0.3414(5)	0.9010(4)	0.3152(6)	3.5(2)
C(30)	0.5800(5)	0.8545(4)	0.3371(6)	3.0(2)
C(31)	0.5522(6)	0.8324(5)	0.2056(6)	4.1(2)
C(32)	0.6026(7)	0.8630(5)	0.1320(7)	5.0(3)
C(33)	0.6809(8)	0.9140(5)	0.1908(8)	5.2(3)
C(34)	0.7097(7)	0.9357(4)	0.3212(8)	4.4(3)
C(35)	0.6595(6)	0.9069(4)	0.3959(7)	3.8(2)
C(40)	0.5260(5)	0.7042(4)	0.3856(6)	3.2(2)
C(41)	0.4509(6)	0.6569(5)	0.3970(9)	5.5(3)
C(42)	0.4708(8)	0.5713(6)	0.3777(11)	7.2(4)
C(43)	0.5596(8)	0.5316(5)	0.3413(9)	6.3(3)
C(44)	0.6314(7)	0.5780(5)	0.3290(8)	5.2(3)
C(45)	0.6166(6)	0.6650(4)	0.3518(7)	4.2(2)
P(2)	0.2135(1)	0.4367(1)	0.0582(2)	2.61(5)
C(50)	0.1514(5)	0.4082(4)	0.1672(6)	2.7(2)
C(51)	0.0707(5)	0.3573(4)	0.1228(6)	3.3(2)
C(52)	0.0264(6)	0.3346(5)	0.2078(7)	4.1(2)
C(53)	0.0605(6)	0.3614(5)	0.3371(8)	4.5(3)
C(54)	0.1397(7)	0.4112(5)	0.3823(7)	4.6(3)
C(55)	0.1871(6)	0.4357(5)	0.2989(7)	4.0(2)
C(60)	0.1542(5)	0.3908(4)	−0.1024(6)	2.7(2)
C(61)	0.1731(6)	0.3051(4)	−0.1450(7)	3.9(2)
C(62)	0.1243(7)	0.2672(5)	−0.2652(7)	4.8(3)
C(63)	0.0589(7)	0.3132(5)	−0.3443(7)	4.8(3)
C(64)	0.0396(6)	0.3971(5)	−0.3049(7)	4.7(2)
C(65)	0.0866(6)	0.4365(4)	−0.1815(6)	3.7(2)
C(70)	0.3444(5)	0.3936(4)	0.0851(6)	3.0(2)
C(71)	0.3792(6)	0.3395(5)	0.1689(8)	4.7(3)
C(72)	0.4790(7)	0.3042(5)	0.1818(9)	5.8(3)
C(73)	0.5430(6)	0.3204(5)	0.1121(9)	5.1(3)
C(74)	0.5080(6)	0.3731(5)	0.0280(8)	4.8(3)
C(75)	0.4091(6)	0.4094(5)	0.0164(7)	4.2(2)
C(80)	0.2054(5)	0.5479(4)	0.0756(6)	2.8(2)
C(81)	0.1751(6)	0.6006(4)	0.1779(7)	4.1(2)
C(82)	0.1708(7)	0.6872(5)	0.1881(8)	5.2(3)
C(83)	0.1942(6)	0.7196(4)	0.1005(9)	4.7(3)
C(84)	0.2247(6)	0.6683(5)	−0.0028(8)	4.3(3)
C(85)	0.2298(5)	0.5816(4)	−0.0173(7)	3.7(2)

Table 3. Fractional coordinates and equivalent isotropic thermal parameters (Å^2) for the non-hydrogen atoms in $[P(C_6H_5)_4]_4[Ag_3CuI_8]$. B_{eq} is defined as in Table 2. Estimated standard deviations are given in parentheses.

Atom	x	y	z	B_{eq}
Ag	0.05707(5)	−0.05965(4)	−0.10349(6)	5.23(2)
AgCu	0.15621(5)	−0.20544(4)	−0.28433(7)	4.20(2)
I(1)	0.03935(3)	0.11677(3)	−0.05957(4)	3.67(1)
I(2)	0.27766(4)	−0.11747(3)	−0.08143(5)	4.48(2)
I(3)	−0.02737(4)	−0.12911(3)	−0.36739(5)	4.36(1)
I(4)	0.21807(4)	−0.35285(3)	−0.40403(5)	4.83(2)
P(1)	0.5139(1)	0.8151(1)	0.4316(1)	2.65(4)
C(10)	0.5767(4)	0.8455(4)	0.5965(5)	2.8(2)
C(11)	0.5305(5)	0.9056(4)	0.6792(6)	3.7(2)
C(12)	0.5871(6)	0.9310(4)	0.8032(7)	4.2(2)
C(13)	0.6847(6)	0.8969(5)	0.8448(6)	4.4(2)
C(14)	0.7306(5)	0.8349(5)	0.7604(7)	4.2(2)
C(15)	0.6766(5)	0.8098(4)	0.6394(6)	3.9(2)
C(20)	0.3820(5)	0.8546(3)	0.4081(6)	2.9(2)
C(21)	0.3194(5)	0.8363(4)	0.4801(7)	3.7(2)
C(22)	0.2186(6)	0.8660(5)	0.4617(7)	4.2(2)
C(23)	0.1767(5)	0.9136(4)	0.3688(7)	3.9(2)
C(24)	0.2376(6)	0.9308(4)	0.2988(7)	4.4(2)
C(25)	0.3411(5)	0.9021(4)	0.3160(6)	3.3(2)
C(30)	0.5808(5)	0.8552(4)	0.3385(6)	3.2(2)
C(31)	0.5521(6)	0.8329(4)	0.2058(7)	4.3(2)
C(32)	0.6035(7)	0.8632(5)	0.1341(7)	5.1(3)
C(33)	0.6834(7)	0.9148(5)	0.1940(8)	4.9(3)
C(34)	0.7130(6)	0.9361(4)	0.3222(8)	4.6(2)
C(35)	0.6607(5)	0.9073(4)	0.3982(6)	3.6(2)
C(40)	0.5267(5)	0.7038(4)	0.3871(6)	3.3(2)
C(41)	0.4526(6)	0.6563(5)	0.3970(10)	5.8(3)
C(42)	0.4662(8)	0.5712(5)	0.3719(12)	7.4(4)
C(43)	0.5553(8)	0.5310(5)	0.3408(10)	6.7(3)
C(44)	0.6308(7)	0.5782(5)	0.3316(8)	5.5(3)
C(45)	0.6165(6)	0.6654(4)	0.3517(7)	4.4(2)
P(2)	0.2131(1)	0.4367(1)	0.0575(1)	2.53(4)
C(50)	0.1505(4)	0.4082(3)	0.1652(6)	2.8(2)
C(51)	0.0708(5)	0.3574(4)	0.1217(6)	3.2(2)
C(52)	0.0258(6)	0.3340(4)	0.2055(7)	4.3(2)
C(53)	0.0612(6)	0.3607(5)	0.3343(8)	4.7(2)
C(54)	0.1415(7)	0.4113(5)	0.3809(7)	4.7(2)
C(55)	0.1878(6)	0.4337(4)	0.2967(7)	4.1(2)
C(60)	0.1536(4)	0.3910(3)	−0.1024(6)	2.6(2)
C(61)	0.1733(6)	0.3057(4)	−0.1445(6)	4.0(2)
C(62)	0.1245(7)	0.2660(4)	−0.2665(7)	4.8(2)
C(63)	0.0579(7)	0.3140(5)	−0.3444(7)	5.2(2)
C(64)	0.0417(6)	0.3989(5)	−0.3055(7)	4.8(2)
C(65)	0.0869(5)	0.4369(4)	−0.1828(6)	3.9(2)
C(70)	0.3440(4)	0.3930(3)	0.0847(6)	3.0(2)
C(71)	0.3777(6)	0.3400(5)	0.1680(9)	5.0(3)
C(72)	0.4774(6)	0.3043(5)	0.1806(10)	5.7(3)
C(73)	0.5421(6)	0.3198(5)	0.1130(9)	5.1(3)
C(74)	0.5064(6)	0.3726(5)	0.0284(9)	5.1(3)
C(75)	0.4084(5)	0.4089(4)	0.0156(7)	4.1(2)
C(80)	0.2050(4)	0.5477(3)	0.0746(6)	2.9(2)
C(81)	0.1735(6)	0.6008(4)	0.1784(7)	4.1(2)
C(82)	0.1680(7)	0.6849(4)	0.1880(8)	5.5(3)
C(83)	0.1946(6)	0.7192(4)	0.0991(9)	4.9(2)
C(84)	0.2258(6)	0.6676(4)	−0.0013(9)	4.7(3)
C(85)	0.2311(5)	0.5826(4)	−0.0144(7)	3.8(2)

Table 4. Fractional coordinates and equivalent isotropic thermal parameters (Å^2) for the non-hydrogen atoms in $[P(C_6H_5)_4]_2[AgCuBr_4]$. B_{eq} is defined as in Table 2. Estimated standard deviations are given in parentheses.

Atom	*x*	*y*	*z*	B_{eq}
AgCu	0.39879(6)	0.0622(1)	0.02620(4)	5.48(3)
Br(1)	0.58416(5)	0.1330(1)	0.07193(4)	4.45(2)
Br(2)	0.27698(7)	0.1631(1)	0.08142(5)	6.09(3)
P	−0.0352(1)	−0.0936(2)	0.17630(9)	2.47(5)
C(10)	−0.1342(4)	−0.2308(8)	0.1716(3)	2.7(2)
C(11)	−0.1487(5)	−0.3107(9)	0.2299(4)	3.2(2)
C(12)	−0.2203(6)	−0.4291(11)	0.2244(5)	4.3(3)
C(13)	−0.2775(6)	−0.4684(11)	0.1619(5)	4.5(3)
C(14)	−0.2643(6)	−0.3888(11)	0.1043(5)	4.5(3)
C(15)	−0.1919(5)	−0.2695(10)	0.1076(4)	3.5(2)
C(20)	−0.0101(5)	0.0210(9)	0.2553(3)	3.0(2)
C(21)	0.0328(5)	−0.0620(10)	0.3164(3)	3.2(2)
C(22)	0.0475(5)	0.0230(11)	0.3780(4)	4.2(2)
C(23)	0.0213(6)	0.1886(12)	0.3797(5)	4.8(3)
C(24)	−0.0193(7)	0.2726(11)	0.3207(5)	5.0(3)
C(25)	−0.0366(5)	0.1891(10)	0.2575(4)	3.7(2)
C(30)	−0.0597(4)	0.0547(9)	0.1067(3)	2.9(2)
C(31)	0.0099(5)	0.1135(10)	0.0751(4)	3.5(2)
C(32)	−0.0099(7)	0.2387(11)	0.0275(4)	4.4(3)
C(33)	−0.0975(7)	0.3069(11)	0.0097(4)	4.4(3)
C(34)	−0.1686(6)	0.2493(11)	0.0390(4)	4.3(3)
C(35)	−0.1490(6)	0.1250(11)	0.0882(4)	4.1(2)
C(40)	0.0662(4)	−0.2245(9)	0.1746(3)	2.8(2)
C(41)	0.0539(5)	−0.3946(9)	0.1638(4)	3.2(2)
C(42)	0.1331(7)	−0.4942(11)	0.1634(4)	4.5(3)
C(43)	0.2215(6)	−0.4232(13)	0.1715(4)	4.7(3)
C(44)	0.2317(5)	−0.2533(14)	0.1807(4)	4.7(3)
C(45)	0.1553(5)	−0.1517(12)	0.1841(4)	4.1(2)

Table 5. Interatomic distances (Å) and angles (°) within the $[Ag_2Cu_2I_8]^{4-}$ and $[Ag_3CuI_8]^{4-}$ anions. Symmetry code: (*i*): $-x, -y, -z$.

$[Ag_2Cu_2I_8]^{4-}$		$[Ag_3CuI_8]^{4-}$	
Ag–I(1)	2.824(1)	Ag–I(1)	2.839(1)
Ag–I(1^i)	2.816(1)	Ag–I(1^i)	2.834(1)
Ag–I(2)	2.948(1)	Ag–I(2)	2.968(1)
Ag–I(3)	2.864(2)	Ag–I(3)	2.880(1)
Cu–I(2)	2.601(2)	AgCu–I(2)	2.670(1)
Cu–I(3)	2.599(1)	AgCu–I(3)	2.678(1)
Cu–I(4)	2.577(1)	AgCu–I(4)	2.638(1)
Ag···Cu	3.119(2)	Ag···AgCu	3.147(1)
Ag···Ag^i	3.195(2)	Ag···Ag^i	3.224(1)
I(1)–Ag–I(1^i)	110.98(4)	I(1)–Ag–I(1^i)	110.74(3)
I(1)–Ag–I(2)	108.72(4)	I(1)–Ag–I(2)	108.51(3)
I(1)–Ag–I(3)	110.60(4)	I(1)–Ag–I(3)	110.43(3)
I(1^i)–Ag–I(2)	115.15(4)	I(1^i)–Ag–I(2)	114.38(3)
I(1^i)–Ag–I(3)	111.79(4)	I(1^i)–Ag–I(3)	111.24(3)
I(2)–Ag–I(3)	99.00(4)	I(2)—Ag–I(3)	101.14(3)
I(2)–Cu–I(3)	116.42(5)	I(2)–AgCu–I(3)	115.30(3)
I(2)–Cu–I(4)	121.49(5)	I(2)–AgCu–I(4)	122.20(4)
I(3)–Cu–I(4)	121.98(5)	I(3)–AgCu–I(4)	122.37(4)
Ag–I(1)–Ag^i	69.02(4)	Ag–I(1)–Ag^i	69.26(3)
Ag–I(2)–Cu	68.06(4)	Ag–I(2)–AgCu	67.62(3)
Ag–I(3)–Cu	69.43(4)	Ag–I(3)–AgCu	68.86(3)

2.846(2), 2.901(2) and 2.991(2) Å.[9] The three-coordinated silver(I) centre in $[P(C_6H_5)_4]_4[Ag_4I_8]$ exhibits Ag–I distances of 2.727(2) (terminal), and 2.763(2) and 2.765(2) Å (bridging). In the analogous $[Cu_4I_8]^{4-}$ anion isolated recently with cobaltocenium as cation, the Cu–I distances associated with the three-coordinated centre are 2.486(2) (terminal) and 2.551(2) and 2.580(2) Å (bridging), whereas Cu–I for the tetrahedrally coordinated centre range from 2.653(2) to 2.761(2) Å.[25] It is thus apparent that there is an overall consistency between stoichiometry and bond lengths in $[Ag_2Cu_2I_8]^{4-}$ and $[Ag_3CuI_8]^{4-}$ (cf. Table 5). That the Ag–I bond lengths in $[Ag_2Cu_2I_8]^{4-}$ are somewhat shorter than Ag–I (tetrahedral) in $[Ag_4I_8]^{4-}$ and the Cu–I bond lengths somewhat longer than Cu–I (trigonal) in $[Cu_4I_8]^{4-}$, could indicate slight mixing of copper(I) and silver(I) in both metal sites. On the other hand, the geometry of a given halometallate(I) ion, e.g. $[Cu_2Br_4]^{2-}$,[1] is known to vary considerably under different environmental constraints. It is thus questionable whether small differences in bond length can be used as stoichiometric indicators in this type of anion.

The Ag···Cu contact in $[Ag_2Cu_2I_8]^{4-}$, 3.119(2) Å, is appreciably longer than that in the trimetallic hexanuclear cluster $[AgCuRu_4(\mu_3\text{-}H)_2(CO)_{12}(P(C_6H_5)_3)_2]$, 2.764(1) Å.[26,27]

Bond lengths and angles in the $[AgCuBr_4]^{2-}$ anion are given in Fig. 2. The AgCu–Br distances are intermediate between the metal–ligand bonds in $[Ag_2Br_4]^{2-}$, 2.491(1) (terminal) and 2.617(1) and 2.752(2) Å (bridging),[8] and those typical for $[Cu_2Br_4]^{2-}$ (Ref. 1 and references therein). Considerable variation has, however, been observed in the

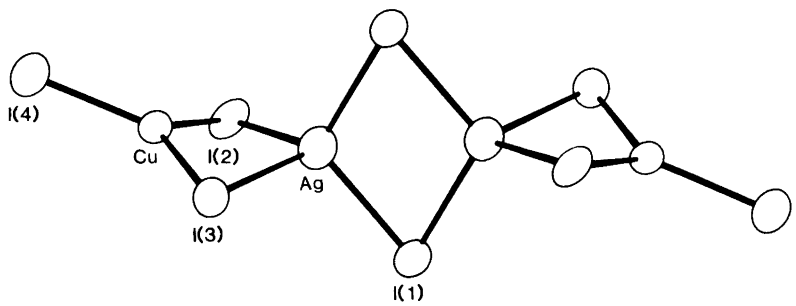

Fig. 1. The $[Ag_2Cu_2I_8]^{4-}$ ion in $[P(C_6H_5)_4]_4[Ag_2Cu_2I_8]$, showing the crystallographic numbering. $[Ag_3CuI_8]^{4-}$ is essentially similar, Cu being replaced by AgCu. The thermal ellipsoids enclose 50 % probability (Ref. 24).

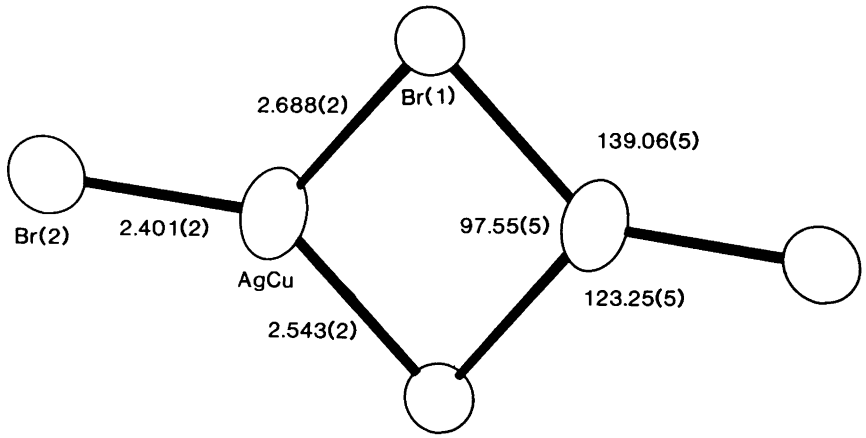

Fig. 2. The $[AgCuBr_4]^{2-}$ ion in $[P(C_6H_5)_4]_2[AgCuBr_4]$, showing the crystallographic numbering. Distances are in Å and angles in °; estimated standard deviations are given in parentheses. The thermal ellipsoids enclose 50 % probability (Ref. 24).

geometry of the $[Cu_2Br_4]^{2-}$ anion, particularly with respect to the four-membered $(Cu–Br)_2$ ring and the Cu···Cu separation. In the present compound, the metal–metal separation is 3.449(2) Å, slightly shorter than that in $[P(C_6H_5)_4]_2[Ag_2Br_4]$, 3.578(2) Å.[8] In $[Cu_2Br_4]^{2-}$ ions, the Cu···Cu separation has been found to vary between 2.660(3) and 2.937(3) Å (Ref. 1 and references therein).

The present investigation has thus demonstrated that it is possible to prepare crystalline heteronuclear (Cu/Ag) halometallates(I) in a similar way to the corresponding homonuclear haloargentates(I) or halocuprates(I). This, in itself, would appear to provide support for the hypothesis that the primary process occurring at the solution–crystal interface during formation of tetraalkylammonium and related crystalline halometallates(I) is cation–halide packing, the "naked" metal ion then diffusing into available interstices, with subsequent rearrangement resulting in the specific anion with the appropriate metal(I) coordination number. In $[Ag_2Cu_2I_8]^{4-}$, copper(I) is three-coordinated, which is the preferential coordination number adopted by copper(I) in crystalline iodocuprates(I) containing unipositive cations similar in size to tetraphenylphosphonium,[15,28,29] whereas silver(I) is four-coordinated. Apart from $[Ag_4I_8]^{4-}$, which contains two trigonal-planar and two tetrahedrally coordinated metal centres, $[Ag_3I_4]^-$ polymers in which silver(I) is solely tetrahedrally coordinated have been obtained with tetraphenylphosphonium,[9] tetraphenylarsonium[9] and tetrabutylammonium.[14] That copper(I) shows preference for the three-coordinated sites in $[Ag_2Cu_2I_8]^{4-}$ and $[Ag_3CuI_8]^{4-}$, whereas silver(I) shows preference for the four-coordinated site in $[Ag_2Cu_2I_8]^{4-}$ but occupies both types of site in $[Ag_3CuI_8]^{4-}$, also appears to be consistent with the tentative mechanism proposed. On the other hand, copper(I) exhibits trigonal-planar coordination geometry in $[AgCuBr_4]^{2-}$, despite the tendency to form digonal monomeric bromocuprate(I) ions with large unipositive cations, cf. tetraphenylphosphonium.[16] Although a three-coordinated $[Cu_4Br_6]^{2-}$ species has been isolated with the slightly smaller tetrapropylammonium cation,[3,4] even smaller cations are required for the isolation of dinuclear $[Cu_2Br_4]^{2-}$ anions.[1,17] Silver(I) may thus perhaps play a more important role than copper(I) in determining the detailed coordination environment of the resulting heteronuclear complex.

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