Preparation and Characterisation of Tetraphenylphosphonium and Tetraphenylarsonium Halogenoargentates(I), including a New Iodoargentate(I) Cluster, $[Ag_4I_8]^{4-}$, containing Three- and Four-co-ordinated Silver(I)†

Göran Helgesson and Susan Jagner*
Department of Inorganic Chemistry, Chalmers University of Technology, S-412 96 Göteborg, Sweden

---

A new iodoargentate(I) cluster $[Ag_4I_8]^{4-}$, containing three- and four-co-ordinated silver(I) has been isolated with the tetraphenylphosphonium and tetraphenylarsonium cations and characterised by means of crystal structure determination. Tetrakis(tetraphenylphosphonium) and tetrakis(tetraphenylarsonium) hexa-μ-iodo-di-iodotetra-argentate(I) [(**1**) and (**2**)] are isostructural and crystallise in the triclinic space group $P\bar{1}$, with $a = 13.453(7)$, $b = 16.607(9)$, $c = 11.068(7)$ Å, $\alpha = 102.83(4)$, $\beta = 103.94(4)$, $\gamma = 82.96(4)°$, $Z = 1$, and $a = 13.446(3)$, $b = 16.712(3)$, $c = 11.293(4)$ Å, $\alpha = 103.36(2)$, $\beta = 103.84(2)$, $\gamma = 83.43(2)°$, $Z = 1$, respectively. The initial phases crystallising from solution during formation of $[PPh_4]_4[Ag_4I_8]$ and $[AsPh_4]_4[Ag_4I_8]$ are $[PPh_4][Ag_3I_4]$ (**3**) and $[AsPh_4][Ag_3I_4]$ (**4**), respectively. The latter compounds are also isostructural with one another and crystallise in the monoclinic space group $P2_1/c$ with $Z = 4$ and $a = 13.380(5)$, $b = 26.536(5)$, $c = 8.504(4)$ Å, $\beta = 108.09(4)°$ for (**3**), and $a = 13.448(7)$, $b = 26.723(4)$, $c = 8.546(4)$, $\beta = 107.99(4)°$ for (**4**). With tetraphenylarsonium as cation, discrete chloroargentate(I) and bromoargentate(I) anions, $[Ag_2X_4]^{2-}$, X = Cl (**5**) or Br (**6**), containing distorted trigonal-planar co-ordinated silver(I), have been obtained. Bis(tetraphenylarsonium) di-μ-chloro-dichlorodiargentate(I) (**5**) and bis(tetraphenylarsonium) di-μ-bromo-dibromodiargentate(I) (**6**) both crystallise in the monoclinic space group $P2_1/n$ with $Z = 2$ and $a = 14.280(6)$, $b = 8.200(4)$, $c = 19.118(8)$ Å, $\beta = 101.19(3)°$. and $a = 14.546(4)$, $b = 8.072(2)$, $c = 19.854(5)$ Å, $\beta = 102.73(2)°$, respectively. The tetranuclear $[Ag_4I_8]^{4-}$ anion is centrosymmetric and can be described in terms of two edge-sharing silver(I)–iodide tetrahedra, each linked *via* a common edge to an approximately planar silver(I)–iodide triangle. In the latter the silver(I) atom is displaced 0.054(1) (**1**) and 0.026(1) Å (**2**) from the plane through the three iodide ligands. The Ag–I distances associated with the three-co-ordinated centre are 2.727(2), 2.763(2), and 2.765(2) Å (**1**), and 2.721(1), 2.757(1), and 2.766(1) Å (**2**), while those involving the four-co-ordinated centre range from 2.842(2) to 2.991(2) (**1**) and 2.846(1) to 2.973(1) Å (**2**). The Ag ··· Ag separations are 3.171(2) and 3.256(2), and 3.198(1) and 3.306(2) Å in (**1**) and (**2**), respectively. The $[Ag_3I_4]^-$ polymers in $[PPh_4][Ag_3I_4]$ (**3**) and $[PPh_4][Ag_3I_4]$ (**4**) consist of triple chains of edge-sharing Ag–I tetrahedra, Ag–I distances ranging from 2.796(2)—2.972(3) (**3**) and 2.798(4)—2.966(4) Å (**4**). The anions in $[AsPh_4]_2[Ag_2Cl_4]$ and $[AsPh_4]_2[Ag_2Br_4]$ are centrosymmetric, approximately planar entities in which silver(I) is displaced 0.004(1) (**5**) and 0.048(1) Å (**6**) from the ligand plane, and the Ag ··· Ag separations are 3.659(2) (**5**) and 3.549(2) Å (**6**). In $[Ag_2Cl_4]^{2-}$, the bridging Ag–Cl distances differ considerably from one another, *i.e.* 2.446(2) and 2.809(2) Å, the terminal Ag–Cl bond being 2.359(2) Å. In $[Ag_2Br_4]^{2-}$, there is less discrepancy between bridging distances: 2.614(1) and 2.741(1) Å; Ag–Br(terminal) is 2.481(1) Å.

In halogenocuprates(I) crystallising with symmetrically substituted tetra-alkylammonium and analogous cations, the co-ordination 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.[1] This has been interpreted as suggesting that cation–halide packing is of importance for the attainment of a particular copper(I) co-ordination number and thus for the resulting anionic configuration in the crystal.[1]

Although the structures of a few salts of symmetrically substituted quaternary ammonium, phosphonium, or arsonium cations with halogenoargentates(I) are known, as yet, structural information appears insufficient to ascertain whether or not the co-ordination number of silver(I) shows a similar dependence on cation size as that of copper(I) in analogous compounds. Those halogenoargentates(I) containing the smaller tetra-alkylammonium cations, *e.g.* tetramethylammonium or tetraethylammonium, characterised hitherto by means of spectroscopic and crystallographic studies, contain polymeric anions of stoicheiometry $[AgX_2]^-$ (X = Cl, Br, or I),[2] $[Ag_2X_3]^-$ (X = Br or I),[2a,3] and $[Ag_{13}X_{15}]^{2-}$ (X = I),[4] all composed of silver(I)–halide tetrahedra. Spectroscopic studies also indicate the presence of polymeric species containing four-co-ordinated silver(I) in $[PEt_4][Ag_2X_3]$ (X = Cl, Br, or I) and in $[PMe_4][AgBr_2]$.[2a] Tetrabutylammonium tetraiodotriargentate(I) contains a polymeric chain in which silver(I) exhibits slightly distorted tetrahedral co-ordination geometry,[5] whereas discrete, dinuclear $[Ag_2X_4]^{2-}$ species (X = Cl or Br), in which silver(I) exhibits distorted trigonal-planar co-ordination geometry have been isolated with the tetraphenylphosphonium cation.[6] The

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

only discrete, mononuclear trigonal iodoargentate(I) anion documented hitherto is that in $[PMePh_3]_2[AgI_3]$ which is similar to $[CuI_3]^{2-}$ in the corresponding iodocuprate(I).[7] We now report the preparation and crystallographic determination of two compounds containing a tetranuclear $[Ag_4I_8]^{4-}$ cluster, composed of three- and four-co-ordinated silver(I), of two compounds containing polymeric $[Ag_3I_4]^-$ anions, and of two further examples of dinuclear trigonal $[Ag_2X_4]^{2-}$ (X = Cl or Br) species. A discrete $[Ag_4I_8]^{4-}$ anion, containing four-co-ordinated silver(I) has been reported previously;[8] and the copper(I) analogue of the $[Ag_4I_8]^{4-}$ reported here, *i.e.* $[Cu_4I_8]^{4-}$, has recently been prepared and characterised.[9] We believe, however, this to be the first example of an $[Ag_4I_8]^{4-}$ ion, containing trigonal-planar and tetrahedrally co-ordinated silver(I). Similarly, the $[Ag_3I_4]^-$ anion does not seem to have been documented previously as a triple chain of edge-sharing Ag–I tetrahedra, although the copper(I) counterpart is known.[10]

Experimental

Preparation of Compounds.—$[PPh_4]_4[Ag_4I_8]$ (**1**). This compound was prepared by refluxing silver iodide (0.10 g, 0.43 mmol) (ICN Biomedicals, K & K) and tetraphenylphosphonium iodide (0.20 g, 0.43 mmol) (Fluka) in acetonitrile (20 cm^3) for approximately 1 h, fine, colourless needles of $[PPh_4][Ag_3I_4]$, m.p. 216.4—217.3 °C (see below), being deposited, together with a small amount of an unidentified phase with m.p. *ca.* 224 °C. The mixture was cooled slowly to room temperature and the solvent allowed to evaporate gradually under nitrogen, the unidentified phase dissolving and the needles being replaced after a few days by colourless irregular-shaped prisms of $[PPh_4]_4[Ag_4I_8]$, m.p. 234.5—235.4 °C.

$[AsPh_4]_4[Ag_4I_8]$ (**2**). This salt, m.p. 228.9—231.0 °C, was prepared in a completely analogous manner from silver iodide (0.10 g, 0.43 mmol), tetraphenylarsonium iodide (0.22 g, 0.43 mmol) (Fluka) and acetonitrile (20 cm^3), microcrystalline $[AsPh_4][Ag_3I_4]$, m.p. 214.2—215.2 °C (see below), gradually undergoing a phase transition to form $[AsPh_4]_4[Ag_4I_8]$.

$[PPh_4][Ag_3I_4]$ (**3**). This compound was prepared by dissolving tetraphenylphosphonium iodide (0.15 g, 0.43 mmol) in a few cm^3 of water. Dimethylformamide (10 cm^3) was added to the solution with stirring, followed by silver iodide (0.10 g, 0.43 mmol). The mixture was heated under reflux for 1 h, after which all the silver(I) iodide had dissolved. Colourless, elongated rectangular prisms of $[PPh_4][Ag_3I_4]$, m.p. 216.4—217.3 °C, were deposited from the solution on slow cooling to room temperature.

$[AsPh_4][Ag_3I_4]$ (**4**). This salt, m.p. 214.2—215.2 °C, was prepared in an analogous manner from silver(I) iodide (0.10 g, 0.43 mmol), tetraphenylarsonium iodide (0.22 g, 0.43 mmol), and dimethylformamide (10 cm^3).

$[AsPh_4]_2[Ag_2Cl_4]$ (**5**). This compound was prepared by dissolving silver(I) chloride (0.12 g, 0.84 mmol) (ICN Biomedicals, K & K) and tetraphenylarsonium chloride (0.35 g, 0.84 mmol) (Fluka) in acetonitrile (15 cm^3), filtering, and then evaporating the solution to dryness. Colourless, elongated prisms of $[AsPh_4]_2[Ag_2Cl_4]$, m.p. 188.2—190.2 °C, were obtained on recrystallization of the resulting white powder from acetonitrile ($\approx$5 cm^3). We were not successful in obtaining the compound $[AsPh_4]_3[Ag_2Cl_5]$, m.p. 172—174 °C, reported by Bowmaker *et al.*[7a]

$[AsPh_4]_2[Ag_2Br_4]$ (**6**). This salt, m.p. 207.1—210.7 °C, was prepared in an analogous manner from silver(I) bromide (0.10 g, 0.53 mmol) (ICN Biomedicals, K & K) and tetraphenylarsonium bromide (0.25 g, 0.53 mmol) (Fluka) in acetonitrile (15 cm^3).

Crystallography.—Crystal data. (**1**) $C_{96}H_{80}Ag_4I_8P_4$, M = 2 804.3, triclinic, a = 13.453(7), b = 16.607(9), c = 11.068(7) Å, α = 102.83(4), β = 103.94(4), γ = 82.96(4)°, U = 2 334(2) Å^3 (by least-squares refinement on diffractometer setting angles for 15 automatically centred reflections, λ = 0.710 69 Å), space group $P\bar{1}$, Z = 1, D_c = 2.00 g cm^{-3}. Colourless, irregular-shaped prisms. Approximate crystal dimensions: 0.15 × 0.09 × 0.12 mm, μ(Mo-K_α) = 3.60 mm^{-1}.

(**2**). $C_{96}H_{80}Ag_4As_4I_8$, M = 2 980.0, triclinic, a = 13.446(3), b = 16.712(3), c = 11.293(4) Å, α = 103.36(2), β = 103.84(2), γ = 83.43(2)°, U = 2 393(1) Å^3 (by least-squares refinement on diffractometer setting angles for 25 automatically centred reflections in the range $25 < 2\theta < 50°$, λ = 0.710 69 Å), space group $P\bar{1}$, Z = 1, D_c = 2.07 g cm^{-3}. Colourless, irregular-shaped prisms. Crystal dimensions (distance to faces from vertex chosen as origin for absorption correction): 0.000, ($\bar{1}0\bar{1}$, $\bar{1}01$, $0\bar{1}0$), 0.345 ($10\bar{1}$), 0.442 (101), 0.402 (010) mm, μ(Mo-K_α) = 4.77 mm^{-1}.

(**3**). $C_{24}H_{20}Ag_3I_4P$, M = 1 170.6, monoclinic, a = 13.380(5), b = 26.536(5), c = 8.504(4) Å, β = 108.09(4)°, U = 2 870(4) Å^3 (by least-squares refinement on diffractometer setting angles for 25 automatically centred reflections in the range $25 < 2\theta < 50°$, λ = 0.710 69 Å), space group $P2_1/c$, Z = 4, D_c = 2.71 g cm^{-3}. Colourless, elongated, rectangular prisms. Crystal dimensions (distance to faces from vertex chosen as origin for absorption correction): 0.000 (110, $1\bar{1}0$, 001), 0.195 ($00\bar{1}$), 0.088 ($\bar{1}\bar{1}0$), 0.071 ($\bar{1}10$) mm, μ(Mo-K_α) = 6.36 mm^{-1}.

(**4**). $C_{24}H_{20}Ag_3AsI_4$, M = 1 214.6, monoclinic, a = 13.448(7), b = 26.723(4), c = 8.546(4) Å, β = 107.99(4)°, U = 2 921(4) Å^3 (by least-squares refinement on diffractometer setting angles for 20 automatically centred reflections, λ = 0.710 69 Å), space group $P2_1/c$, Z = 4, D_c = 2.76 g cm^{-3}. Colourless, elongated, rectangular prisms. Crystal dimensions (distances to faces from origin at crystal centroid): 0.079 (001, $00\bar{1}$), 0.115 (010, $0\bar{1}0$), 0.071 (110, $\bar{1}\bar{1}0$), 0.084 ($1\bar{1}0$, $\bar{1}10$) mm, μ(Mo-K_α) = 7.29 mm^{-1}.

(**5**). $C_{48}H_{40}Ag_2As_2Cl_4$. M = 1 124.2, monoclinic, a = 14.280(6), b = 8.200(4), c = 19.118(8) Å, β = 101.19(3)°, U = 2 196(2) Å^3 (by least-squares refinement on diffractometer setting angles for 15 automatically centred reflections, λ = 0.710 69 Å), space group $P2_1/n$ (alt. $P2_1/c$, no. 14), Z = 2, D_c = 1.70 g cm^{-3}. Colourless elongated prisms. Crystal dimensions (distance to faces from vertex chosen as origin for absorption correction): 0.000 ($\bar{1}0\bar{1}$, 010, $00\bar{1}$), 0.150 (101), 0.181 (001), 0.265 ($0\bar{1}0$), 0.077 ($10\bar{1}$), 0.108 ($\bar{1}01$) mm, μ(Mo-K_α) = 2.65 mm^{-1}.

(**6**). $C_{48}H_{40}Ag_2As_2Br_4$, M = 1 302.1, monoclinic, a = 14.546(4), b = 8.072(2), c = 19.854(5) Å, β = 102.73(2)°, U = 2 274(2) Å^3 (by least-squares refinement on diffractometer setting angles for 15 automatically centred reflections, λ = 0.710 69 Å), space group $P2_1/n$ (alt. $P2_1/c$, no. 14), Z = 2, D_c = 1.70 g cm^{-3}. Colourless, elongated prisms. Crystal dimensions (distance to faces from origin at crystal centroid): 0.150 (100, $\bar{1}00$), 0.146 (010, $0\bar{1}0$), 0.137 (001, $00\bar{1}$), 0.141 ($10\bar{1}$, $\bar{1}01$) mm, μ(Mo-K_α) = 5.81 mm^{-1}.

Data collection and processing. (**1**). Syntex $P2_1$ diffractometer, approx. 290 K, ω—2θ scan mode, variable 2θ scan rate 2.5—29.3° min^{-1}, Mo-K_α radiation; 8 255 unique reflections ($3.5 < 2\theta < 50°$); 96-step profile recorded for each reflection; intensities calculated using the Lehmann and Larsen profile-analysis method;[11] no absorption correction owing to difficulties in measuring and indexing the large number of crystal faces; 6 096 reflections with $I > 3\sigma(I)$.

(**2**). Rigaku AFC6R diffractometer, approx. 290 K, ω—2θ scan mode with an ω scan rate of 32° min^{-1} and a scan width of $(1.42 + 0.30\tan\theta)°$, graphite-monochromated Mo-K_α radiation from a RU200 rotating anode operated at 9 kW (50 kV; 180 mA); weak reflections $[F < 10\sigma(F)]$ were rescanned up to three times and counts accumulated to improve counting statistics. Stationary background counts were recorded on each side of the

Table 1. Fractional atomic co-ordinates for the non-hydrogen atoms in $[PPh_4]_4[Ag_4I_8]$ (**1**)

Atom	*x*	*y*	*z*
Ag(1)	0.057 39(5)	−0.059 36(4)	−0.104 84(6)
Ag(2)	0.157 08(5)	−0.206 73(3)	−0.284 29(6)
I(1)	0.039 59(8)	0.116 80(3)	−0.058 33(4)
I(2)	0.280 29(4)	−0.115 60(3)	−0.074 05(5)
I(3)	−0.031 32(4)	−0.127 04(3)	−0.368 83(5)
I(4)	0.220 19(4)	−0.358 30(3)	−0.407 95(5)
P(1)	0.513 9(1)	0.815 4(1)	0.431 5(1)
C(10)	0.575 3(5)	0.844 2(4)	0.595 9(6)
C(11)	0.529 8(5)	0.904 5(4)	0.678 7(6)
C(12)	0.584 4(6)	0.931 0(4)	0.802 9(7)
C(13)	0.682 1(6)	0.897 2(4)	0.843 7(6)
C(14)	0.727 5(5)	0.836 3(5)	0.763 3(6)
C(15)	0.674 1(5)	0.810 2(5)	0.638 5(6)
C(20)	0.380 9(5)	0.854 0(4)	0.407 0(6)
C(21)	0.319 2(5)	0.835 4(4)	0.480 1(7)
C(22)	0.216 5(5)	0.864 1(5)	0.458 4(7)
C(23)	0.178 1(5)	0.912 0(4)	0.369 9(7)
C(24)	0.238 0(6)	0.930 8(4)	0.298 5(7)
C(25)	0.341 3(5)	0.902 2(4)	0.316 0(6)
C(30)	0.581 0(5)	0.855 9(4)	0.339 5(5)
C(31)	0.552 4(6)	0.833 5(5)	0.206 1(7)
C(32)	0.603 4(7)	0.863 8(5)	0.135 3(7)
C(33)	0.684 3(7)	0.914 2(5)	0.193 4(8)
C(34)	0.713 9(6)	0.936 5(5)	0.324 4(8)
C(35)	0.660 9(6)	0.906 9(4)	0.397 8(7)
C(40)	0.526 4(5)	0.704 3(4)	0.386 1(6)
C(41)	0.451 6(6)	0.656 5(5)	0.394 1(10)
C(42)	0.466 7(8)	0.571 4(5)	0.369 1(10)
C(43)	0.555 1(7)	0.532 1(5)	0.337 9(9)
C(44)	0.630 0(7)	0.579 8(5)	0.328 4(7)
C(45)	0.615 7(6)	0.666 0(4)	0.352 4(7)
P(2)	0.213 0(1)	0.436 3(1)	0.056 4(1)
C(50)	0.150 1(5)	0.408 1(4)	0.164 7(6)
C(51)	0.070 7(5)	0.356 5(4)	0.119 5(6)
C(52)	0.025 0(5)	0.333 0(5)	0.204 4(8)
C(53)	0.059 0(6)	0.359 6(5)	0.331 6(7)
C(54)	0.141 0(6)	0.410 0(5)	0.380 8(7)
C(55)	0.186 9(6)	0.434 5(5)	0.294 0(7)
C(60)	0.153 4(5)	0.390 6(4)	−0.103 9(6)
C(61)	0.173 0(6)	0.306 3(4)	−0.144 5(6)
C(62)	0.122 9(6)	0.268 1(5)	−0.266 7(7)
C(63)	0.059 1(6)	0.313 7(5)	−0.346 0(7)
C(64)	0.041 3(7)	0.398 7(5)	−0.305 7(7)
C(65)	0.087 1(6)	0.436 4(4)	−0.184 9(7)
C(70)	0.344 2(5)	0.394 1(4)	0.085 6(6)
C(71)	0.377 9(6)	0.339 8(5)	0.167 7(8)
C(72)	0.476 8(7)	0.303 6(5)	0.178 5(9)
C(73)	0.541 7(5)	0.320 1(5)	0.110 8(9)
C(74)	0.506 1(6)	0.371 4(5)	0.026 2(8)
C(75)	0.408 8(5)	0.409 8(5)	0.015 2(8)
C(80)	0.206 3(5)	0.547 2(4)	0.074 8(6)
C(81)	0.172 9(6)	0.597 9(4)	0.174 5(7)
C(82)	0.167 8(7)	0.684 5(4)	0.186 7(8)
C(83)	0.196 0(6)	0.717 9(4)	0.099 9(9)
C(84)	0.226 0(6)	0.666 2(5)	−0.004 2(8)
C(85)	0.231 5(5)	0.581 3(4)	−0.016 4(7)

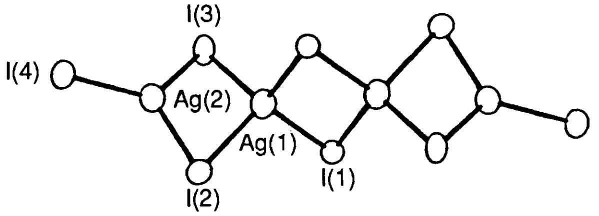

Figure 1. The $[Ag_4I_8]^{4-}$ ion in $[AsPh_4]_4[Ag_4I_8]$ (**2**). The anion in $[PPh_4]_4[Ag_4I_8]$ (**1**) is essentially similar. The $[Ag_4I_8]^{4-}$ ion is centrosymmetric; the thermal ellipsoids enclose 50% probability

reflection; ratio of peak counting time *vs.* background counting time 2:1; 8 824 unique reflections ($3.5 < 2\theta < 50°$); analytical absorption correction;[12] 5 814 reflections with $I > 3\sigma(I)$.

(**3**). Rotation and Weissenberg photographs indicated an orthorhombic cell with $a \approx 8.49$, $b \approx 25.39$, $c \approx 26.49$ Å, space group *Cmca*, three reflections $h0l$, $l = 2n + 1$, being observed. From a preliminary data set measured with a Syntex $P2_1$ diffractometer, it was possible to locate the atoms of the anion, with the phosphorus atom disordered in site 16g; it was not, however, possible to locate more than a few carbon atoms unambiguously as half-atoms. Closer inspection of reflection profiles from a large number of crystals established the presence of twinning, the true Laue symmetry being $2/m$ (transformation matrix from metric orthorhombic to monoclinic cell (true space group $P2_1/c$): −0.5, 0.5, 0/0, 0, 1/1, 0, 0). Data were collected for a crystal exhibiting a minimum amount of twinning on a Rigaku AFC6R diffractometer [*cf.* compound (**2**)] approx. 290 K; ω—2θ scan mode with an ω scan rate of 8° min^{-1} and a scan width of $(1.20 + 0.30\tan\theta)°$, 5 177 unique reflections ($3.5 < 2\theta < 50°$); analytical absorption correction[12] (max., min. transmission factors = 0.710, 0.451); 2 690 reflections with $I > 3\sigma(I)$.

(**4**). Twinning analogous to that for compound (**3**) exhibited; intensity data collection as for (**3**); approx. 290 K; ω—2θ scan mode with an ω scan rate of 16° min^{-1} and a scan width of $(1.09 + 0.30\tan\theta)°$, 5 246 unique reflections ($3.5 < 2\theta < 50°$); analytical absorption correction[12] (max., min. transmission factors = 0.475, 0.304); 2 684 reflections with $I > 3\sigma(I)$.

(**5**). Syntex $P2_1$ diffractometer; *cf.* compound (**1**) variable 2θ scan rate 2.0—15.0° min^{-1}, 3 899 unique reflections ($3.5 < 2\theta < 50°$); absorption correction[13] (max., min. transmission factors = 0.708, 0.625); 2 728 reflections with $I > 3\sigma(I)$.

(**6**). Syntex $P2_1$ diffractometer; variable 2θ scan rate 2.0—15.0° min^{-1}, 4 026 unique reflections ($3.5 < 2\theta < 50°$); absorption correction[13] (max., min. transmission factors = 0.301, 0.227); 2 581 reflections with $I > 3\sigma(I)$.

Structure analysis and refinement. (**1**). The structure was solved from Patterson and subsequent electron density maps. 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) gave final $R = 0.046$, $R' = 0.060$ for 505 parameters and 6 096 reflections; maximum residual electron density = 0.94 e Å^{-3}. Weighting scheme: $w = [\sigma^2(F_o) + 0.0008F_o^2]^{-1}$. Atomic scattering factors and anomalous dispersion corrections from ref. 14; computer programs used described in ref. 15.

(**2**). The atomic co-ordinates of (**1**) were used as starting point for the refinement of (**2**). 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, $B = B_{eq}$ of the carrying carbon atom*) gave final $R = 0.041$, $R' = 0.056$ for 505 parameters and 5 814 reflections; maximum residual electron density = 0.69 e Å^{-3}. Weighting scheme: $w = [\sigma^2(F_o)]^{-1}$. For atomic scattering factors, anomalous dispersion corrections, and computer programs used, see ref. 16.

(**3**). The co-ordinates of the silver and iodine atoms determined in space group *Cmca* (MITHRIL),[17] see above,

---

* $B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

Table 2. Fractional atomic co-ordinates for the non-hydrogen atoms in $[AsPh_4]_4[Ag_4I_8]$ (**2**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ag(1)	0.059 95(7)	−0.059 23(5)	−0.103 62(8)	C(43)	0.557 0(11)	0.528 8(7)	0.334 8(14)
Ag(2)	0.161 81(6)	−0.204 64(5)	−0.284 26(8)	C(44)	0.632 6(10)	0.576 4(8)	0.326 7(11)
I(1)	0.039 74(4)	0.116 08(4)	−0.054 38(6)	C(45)	0.616 6(9)	0.661 6(7)	0.348 8(10)
I(2)	0.281 05(5)	−0.114 48(4)	−0.072 80(7)	As(2)	0.2096 9(6)	0.4357 2(5)	0.053 35(8)
I(3)	−0.026 56(5)	−0.125 95(4)	−0.364 09(6)	C(50)	0.146 4(6)	0.407 8(5)	0.171 6(8)
I(4)	0.223 88(5)	−0.354 62(4)	−0.408 53(7)	C(51)	0.066 5(6)	0.352 9(5)	0.125 9(8)
As(1)	0.514 36(6)	0.816 40(5)	0.430 19(8)	C(52)	0.024 1(8)	0.329 8(6)	0.212 8(10)
C(10)	0.578 5(6)	0.847 9(5)	0.602 3(7)	C(53)	0.060 1(9)	0.358 2(7)	0.337 5(10)
C(11)	0.530 6(7)	0.904 8(6)	0.683 6(8)	C(54)	0.138 4(9)	0.412 0(7)	0.380 1(8)
C(12)	0.582 5(8)	0.929 2(6)	0.807 9(9)	C(55)	0.182 2(8)	0.435 8(6)	0.296 0(9)
C(13)	0.680 1(8)	0.899 0(6)	0.846 5(8)	C(60)	0.144 5(6)	0.384 9(5)	−0.114 9(8)
C(14)	0.727 4(7)	0.840 3(6)	0.763 3(8)	C(61)	0.160 1(8)	0.301 5(6)	−0.154 3(9)
C(15)	0.677 0(7)	0.815 3(6)	0.642 7(8)	C(62)	0.112 4(9)	0.265 0(6)	−0.270 0(10)
C(20)	0.374 4(6)	0.857 0(5)	0.403 3(8)	C(63)	0.050 0(9)	0.309 5(6)	−0.350 2(9)
C(21)	0.310 0(7)	0.839 2(6)	0.473 5(9)	C(64)	0.037 1(9)	0.394 2(7)	−0.309 3(10)
C(22)	0.208 7(7)	0.866 3(6)	0.453 1(10)	C(65)	0.082 7(7)	0.432 2(6)	−0.193 0(9)
C(23)	0.171 9(7)	0.914 3(6)	0.366 0(10)	C(70)	0.348 2(6)	0.389 3(5)	0.079 8(8)
C(24)	0.233 2(7)	0.932 6(6)	0.296 5(9)	C(71)	0.380 2(8)	0.337 9(6)	0.161 2(12)
C(25)	0.335 6(7)	0.904 6(6)	0.314 7(8)	C(72)	0.479 5(9)	0.300 7(7)	0.172 7(13)
C(30)	0.588 2(6)	0.859 7(5)	0.336 7(8)	C(73)	0.543 0(8)	0.317 1(8)	0.103 4(13)
C(31)	0.558 8(8)	0.837 0(6)	0.204 9(9)	C(74)	0.509 0(8)	0.367 8(7)	0.021 2(12)
C(32)	0.612 3(9)	0.867 9(7)	0.137 0(10)	C(75)	0.412 5(7)	0.405 2(7)	0.011 1(10)
C(33)	0.694 3(9)	0.915 7(7)	0.196 5(11)	C(80)	0.203 6(6)	0.551 2(5)	0.070 4(8)
C(34)	0.723 2(8)	0.937 3(6)	0.327 0(10)	C(81)	0.173 2(8)	0.604 1(5)	0.171 2(9)
C(35)	0.669 1(7)	0.908 4(6)	0.394 7(9)	C(82)	0.168 0(9)	0.689 5(6)	0.183 1(11)
C(40)	0.527 6(7)	0.698 9(5)	0.381 7(8)	C(83)	0.192 4(8)	0.721 0(5)	0.094 1(13)
C(41)	0.452 2(8)	0.650 8(7)	0.390 1(14)	C(84)	0.220 8(8)	0.670 3(7)	−0.008 8(13)
C(42)	0.469 8(11)	0.564 9(7)	0.365 1(18)	C(85)	0.226 9(7)	0.585 6(6)	−0.021 7(10)

were transformed to space group $P2_1/c$ and the remaining non-hydrogen atoms were located from a subsequent difference map. 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, $B = B_{eq}$ of the carrying carbon atom) gave final $R = 0.050$, $R' = 0.057$ for 289 parameters and 2 690 reflections; maximum residual electron density = 1.1 e Å^{-3}. Weighting scheme: $w = [\sigma^2(F_o)]^{-1}$. For atomic scattering factors, anomalous dispersion corrections and computer programs used, see ref. 16.

(**4**). The co-ordinates of (**3**) were used as starting point for the refinement of (**4**), which was carried out in a completely analogous manner, yielding a final $R = 0.080$, $R' = 0.11$ for 289 parameters and 2 684 reflections. The maximum residual electron density was 4.1 e Å^{-3}, located at the phosphorus site corresponding to the twinned form. Despite many attempts, we were not successful in finding a better quality crystal of (**4**).

(**5**). The Patterson function and a subsequent electron density calculation confirmed that (**5**) is isostructural with $[PPh_4]_2[Ag_2Cl_4]$,[6] the atomic co-ordinates of the latter compound being used as starting point for the refinement. Full-matrix least-squares refinement, including anisotropic thermal parameters for all non-hydrogen atoms, and with isotropic thermal parameters for H set equal to B_{eq} of the carrying carbon atom and not refined gave a final $R = 0.042$, $R' = 0.048$ for 313 parameters and 2 728 reflections; weighting scheme: $w = [\sigma^2(F_o) + 0.001F_o^2]^{-1}$; maximum residual electron density = 0.97 e Å^{-3}. Atomic scattering factors and anomalous dispersion correction from ref. 14; computer programs used described in ref. 15.

(**6**). Refinement as for (**5**) yielded a final $R = 0.040$, $R' = 0.043$ for 313 parameters and 2 581 reflections; weighting scheme: $w = [\sigma^2(F_o) + 0.0005F_o^2]^{-1}$; maximum residual electron density = 0.65 e Å^{-3}. Atomic scattering factors and anomalous dispersion corrections from ref. 14; computer programs used described in ref. 15.

The figures were drawn using ORTEP.[18] Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and bond distances and angles within the cations.

Results and Discussion

Fractional co-ordinates for the six compounds are given in Tables 1—6. The $[Ag_4I_8]^{4-}$ cluster determined in compounds (**1**) and (**2**) (Figure 1, Table 7) is comprised of two three-co-ordinated and two four-co-ordinated silver(I) centres and is very similar to the $[Cu_4I_8]^{4-}$ anion isolated with cobaltocenium as cation.[9] As is apparent from Table 7, there is considerable difference between the silver(I)–iodide distances associated with the trigonal-planar and tetrahedrally co-ordinated silver(I) atoms, the former being similar to the Ag–I distances determined in the mononuclear $[AgI_3]^{2-}$ ion, *viz.* 2.742(1), 2.746(1), and 2.755(1) Å.[7b] It is notable that the non-bridged Ag–I bond associated with the trigonal centre in both $[Ag_4I_8]^{4-}$ ions (Table 7) is appreciably shorter than the Ag–I bonds in $[AgI_3]^{2-}$. The Ag ··· Ag separations in $[Ag_4I_8]^{4-}$ are relatively short, *i.e.* of the same order or slightly shorter than those in *e.g.* $[NMe_4][AgI_2]$, *viz.* 3.265 and 3.634 Å.[2b] The $[Ag_4I_8]^{4-}$ ion determined previously[8] has a completely different structure from the anion in (**1**) and (**2**) and is composed of edge-sharing Ag–I tetrahedra yielding a planar rhombic core of silver(I) atoms in which the rhomb edges are 3.125(4) and 3.283(4) Å, one of the diagonal Ag ··· Ag distances being marginally shorter, *i.e.* 2.967(4) Å.[8]

The $[Ag_3I_4]^-$ ion in compounds (**3**) and (**4**) is depicted in Figure 2 and interatomic distances and angles are given in Table 8. The anion is a triple chain of Ag–I tetrahedra in which the outer tetrahedra share three edges and the inner four. It thus differs from that determined in $[NBu_4][Ag_3I_4]$[5] but is analogous to the anion in $[PMePh_3][Cu_3I_4]$.[10] Again, the Ag ··· Ag separations are relatively short (Table 8). That (**3**) and (**4**) both readily form twinned structures can be attributed

Table 3. Fractional atomic co-ordinates for the non-hydrogen atoms in $[PPh_4][Ag_3I_4]$ (**3**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ag(1)	0.701 1(1)	0.165 70(7)	0.155 5(2)	C(22)	0.425 7(14)	0.136 6(7)	0.713 1(24)
Ag(2)	0.717 8(2)	0.233 90(7)	−0.138 1(3)	C(23)	0.365 0(19)	0.147 6(8)	0.809 4(26)
Ag(3)	0.705 4(1)	0.161 46(7)	0.552 8(2)	C(24)	0.259 8(17)	0.140 5(7)	0.754 7(25)
I(1)	0.600 9(1)	0.095 00(5)	0.300 0(2)	C(25)	0.211 2(14)	0.123 3(6)	0.601 8(25)
I(2)	0.881 4(1)	0.195 39(5)	0.445 6(2)	C(30)	0.180 4(17)	0.143 0(7)	0.161 2(23)
I(3)	0.776 8(1)	0.131 43(5)	−0.108 6(2)	C(31)	0.258 9(16)	0.180 1(7)	0.186 2(28)
I(4)	0.562 1(1)	0.252 29(5)	0.034 8(2)	C(32)	0.238 8(20)	0.223 4(7)	0.092 6(30)
P	0.208 0(4)	0.088 9(2)	0.290 3(6)	C(33)	0.142 3(24)	0.231 3(9)	−0.029 2(32)
C(10)	0.295 1(14)	0.047 5(7)	0.230 1(23)	C(34)	0.065 1(18)	0.194 0(9)	−0.050 5(28)
C(11)	0.353 6(16)	0.011 4(7)	0.335 6(24)	C(35)	0.084 7(15)	0.149 9(8)	0.041 3(26)
C(12)	0.411 5(14)	−0.023 0(7)	0.277 4(27)	C(40)	0.091 4(14)	0.053 5(6)	0.279 2(21)
C(13)	0.413 5(15)	−0.021 9(7)	0.123 1(27)	C(41)	0.002 6(15)	0.079 3(8)	0.293 7(24)
C(14)	0.354 0(15)	0.012 5(8)	0.013 1(26)	C(42)	−0.083 6(19)	0.049 4(11)	0.294 8(31)
C(15)	0.293 8(14)	0.048 7(7)	0.067 8(24)	C(43)	−0.083 9(18)	−0.001 0(11)	0.280 1(32)
C(20)	0.269 8(14)	0.110 0(7)	0.497 5(22)	C(44)	0.005 6(22)	−0.026 5(10)	0.268 0(33)
C(21)	0.376 6(17)	0.118 3(7)	0.550 6(24)	C(45)	0.089 8(17)	0.002 4(7)	0.263 8(26)

Table 4. Fractional atomic co-ordinates for the non-hydrogen atoms in $[AsPh_4][Ag_3I_4]$ (**4**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ag(1)	0.700 0(2)	0.165 27(11)	0.156 6(4)	C(22)	0.427 0(32)	0.139 4(14)	0.708 1(54)
Ag(2)	0.717 4(3)	0.234 45(11)	−0.136 3(4)	C(23)	0.363 8(35)	0.147 8(18)	0.809 3(44)
Ag(3)	0.703 6(2)	0.161 51(11)	0.553 7(4)	C(24)	0.262 5(35)	0.141 7(13)	0.762 6(52)
I(1)	0.598 3(2)	0.096 01(9)	0.301 5(3)	C(25)	0.214 2(25)	0.123 7(12)	0.608 3(41)
I(2)	0.878 8(2)	0.194 08(9)	0.445 4(3)	C(30)	0.174 5(29)	0.147 5(12)	0.142 4(44)
I(3)	0.775 8(2)	0.132 58(8)	−0.106 8(3)	C(31)	0.260 2(30)	0.182 9(14)	0.179 8(51)
I(4)	0.562 9(2)	0.251 97(8)	0.037 8(3)	C(32)	0.235 6(35)	0.226 6(10)	0.084 4(48)
As	0.206 9(3)	0.089 1(1)	0.287 6(4)	C(33)	0.141 9(37)	0.232 2(16)	−0.036 2(44)
C(10)	0.300 6(22)	0.044 8(11)	0.231 1(45)	C(34)	0.058 6(34)	0.197 5(14)	−0.057 1(68)
C(11)	0.356 8(29)	0.010 6(13)	0.332 8(37)	C(35)	0.086 4(29)	0.151 7(13)	0.048 7(46)
C(12)	0.418 1(27)	−0.023 9(14)	0.284 0(52)	C(40)	0.083 5(24)	0.052 6(10)	0.279 1(40)
C(13)	0.417 7(27)	−0.025 8(12)	0.125 6(47)	C(41)	−0.002 6(26)	0.079 0(13)	0.286 8(49)
C(14)	0.361 0(27)	0.008 6(14)	0.022 0(45)	C(42)	−0.094 3(31)	0.048 5(15)	0.291 0(48)
C(15)	0.297 7(27)	0.044 7(12)	0.060 6(43)	C(43)	−0.086 6(32)	−0.002 0(16)	0.284 5(56)
C(20)	0.272 8(27)	0.115 0(13)	0.503 2(43)	C(44)	−0.003 4(39)	−0.030 1(16)	0.261 9(58)
C(21)	0.381 6(29)	0.124 1(18)	0.557 5(46)	C(45)	0.088 6(29)	0.002 8(12)	0.277 0(53)

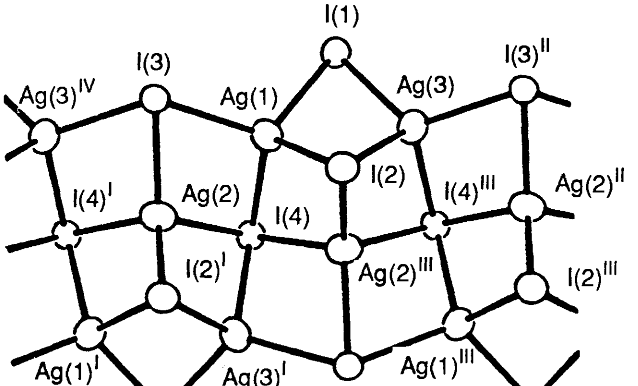

Figure 2. The $[Ag_3I_4]^-$ ion in $[PPh_4][Ag_3I_4]$ (**3**). The anion in $[AsPh_4][Ag_3I_4]$ (**4**) is essentially similar. The thermal ellipsoids enclose 50% probability. For symmetry codes see Table 8

to the relatively high symmetry of the anion *i.e.* pseudo-mirror planes perpendicular to *c* through Ag(2), I(1), I(2), and I(3) and through I(4), providing two equally favourable orientations of the cation.

The $[Ag_2Cl_4]^{2-}$ and $[Ag_2Br_4]^{2-}$ ions in compounds (**5**) and (**6**) are practically identical with those determined previously in the isostructural tetraphenylphosphonium salts.[6] Silver(I) exhibits distorted trigonal-planar co-ordination geometry, with the metal atom displaced 0.004(1) and 0.048(1) Å from the ligand plane in $[Ag_2Cl_4]^{2-}$ and $[Ag_2Br_4]^{2-}$ respectively. As in the tetraphenylphosphonium counterpart,[6] the bridging metal–chloride bonds in $[Ag_2Cl_4]^{2-}$ differ considerably from one another (*cf.* Figure 3) and marked deviation from trigonal co-ordination geometry is, moreover, evident from the bond angles. The $Ag \cdots Ag^{I}$ and $Cl \cdots Cl^{I}$ separations are 3.659(2) and 3.789(3) Å, respectively. The co-ordination geometry of silver(I) in $[Ag_2Br_4]^{2-}$ is more regular (Figure 3), and the $Ag \cdots Ag^{I}$ and $Br \cdots Br^{I}$ separations are 3.549(2) and 4.013(2) Å, respectively [symmetry code: I $1 - x, -y, -z$].

Severely distorted trigonal-planar co-ordination geometry for silver(I) has been observed, for example, in the $[Ag_2Cl_5]^{3-}$ anion in ammonium tris[tetrachloroaurate(III)] μ-chloro-bis[dichloroargentate(I)], in which the Cl–Ag–Cl angle involving terminal chlorines is 152.5° and the bridging Ag–Cl distance 2.69 Å, as opposed to the terminal distance of 2.46 Å.[19] A description in terms of 'chlorine bridged $AgCl_2^-$ ions' was suggested as being appropriate for this ion.[19] As mentioned previously,[6] a similar description could also be employed for the dinuclear $[Ag_2X_4]^{2-}$ ions, and in particular for $[Ag_2Cl_4]^{2-}$, *viz.* two bent $[AgCl_2]^-$ moieties joined *via* weak Ag–Cl interactions. Pseudo-three-co-ordinated silver (I), with one very large bond angle [160.3(1)°] has also been found in $[Ag\{P(C_6H_4\text{-Me-}p)_3\}\{BPh_2(pz)_2\}]$ (pz = pyrazolyl).[20]

The atom numbering system employed for the cations in the

Table 5. Fractional atomic co-ordinates for the non-hydrogen atoms in $[AsPh_4]_2[Ag_2Cl_4]$ (**5**)

Atom	*x*	*y*	*z*
Ag	0.386 56(4)	0.054 60(7)	0.024 80(3)
Cl(1)	0.582 1(1)	0.114 1(2)	0.073 6(1)
Cl(2)	0.275 6(1)	0.172 3(2)	0.086 6(1)
As	−0.032 24(3)	−0.107 76(6)	0.179 36(3)
C(10)	−0.136 7(3)	−0.256 7(6)	0.170 5(3)
C(11)	−0.150 2(4)	−0.343 2(7)	0.230 0(3)
C(12)	−0.216 8(4)	−0.464 5(8)	0.221 9(4)
C(13)	−0.271 0(5)	−0.500 4(9)	0.156 0(4)
C(14)	−0.259 0(4)	−0.410 6(8)	0.097 8(4)
C(15)	−0.190 3(4)	−0.289 4(7)	0.103 9(3)
C(20)	−0.012 6(3)	0.005 6(6)	0.268 1(3)
C(21)	0.026 2(4)	−0.078 0(7)	0.330 4(3)
C(22)	0.037 3(5)	0.003 2(9)	0.394 6(3)
C(23)	0.013 9(5)	0.166 2(9)	0.396 7(4)
C(24)	−0.023 0(5)	0.246 7(8)	0.335 2(4)
C(25)	−0.036 4(4)	0.169 1(7)	0.269 8(3)
C(30)	−0.058 3(4)	0.051 5(6)	0.105 3(3)
C(31)	0.014 8(4)	0.119 9(8)	0.077 4(3)
C(32)	−0.007 7(5)	0.245 6(8)	0.029 1(4)
C(33)	−0.099 0(6)	0.301 3(8)	0.008 7(3)
C(34)	−0.170 8(5)	0.232 7(8)	0.036 4(4)
C(35)	−0.151 9(4)	0.105 4(7)	0.085 5(3)
C(40)	0.078 3(4)	−0.235 9(7)	0.175 2(3)
C(41)	0.068 7(4)	−0.404 2(7)	0.168 9(3)
C(42)	0.148 9(6)	−0.497 1(9)	0.167 0(4)
C(43)	0.234 2(6)	−0.425 0(11)	0.169 1(4)
C(44)	0.244 9(4)	−0.259 5(11)	0.175 5(4)
C(45)	0.166 2(4)	−0.163 1(9)	0.179 8(3)

Table 6. Fractional atomic co-ordinates for the non-hydrogen atoms in $[AsPh_4]_2[Ag_2Br_4]$ (**6**)

Atom	*x*	*y*	*z*
Ag	0.397 74(5)	0.064 36(8)	0.027 79(4)
Br(1)	0.585 85(5)	0.132 14(10)	0.073 56(4)
Br(2)	0.273 53(5)	0.169 05(12)	0.084 73(5)
As	−0.034 52(4)	−0.096 96(8)	0.175 30(3)
C(10)	−0.139 0(4)	−0.244 3(7)	0.169 0(3)
C(11)	−0.150 5(5)	−0.321 0(9)	0.229 2(4)
C(12)	−0.221 8(6)	−0.440 2(10)	0.223 8(4)
C(13)	−0.277 9(6)	−0.476 9(10)	0.160 2(5)
C(14)	−0.265 7(5)	−0.395 5(11)	0.102 9(4)
C(15)	−0.195 9(5)	−0.277 4(10)	0.105 9(4)
C(20)	−0.010 3(4)	0.021 9(8)	0.260 1(3)
C(21)	0.031 6(5)	−0.059 0(8)	0.320 7(4)
C(22)	0.045 8(5)	0.026 4(10)	0.382 2(4)
C(23)	0.019 7(6)	0.188 4(12)	0.383 0(4)
C(24)	−0.020 3(7)	0.270 0(10)	0.323 4(5)
C(25)	−0.036 3(5)	0.187 8(9)	0.260 3(4)
C(30)	−0.061 4(4)	0.061 0(8)	0.102 6(3)
C(31)	0.010 9(5)	0.119 8(10)	0.073 4(4)
C(32)	−0.010 1(7)	0.248 0(11)	0.025 1(4)
C(33)	−0.098 1(7)	0.308 8(11)	0.005 6(4)
C(34)	−0.169 4(6)	0.247 6(10)	0.034 1(4)
C(35)	−0.151 3(5)	0.123 8(9)	0.083 1(4)
C(40)	0.072 2(4)	−0.232 5(8)	0.174 0(3)
C(41)	0.061 0(5)	−0.402 2(10)	0.167 9(4)
C(42)	0.138 2(7)	−0.500 0(11)	0.167 4(4)
C(43)	0.225 0(6)	−0.429 6(13)	0.172 6(5)
C(44)	0.235 9(5)	−0.263 7(13)	0.179 0(5)
C(45)	0.160 1(5)	−0.160 0(10)	0.180 3(4)

six compounds is analogous to that used previously.[6] None of the cations exhibits any abnormal features. Nor are there any anion–cation contacts < 3.6 Å in any of the compounds.

The preference of silver(I) for co-ordination number three over co-ordination number four as a function of cation size and concentration of halide ligand in crystalline halogenoargentates(I) containing symmetrically substituted quaternary ammonium and phosphonium cations is illustrated in Table 9. The relative sizes of the tetraphenylphosphonium and tetrabutylammonium cations have been estimated from crystalline volume increments for the organic substituents.[21] As

Table 7. Interatomic distances (Å) and angles (°) within the $[Ag_4I_8]^{4-}$ anions in $[PPh_4]_4[Ag_4I_8]$ (**1**) and $[AsPh_4]_4[Ag_4I_8]$ (**2**). Primed atoms related to unprimed atoms by inversion centre

	(**1**)	(**2**)
Ag(1)–I(1)	2.846(2)	2.847(1)
Ag(1)–I(1′)	2.842(2)	2.846(1)
Ag(1)–I(2)	2.991(2)	2.973(1)
Ag(1)–I(3)	2.901(2)	2.897(1)
Ag(2)–I(2)	2.765(2)	2.757(1)
Ag(2)–I(3)	2.763(2)	2.766(1)
Ag(2)–I(4)	2.727(2)	2.721(1)
Ag(1) ··· Ag(2)	3.171(2)	3.198(1)
Ag(1) ··· Ag(1′)	3.256(2)	3.306(2)
I(1)–Ag(1)–I(1′)	110.15(5)	108.99(4)
I(1)–Ag(1)–I(2)	108.07(5)	109.21(4)
I(1)–Ag(1)–I(3)	110.53(5)	110.17(4)
I(1′)–Ag(1)–I(2)	113.26(5)	113.46(4)
I(1′)–Ag(1)–I(3)	110.56(5)	111.07(4)
I(2)–Ag(1)–I(3)	104.10(5)	103.82(4)
I(2)–Ag(2)–I(3)	114.36(5)	113.55(4)
I(2)–Ag(2)–I(4)	123.03(5)	123.79(4)
I(3)–Ag(2)–I(4)	122.49(5)	122.63(4)
Ag(1)–I(1)–Ag(1′)	69.85(5)	71.00(4)
Ag(1)–I(2)–Ag(2)	66.72(5)	67.73(3)
Ag(1)–I(3)–Ag(2)	68.03(5)	68.72(3)

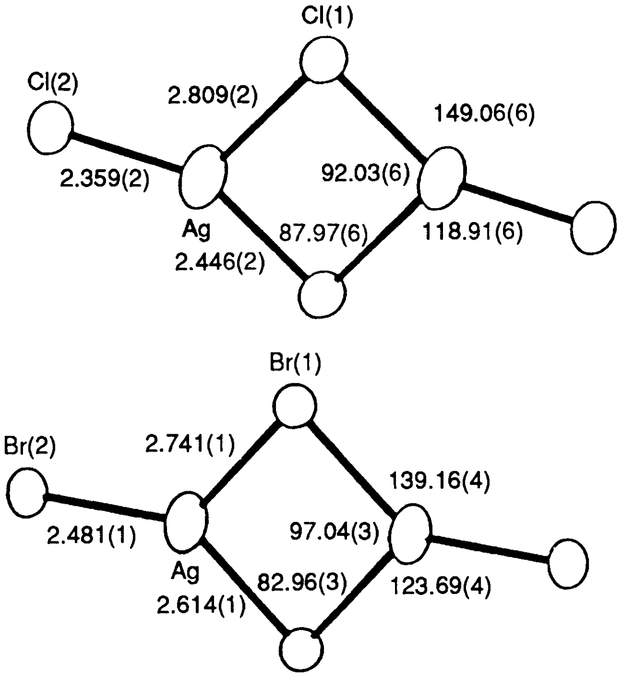

Figure 3. The $[Ag_2Cl_4]^{2-}$ ion (*a*) and the $[Ag_2Br_4]^{2-}$ ion (*b*) in $[AsPh_4]_2[Ag_2Cl_4]$ (**5**) and $[AsPh_4]_2[Ag_2Br_4]$ (**6**), respectively. The anions are centrosymmetric. Distances are in Å and angles °; estimated standard deviations are given in parentheses. The thermal ellipsoids enclose 50% probability

Table 8. Interatomic distances (Å) and angles (°) within the $[Ag_3I_4]^-$ anions in $[PPh_4][Ag_3I_4]$ (**3**) and $[AsPh_4][Ag_3I_4]$ (**4**). Symmetry code: I $x, \frac{1}{2} - y, z - \frac{1}{2}$; II $x, y, 1 + z$; III $x, \frac{1}{2} - y, \frac{1}{2} + z$; IV $x, y, z - 1$

	(**3**)	(**4**)		(**3**)	(**4**)
Ag(1)–I(1)	2.801(2)	2.807(4)	Ag(3)–I(2)	2.919(2)	2.919(4)
Ag(1)–I(2)	2.972(3)	2.966(4)	Ag(3)–I(3^{II})	2.852(3)	2.866(4)
Ag(1)–I(3)	2.882(2)	2.879(4)	Ag(3)–I(4^{III})	2.960(2)	2.964(4)
Ag(1)–I(4)	2.934(2)	2.940(4)	Ag(1) · · · Ag(2)	3.147(3)	3.178(5)
Ag(2)–I(2^{I})	2.802(2)	2.812(4)	Ag(1) · · · Ag(2^{III})	3.160(3)	3.180(4)
Ag(2)–I(3)	2.821(2)	2.823(4)	Ag(1) · · · Ag(3)	3.363(3)	3.381(5)
Ag(2)–I(4)	2.940(2)	2.944(4)	Ag(2) · · · Ag(3^{I})	3.246(3)	3.254(5)
Ag(2)–I(4^{I})	2.935(3)	2.938(4)	Ag(2) · · · Ag(3^{IV})	3.219(3)	3.247(5)
Ag(3)–I(1)	2.796(2)	2.798(4)			
I(1)–Ag(1)–I(2)	100.90(7)	100.62(12)	I(2)–Ag(3)–I(4^{III})	108.55(6)	108.63(12)
I(1)–Ag(1)–I(3)	117.53(8)	118.91(13)	I(3^{II})–Ag(3)–I(4^{III})	106.06(7)	105.59(12)
I(1)–Ag(1)–I(4)	109.89(8)	109.43(13)	Ag(1)–I(1)–Ag(3)	73.85(7)	74.21(11)
I(2)–Ag(1)–I(3)	109.83(8)	109.73(13)	Ag(1)–I(2)–Ag(2^{III})	66.28(6)	66.72(11)
I(2)–Ag(1)–I(4)	110.24(7)	110.09(12)	Ag(1)–I(2)–Ag(3)	69.61(7)	70.13(10)
I(3)–Ag(1)–I(4)	108.21(7)	107.77(12)	Ag(2^{III})–I(2)–Ag(3)	69.10(6)	69.16(11)
I(2^{I})–Ag(2)–I(3)	116.60(8)	117.43(13)	Ag(1)–I(3)–Ag(2)	66.97(6)	67.74(11)
I(2^{I})–Ag(2)–I(4)	112.40(8)	112.20(13)	Ag(1)–I(3)–Ag(3^{IV})	127.60(7)	128.20(12)
I(2^{I})–Ag(2)–I(4^{I})	115.20(8)	114.65(13)	Ag(2)–I(3)–Ag(3^{IV})	69.15(6)	69.61(11)
I(3)–Ag(2)–I(4)	109.74(7)	109.19(12)	Ag(1)–I(4)–Ag(2)	64.80(6)	65.38(10)
I(3)–Ag(2)–I(4^{I})	107.54(7)	107.43(12)	Ag(1)–I(4)–Ag(2^{III})	65.15(6)	65.51(10)
I(4)–Ag(2)–I(4^{I})	92.78(8)	93.23(12)	Ag(1)–I(4)–Ag(3^{I})	104.90(7)	105.98(11)
I(1)–Ag(3)–I(2)	102.34(7)	102.01(12)	Ag(2)–I(4)–Ag(2^{III})	95.16(8)	95.49(12)
I(1)–Ag(3)–I(3^{II})	122.06(8)	122.93(13)	Ag(2)–I(4)–Ag(3^{I})	66.77(6)	66.85(10)
I(1)–Ag(3)–I(4^{III})	106.65(8)	106.79(13)	Ag(2^{III})–I(4)–Ag(3^{I})	66.20(6)	66.77(10)
I(2)–Ag(3)–I(3^{II})	110.61(8)	110.31(13)			

Table 9. Co-ordination of silver(I) in halogenoargentates(I) crystallising with symmetrically substituted quaternary ammonium and phosphonium cations. Infinite polymeric anions are denoted as such. [X] is the concentration (mol dm^{-3}) of halide ligand in the crystalline phase

Cation	Anion	Co-ord. no. of Ag^I	[X]	Ref.
Chloroargentates(I)				
$AsPh_4^+$	$[Ag_2Cl_4]^{2-}$	3	6.0	This work
PPh_4^+	$[Ag_2Cl_4]^{2-}$	3	6.2	6
NEt_4^+	$(Ag_2Cl_3^-)_\infty$	4	14.5	3*d*
NMe_4^+	$(AgCl_2^-)_\infty$	4	15.8	2*c*
Bromoargentates(I)				
$AsPh_4^+$	$[Ag_2Br_4]^{2-}$	3	5.8	This work
PPh_4^+	$[Ag_2Br_4]^{2-}$	3	5.9	6
NEt_4^+	$(Ag_2Br_3^-)_\infty$	4	13.4	3*d*
NMe_4^+	$(Ag_2Br_3^-)_\infty$	4	17.1	3*a*
Iodoargentates(I)				
$AsPh_4^+$	$[Ag_4I_8]^{4-}$	3 and 4	5.6	This work
$AsPh_4^+$	$(Ag_3I_4^-)_\infty$	4	9.1	This work
PPh_4^+	$[Ag_4I_8]^{4-}$	3 and 4	5.7	This work
PPh_4^+	$(Ag_3I_4^-)_\infty$	4	9.3	This work
NBu_4^+	$(Ag_3I_4^-)_\infty$	4	9.6	5
NMe_4^+	$(AgI_2^-)_\infty$	4	13.6	2*b*
	$(Ag_2I_3^-)_\infty$	4	15.0	3*c*
	$(Ag_{13}I_{15}^{2-})_\infty$	4	19.9	4
NH_4^+	$(AgI_3^{2-})_\infty$	4	18.6	*

* C. Brink and H. A. Stenfert Eroese, *Acta Crystallogr.*, 1952, **5**, 433.

for copper(I) in halogenocuprates(I),[1] silver(I) would appear to show a trend towards a higher co-ordination number with decreasing cation size and increasing concentration of ligand ion, indicating that cation–halide packing is relevant for the attainment of a particular silver(I) co-ordination number. For halogenocuprates(I), the various results have been interpeted as suggesting cation–halide packing as a primary process at the solution-crystal interface, copper(I) then diffusing into available interstices, with subsequent rearrangement resulting in the specific anion with the appropriate copper(I) co-ordination number, the tentative mechanism implying a rapid ligand exchange rate for copper(I) in solution.[1e] The present results suggest that such a mechanism may also be applicable to the formation of crystalline halogenoargentates(I) containing bulky, unipositive cations. The recent preparation of heteronuclear $[Ag_2Cu_2I_8]^{4-}$ and $[Ag_3CuI_8]^{4-}$ clusters, analogous to $[Ag_4I_8]^{4-}$, but with copper(I) occupying or partially occupying the three-co-ordinated site also lends support to this hypothesis.[22]

Accordingly, the $[Ag_4I_8]^{4-}$ ion, containing three- and four-co-ordinated silver(I), would appear to be the more stable iodoargentate(I) species isolable with the tetraphenylarsonium and tetraphenylphosphonium cations. That the polymeric $[Ag_3I_4]^-$ species in which silver(I) is tetrahedrally co-ordinated is the primary product crystallising from dimethylformamide may be due to the enhanced solubility of silver(I) iodide and tetraphenylarsonium or tetraphenylphosphonium iodide in this solvent, providing and maintaining the requisite local concentration of iodide.

Acknowledgements

Financial support from the Swedish Natural Science Research Council (NFR) is gratefully acknowledged.

References

1 (*a*) S. Andersson and S. Jagner, *Acta Chem. Scand., Ser. A*, 1986, **40**, 52 and refs. therein; (*b*) *ibid.*, p. 177; (*c*) *ibid.*, 1987, **41**, 230; (*d*) *ibid.*, 1988, **42**, 691; (*e*) S. Andersson, M. Håkansson, and S. Jagner, *J. Cryst. Spec. Res.*, 1989, **19**, 147.

2 (*a*) G. L. Bottger and A. L. Geddes, *Spectrochim. Acta, Part A*, 1967, **23**, 1551; (*b*) K. Peters, H. G. von Schnering, W. Ott, and H-M. Seidenspinner, *Acta Crystallogr., Sect. C*, 1984, **40**, 789; (*c*) G. Helgesson, M. Josefsson, and S. Jagner, *ibid*, 1988, **44**, 1729.

3 (*a*) S. Jagner, S. Olson, and R. Stomberg, *Acta Chem. Scand., Ser. A*, 1986, **40**, 230; (*b*) H-J. Meyer, *Acta Crystallogr.*, 1963, **16**, 788; (*c*) J. D. Kildea, B. W. Skelton, and A. H. White, *Aust. J. Chem.*, 1986, **39**, 171; (*d*) G. Helgesson and S. Jagner, *Acta Crystallogr., Sect. C*, 1988, **44**, 2059.

4 S. Geller and M. D. Lind, *J. Chem. Phys.*, 1970, **52**, 5854.

5 C. J. Gilmore, P. A. Tucker, and P. Woodward, *J. Chem. Soc. A*, 1971, 1337.

6 G. Helgesson and S. Jagner, *J. Chem. Soc., Dalton Trans.*, 1988, 2117.

7 (*a*) G. A. Bowmaker, G. R. Clark, D. A. Rogers, A. Camus, and N. Marsich, *J. Chem. Soc., Dalton Trans.*, 1984, 37; (*b*) G. A. Bowmaker, A. Camus, B. W. Skelton, and A. H. White, *ibid.*, 1990, 727.

8 J. Estienne, *Acta Crystallogr., Sect. C*, 1986, **42**, 1512.

9 H. Hartl, *Angew. Chem.*, 1987, **99**, 925.

10 H. Hartl and F. Mahdjour-Hassan-Abadi, *Z. Naturforsch., Teil B*, 1984, **39**, 149.

11 M. S. Lehmann and F. K. Larsen, *Acta Crystallogr., Sect. A*, 1974, **30**, 580; O. Lindqvist and E. Ljungström, *J. Appl. Crystallogr.*, 1979, **12**, 134.

12 J. de Meulenaer and H. Tompa, *Acta Crystallogr.*, 1965, **19**, 1014.

13 G. T. DeTitta, *J. Appl. Crystallogr.*, 1985, **18**, 75.

14 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, pp. 71, 148.

15 O. Lindgren, Ph.D. Thesis, Chalmers University of Technology and University of Göteborg, 1977; L. Andersen, Ph.D. Thesis, Chalmers University of Technology and University of Göteborg, 1985.

16 TEXSAN Structure Solution Package, Molecular Structure Corporation, The Woodlands, Texas, 1989.

17 C. J. Gilmore, *J. Appl. Crystallogr.*, 1984, **17**, 42.

18 C. J. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Tennessee, 1965.

19 J. C. Bowles and D. Hall, *Chem. Commun.*, 1971, 1523; *Acta Crystallogr., Sect. B*, 1975, **31**, 2149.

20 M. I. Bruce, J. D. Walsh, B. W. Skelton, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1981, 956.

21 A. Immirzi and B. Perini, *Acta Crystallogr., Sect. A*, 1977, **33**, 216.

22 S. Andersson, G. Helgesson, S. Jagner, and S. Olson, *Acta Chem. Scand.*, 1989, **43**, 946.

Received 3rd *February* 1990; *Paper* 0/00513D