Two Compounds containing Dinuclear Three-co-ordinated Halogenoargentate(I) Anions: Crystal Structures of Bis(tetraphenylphosphonium) Di-μ-chloro-dichlorodiargentate(I) and Bis(tetraphenylphosphonium) Di-μ-bromo-dibromodiargentate(I)†

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Two new dinuclear halogenoargentate(I) anions, $[Ag_2Cl_4]^{2-}$ and $[Ag_2Br_4]^{2-}$, containing distorted trigonal-planar co-ordinated silver(I), have been characterised by means of crystal structure determination. Bis(tetraphenylphosphonium) di-μ-chloro-dichlorodiargentate(I) and bis(tetraphenylphosphonium) di-μ-bromo-dibromodiargentate(I) both crystallize in the monoclinic space group $P2_1/n$ with $Z = 2$ and $a = 14.190(9)$, $b = 8.062(3)$, $c = 19.177(10)$ Å, $\beta = 101.64(4)°$, and $a = 14.525(9)$, $b = 7.914(3)$, $c = 20.010(10)$ Å, $\beta = 103.16(5)°$, respectively. Both anions are centrosymmetric and planar or approximately planar, silver(I) being displaced 0.0014(8) and 0.0587(6) Å from the ligand plane in $[Ag_2Cl_4]^{2-}$ and $[Ag_2Br_4]^{2-}$, respectively. In $[Ag_2Cl_4]^{2-}$ the bridging Ag–Cl distances differ considerably from one another, *i.e.* 2.447(1) and 2.792(2) Å, the terminal Ag–Cl bond being 2.358(2) Å. In $[Ag_2Br_4]^{2-}$ there is less discrepancy between bridging distances: 2.617(1) and 2.752(2) Å; Ag–Br(terminal) is 2.491(1) Å.

In halogenocuprates(I) crystallizing with symmetrically substituted tetra-alkylammonium and analogous cations with low effective positive charge, 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 dilution of the ligand ions by the cations 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 some halogenoargentates(I) crystallizing with this type of cation are known, there would not yet appear to be sufficient structural information to ascertain whether or not the co-ordination number of silver(I) shows a similar dependency on cation size as that of copper(I). The salts of the smaller tetra-alkylammonium cations, *e.g.* tetramethylammonium, 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 indicate the presence of polymeric species containing four-co-ordinated silver(I) in $[NEt_4][Ag_2X_3]$ and $[PEt_4][Ag_2X_3]$ (X = Cl, Br, or I), and in $[PMe_4][AgBr_2]$.[2a] Tetrabutylammonium tetraiodotriargentate(I) also contains a polymeric chain in which silver(I) is tetrahedrally co-ordinated.[5] Mononuclear or dinuclear halogenoargentates(I) appear to be less common, the only conclusive evidence hitherto for the existence of a discrete anionic species in a quaternary ammonium or phosphonium compound having been obtained for the mononuclear trigonal $[AgI_3]^{2-}$ ion in $[PMePh_3]_2[AgI_3]$, which is similar to $[CuI_3]^{2-}$ in the corresponding iodocuprate(I).[6] A linear, monomeric dibromoargentate(I) ion has been determined in bis(*N*,*N*-di-n-butyldithiocarbamato)gold(III) dibromoargentate(I);[7] hexa-ammonium tris[tetrachloroaurate(III)] μ-chloro-bis[dichloroargentate(I)] contains a planar dinuclear $[Ag_2Cl_5]^{3-}$ ion, in which silver(I) is three-co-ordinated;[8] while a dinuclear $[Ag_2I_6]^{4-}$ ion, composed of silver(I)–iodide tetrahedra has been determined in bis[(ethylenediamine)di-iodoplatinum(IV)] di-μ-iodo-bis[di-iodoargentate(I)].[9] We wish to report the crystallographic determination of dinuclear $[Ag_2Cl_4]^{2-}$ and $[Ag_2Br_4]^{2-}$ ions, containing three-co-ordinated silver(I). Although chlorocuprate(I),[10] bromocuprate(I),[1c,11] and iodocuprate(I)[12] analogues have been found recently in a variety of compounds, we know of no previous structural determination of a discrete $[Ag_2X_4]^{2-}$ dimer.

Experimental

Preparation of Compounds.—$[PPh_4]_2[Ag_2Br_4]$ was prepared by the method of Bowmaker *et al.*[6] using silver bromide (0.10 g, 0.53 mmol) (ICN Biomedicals, K & K), tetraphenylphosphonium bromide (0.22 g, 0.53 mmol) (Fluka), and acetonitrile (20 cm³). Colourless needles, m.p. 221—222 °C, were obtained after a few days. $[PPh_4]_2[Ag_2Cl_4]$ was prepared in an analogous manner, using silver chloride (0.10 g, 0.70 mmol) (ICN Biomedicals, K & K), tetraphenylphosphonium chloride (0.26 g, 0.70 mmol) (Fluka), and acetonitrile (20 cm³). Colourless needles, m.p. 195—196 °C, were deposited from the solution after a few days.

Crystal-Structure Determinations.—*Crystal data.* $[PPh_4]_2[Ag_2Cl_4]$. $C_{48}H_{40}Ag_2Cl_4P_2$, $M = 1\,036.4$, monoclinic, $a = 14.190(9)$, $b = 8.062(3)$, $c = 19.177(10)$ Å, $\beta = 101.64(4)°$ (by least-squares refinement on diffractometer setting angles for 15 automatically centred reflections, $\lambda = 0.710\,69$ Å), $U = 2\,149(2)$ Å³, space group $P2_1/n$ (alt. $P2_1/c$, no. 14), $Z = 2$, $D_c = 1.60$ g cm⁻³, $F(000) = 1\,040$. Colourless needles. Crystal dimensions (distance to faces from vertex chosen as origin for absorption correction): 0.000 $(10\bar{1}, 0\bar{1}0, 001)$, 0.212 $(\bar{1}01)$, 0.230 $(00\bar{1})$, 0.429 (010) mm, $\mu(Mo\text{-}K_\alpha) = 1.26$ mm⁻¹.

$[PPh_4]_2[Ag_2Br_4]$ $C_{48}H_{40}Ag_2Br_4P_2$, $M = 1214.2$, monoclinic, $a = 14.525(9)$, $b = 7.914(3)$, $c = 20.010(10)$ Å, $\beta = 103.16(5)°$ (by least-squares refinement on diffractometer setting angles for 15 automatically centred reflections, $\lambda = 0.710\,69$ Å),

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Fractional atomic co-ordinates for the non-hydrogen atoms in $[PPh_4]_2[Ag_2Cl_4]$

Atom	*x*	*y*	*z*
Ag	0.385 50(3)	0.055 11(5)	0.023 74(2)
Cl(1)	0.581 05(7)	0.118 73(13)	0.073 01(5)
Cl(2)	0.273 45(8)	0.174 52(16)	0.084 53(7)
P	−0.033 42(6)	−0.102 46(11)	0.179 21(5)
C(10)	−0.133 1(2)	−0.242 0(4)	0.172 2(2)
C(11)	−0.147 7(3)	−0.327 7(5)	0.232 0(2)
C(12)	−0.217 3(3)	−0.451 9(5)	0.224 1(3)
C(13)	−0.271 2(3)	−0.488 3(6)	0.157 8(3)
C(14)	−0.257 4(3)	−0.401 7(5)	0.099 4(3)
C(15)	−0.188 0(3)	−0.278 7(5)	0.105 3(2)
C(20)	−0.012 0(2)	0.007 0(5)	0.262 4(2)
C(21)	0.028 7(3)	−0.077 5(5)	0.324 7(2)
C(22)	0.041 1(3)	0.004 2(6)	0.389 0(2)
C(23)	0.015 8(3)	0.168 9(6)	0.391 4(3)
C(24)	−0.022 2(3)	0.252 0(6)	0.330 1(3)
C(25)	−0.037 8(3)	0.173 1(5)	0.265 2(2)
C(30)	−0.059 0(3)	0.046 7(4)	0.109 1(2)
C(31)	0.013 2(3)	0.113 1(5)	0.078 5(2)
C(32)	−0.008 4(4)	0.241 6(6)	0.029 9(2)
C(33)	−0.101 3(4)	0.301 6(6)	0.011 2(2)
C(34)	−0.172 1(3)	0.235 5(5)	0.040 6(2)
C(35)	−0.152 2(3)	0.108 8(5)	0.090 0(2)
C(40)	0.069 9(2)	−0.226 1(5)	0.175 4(2)
C(41)	0.061 7(3)	−0.396 7(5)	0.165 7(2)
C(42)	0.142 9(4)	−0.488 9(6)	0.163 2(3)
C(43)	0.229 4(4)	−0.416 8(7)	0.168 8(3)
C(44)	0.239 4(3)	−0.247 2(8)	0.178 7(3)
C(45)	0.160 0(3)	−0.150 7(6)	0.183 6(2)

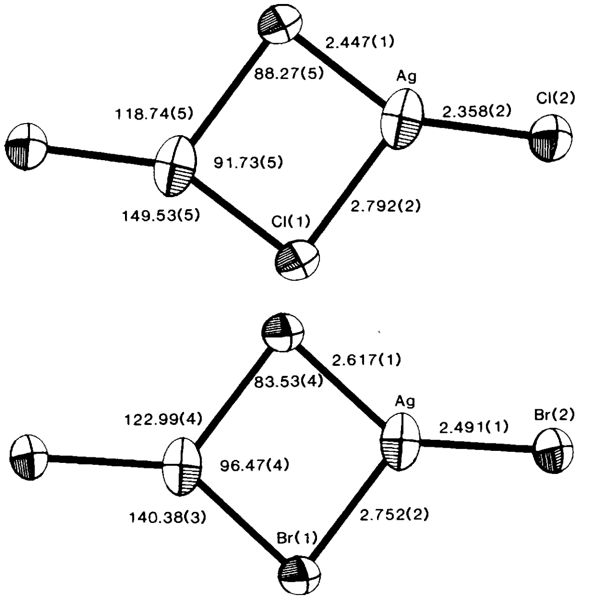

Figure 1. The $[Ag_2Cl_4]^{2-}$ and $[Ag_2Br_4]^{2-}$ ions in $[PPh_4]_2[Ag_2Cl_4]$ and $[PPh_4]_2[Ag_2Br_4]$, respectively. Both anions are centrosymmetric. Distances are in Å and angles in °; estimated standard deviations are given in parentheses. The thermal ellipsoids enclose 50% probability

U = 2 240(2) Å^3, space group $P2_1/n$ (alt. $P2_1/c$, no. 14), $Z = 2$, D_c = 1.80 g cm^{-3}, $F(000)$ = 1 184. Colourless needles. Crystal dimensions (distance to faces from vertex chosen as origin for absorption correction): 0.000 ($\bar{1}00$, $\bar{1}0\bar{1}$, 010), 0.195 (100), 0.227 (001), 0.085 ($00\bar{1}$), 0.149 ($10\bar{1}$), 0.269 (102), 0.349 ($0\bar{1}0$) mm, μ(Mo-K_α) = 4.50 mm^{-1}.

Table 2. Fractional atomic co-ordinates for the non-hydrogen atoms in $[PPh_4]_2[Ag_2Br_4]$

Atom	*x*	*y*	*z*
Ag	0.395 37(3)	0.064 88(6)	0.025 89(2)
Br(1)	0.584 23(3)	0.138 86(7)	0.072 73(2)
Br(2)	0.270 68(4)	0.171 75(8)	0.082 38(3)
P	−0.035 66(7)	−0.090 47(14)	0.175 85(5)
C(10)	−0.135 0(3)	−0.225 8(5)	0.171 0(2)
C(11)	−0.149 4(3)	−0.304 5(6)	0.230 4(2)
C(12)	−0.220 5(4)	−0.423 2(7)	0.225 3(3)
C(13)	−0.277 0(4)	−0.462 5(7)	0.161 9(3)
C(14)	−0.264 2(4)	−0.384 8(7)	0.104 0(3)
C(15)	−0.192 5(3)	−0.267 8(6)	0.107 6(2)
C(20)	−0.010 3(3)	0.024 3(5)	0.255 2(2)
C(21)	0.033 9(3)	−0.058 5(6)	0.315 8(2)
C(22)	0.049 4(4)	0.029 1(7)	0.377 3(2)
C(23)	0.022 3(4)	0.193 1(7)	0.378 6(3)
C(24)	−0.019 3(5)	0.276 8(7)	0.319 2(3)
C(25)	−0.036 5(4)	0.194 4(6)	0.257 2(3)
C(30)	−0.062 0(3)	0.058 4(5)	0.106 6(2)
C(31)	0.008 5(3)	0.113 7(6)	0.074 8(2)
C(32)	−0.011 7(4)	0.241 8(8)	0.026 5(3)
C(33)	−0.100 5(5)	0.308 9(7)	0.008 8(3)
C(34)	−0.171 0(4)	0.251 1(7)	0.038 2(3)
C(35)	−0.152 2(3)	0.127 5(7)	0.088 0(2)
C(40)	0.065 0(3)	−0.220 7(5)	0.173 9(2)
C(41)	0.053 5(4)	−0.391 8(6)	0.163 4(2)
C(42)	0.132 1(4)	−0.492 7(7)	0.163 5(3)
C(43)	0.220 1(4)	−0.419 3(8)	0.171 3(3)
C(44)	0.230 4(3)	−0.251 0(9)	0.180 9(3)
C(45)	0.153 8(3)	−0.149 2(7)	0.183 1(2)

Data collection and processing. $[PPh_4]_2[Ag_2Cl_4]$. Syntex $P2_1$ diffractometer, T *ca.* 290 K, ω–2θ scan mode, variable 2θ scan rate 2.5—29.3° min^{-1}, Mo-K_α radiation; 3 810 unique reflections ($3.5 < 2\theta < 50°$); 96-step profile recorded for each reflection; intensities calculated using the Lehmann and Larsen profile-analysis method;[13] absorption correction[14] (max., min. transmission factors = 0.809, 0.703); 3 057 reflections with $I > 3\sigma(I)$.

$[PPh_4]_2[Ag_2Br_4]$. As above; 3 979 unique reflections ($3.5 < 2\theta < 50°$); absorption correction[14] (max., min. transmission factors = 0.472, 0.306); 3 173 reflections with $I > 3\sigma(I)$.

Structure analysis and refinement. $[PPh_4]_2[Ag_2Cl_4]$. The structure was solved from Patterson and subsequent electron-density maps. Full-matrix least-squares refinement, including anisotopic 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 atom and not refined, gave final R = 0.043, R' = 0.050 for 313 parameters and 3 057 reflections; maximum residual electron density = 0.73 e Å^{-3}. Weighting scheme: $w = [\sigma^2(F_o) + 0.0008F_o^2]^{-1}$. Atomic scattering factors and anomalous dispersion corrections from ref. 15; computer programs used described in ref. 16.

$[PPh_4]_2[Ag_2Br_4]$. The Patterson function and subsequent electron-density calculations confirmed that $[PPh_4]_2[Ag_2Br_4]$ was isostructural with $[PPh_4]_2[Ag_2Cl_4]$. Refinement as above gave a final R = 0.040, R' = 0.045 for 313 parameters and 3 173 reflections; weighting scheme: $w = [\sigma^2(F_o) + 0.0008F_o^2]^{-1}$; maximum residual electron density = 0.66 e Å^{-3}.

The figures were drawn using ORTEP.[17] Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters, H-atom co-ordinates, remaining bond distances and angles.

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* $B_{eq} = \frac{8\pi^2}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$.

Table 3. Connectivity relationships (distances in Å, angles in °) reported for planar $[Cu_2X_4]^{2-}$ and $[Ag_2X_4]^{2-}$ ions[a]

Compound	M–X$_t$	M–X$_b$	M ··· M	M–X$_b$–M	X$_b$–M–X$_b$	X$_b$–M–X$_t$	d	X$_b$ ··· X$_b$	Ref.
$[VO(salen)(H_2O)]_2$-$[Cu_2Cl_4]$[b]	2.161(2)	2.224(3) 2.427(3)			96.8(2)	143.9(1)			10
$[ttt]_2[Cu_2Br_4]$[c]	2.328(3)	2.472(3) 2.490(2)	2.660(3)	64.7(1)	115.4(1)	125.0(1) 117.9(1)	0.196		11(*a*)
$[NEt_4]_2[Cu_2Br_4]$	2.319(2)	2.441(2) 2.454(2)	2.937(3)	73.7(1)	106.3(1)	125.7(1) 127.9(1)	0.06(1)	3.916(3)	11(*b*)
$[NPhMe_3]_2[Cu_2Br_4]$	2.310(1)	2.417(1) 2.421(1)	2.738(2)	68.95(4)	111.05(4)	124.70(4) 124.12(4)	0.049(1)	3.988(2)	11(*c*)
$[PMePh_3]_2[Cu_2Br_4]$	2.337(2)	2.426(2) 2.455(1)	2.697(2)	67.09(5)	112.91(5)	124.60(6) 122.47(5)	0.012(1)	4.068(2)	11(*d*)
$[PEt_4]_2[Cu_2Br_4]$	2.263(4)	2.423(4) 2.436(3)	2.870(5)	72.4(1)	107.6(1)	128.2(1) 124.1(1)	0.032(3)	3.921(5)	1(*c*)
$[NBu_4]_2[Cu_2I_4]$	2.514(2)	2.566(2) 2.592(2)	2.726(4)	63.8(1)	116.2(1)	117.9(1) 125.8(1)	0.03(3)	4.380(3)	12(*a*)
$[NPr_4]_2[Cu_2I_4]$	2.499(1)	2.571(1) 2.582(1)	2.698(2)	63.14(3)	116.86(3)	120.15(4) 122.98(4)	0.013(1)	4.390(1)	12(*c*)
$[PPh_4]_2[Cu_2I_4]$	2.497(0)	2.580(0) 2.595(1)	2.957(1)		110.29(3)	122.35(4) 127.05(4)	0.08		12(*d*)
$[PPh_4]_2[Ag_2Cl_4]$	2.358(2)	2.447(1) 2.792(2)	3.657(2)	88.27(5)	91.73(5)	149.53(5) 118.74(5)	0.001 4(8)	3.768(3)	This work
$[PPh_4]_2[Ag_2Br_4]$	2.491(1)	2.617(1) 2.752(2)	3.578(2)	83.53(4)	96.47(4)	140.38(3) 122.99(4)	0.058 7(6)	4.006(2)	This work

[a] X$_t$ is a terminal and X$_b$ a bridging halide ligand; *d* is the displacement (Å) of the metal atom from the plane through the ligand atoms. [b] H_2salen = *N*,*N'*-ethylenebis(salicylideneimine). [c] ttt = tetrathiotetracene (naphthaceno[5,6-*cd*:11,12-*c'd'*]bis[1,2]dithiole) radical cation.

Results and Discussion

Fractional atomic co-ordinates for $[PPh_4]_2[Ag_2Cl_4]$ and $[PPh_4]_2[Ag_2Br_4]$ are given in Tables 1 and 2 respectively. The anions are depicted in Figure 1. Silver(I) exhibits distorted trigonal-planar co-ordination geometry in both anions, with the metal atom displaced 0.0014(8) Å from the ligand plane in $[Ag_2Cl_4]^{2-}$ and 0.0587(6) Å in $[Ag_2Br_4]^{2-}$. As in the corresponding halogenocuprate(I) ions (*cf.* Table 3), the bridging metal–halide bonds are longer than the terminal. In $[Ag_2Cl_4]^{2-}$ (Figure 1), the bridging Ag–Cl distances differ considerably from one another, whereas $[Ag_2Br_4]^{2-}$ is less distorted in this respect. Marked deviation from trigonal co-ordination geometry is, however, evident from the bond angles in both anions. The Ag ··· Ag^i separation is 3.657(2) Å in $[Ag_2Cl_4]^{2-}$ and 3.578(2) Å in $[Ag_2Br_4]^{2-}$; Cl ··· Cl^i and Br ··· Br^i are 3.768(3) Å and 4.006(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 $[Ag_2Cl_5]^{3-}$, 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.[8] A description in terms of 'chlorine-bridged $[AgCl_2]^-$ ions' was suggested as perhaps being appropriate for this ion.[8] A similar description could also be employed for the dinuclear $[Ag_2X_4]^{2-}$ ions reported here, and in particular for $[Ag_2Cl_4]^{2-}$ (Figure 1), *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 been found in $[Ag\{P(C_6H_4Me\text{-}p)_3\}\{BPh_2(pz)_2\}]$ (pz = pyrazol-1-yl).[18]

Considerable flexibility has been observed in the geometry of the planar di-μ-halogeno-dihalogenodicuprate(I) anions determined hitherto (*cf.* Table 3). In addition, a non-planar $[Cu_2I_4]^{2-}$ ion, folded 147° about the bridging I ··· I contact, has been determined in the tetraphenylarsonium[12b] and tetraphenylphosphonium[12d] compounds, the latter cation also crystallizing with a planar, centrosymmetric $[Cu_2I_4]^{2-}$ dimer.[12d] The bromocuprate(I) analogue of the $[Ag_2Cl_5]^{3-}$ ion,[8] *viz.* $[Cu_2Br_5]^{3-}$, is non-planar, the angle subtended by the copper(I) atoms at the bridging bromide ligand being 72.8(1)°, *i.e.* of the same magnitude as in the doubly-bridged dinuclear species (*cf.* Table 3); there is, moreover, no difference between terminal and bridging bond lengths in this anion.[19] In view of the large variations in geometry associated with trigonal-planar dinuclear halogenocuprate(I) anions, and in the co-ordination geometry of the metal in these species, it seems likely that similar flexibility will be observed in dinuclear halogenoargentates(I) containing three-co-ordinated silver(I) in different environments.

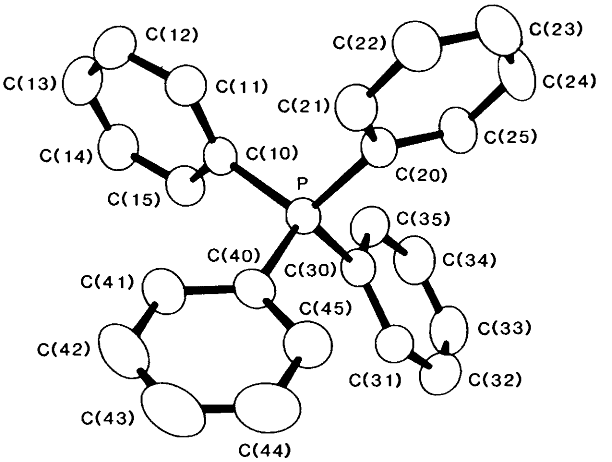

Figure 2. The cation in $[PPh_4]_2[Ag_2Cl_4]$ showing the atom-numbering system. The same system has been used for the cation in $[PPh_4]_2[Ag_2Br_4]$. The thermal ellipsoids enclose 50% probability

The atom numbering system employed for the cations in the two compounds is illustrated in Figure 2. There are no unusual features associated with these ions. The closest silver(I)–carbon contacts are Ag ··· C(23^{ii}) = 3.658(5) Å in $[PPh_4]_2[Ag_2Cl_4]$ and 3.563(6) Å in $[PPh_4]_2[Ag_2Br_4]$. The shortest halide–cation approaches are Cl(2) ··· C(21^{iii}) = 3.597(4) Å and Br(2) ···

$C(21^{iii}) = 3.759(5)$ Å, there being several halide–carbon packing distances only slightly longer than these values (symmetry code: ii $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; iii $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$).

That discrete halogenoargentate(I) species, containing three-co-ordinated silver(I), have been isolated with the tetraphenylphosphonium cation, whereas polymeric species in which silver(I) is tetrahedrally co-ordinated have been obtained with the smaller cation $[NMe_4]^+$,[2–4] and presumably also occur in the tetraethylammonium, tetramethylphosphonium, and tetraethylphosphonium salts, [2a] suggests that the co-ordination number of silver(I) in this type of compound may show a dependency on cation size and concentration of halide ligand in the crystalline phase similar to that noted previously for copper(I).[1]

Acknowledgements

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References

1 (*a*) S. Andersson and S. Jagner, *Acta Chem. Scand., Ser. A*, 1986, **40**, 52; (*b*) *ibid.*, 1986, **40**, 177; (*c*) *ibid.*, 1987, **41**, 230.

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.

3 S. Jagner, S. Olson, and R. Stomberg, *Acta Chem. Scand., Ser. A*, 1986, **40**, 230; H.-J. Meyer, *Acta Crystallogr.*, 1963, **16**, 788; J. D. Kildea, B. W. Skelton, and A. H. White, *Aust. J. Chem.*, 1986, **39**, 171.

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. A. Bowmaker, G. R. Clark, D. A. Rogers, A. Camus, and N. Marsich, *J. Chem. Soc., Dalton Trans.*, 1984, 37.

7 J. A. Cras, J. H. Noordik, P. T. Beurskens, and A. M. Verhoeven, *J. Cryst. Mol. Struct.*, 1971, **1**, 155.

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

9 H. J. Keller, B. Keppler, and H. Pritzkow, *Acta Crystallogr., Sect. B*, 1982, **38**, 1603.

10 L. Banci, A. Bencini, A. Dei, and D. Gatteschi, *Inorg. Chim. Acta*, 1984, **84**, L11.

11 (*a*) R. P. Shibaeva and V. F. Kaminskii, *Kristallografiya*, 1981, **26**, 332; (*b*) M. Asplund and S. Jagner, *Acta Chem. Scand., Ser. A*, 1984, **38**, 135; (*c*) S. Andersson and S. Jagner, *ibid.*, 1985, **39**, 423; (*d*) S. Andersson and S. Jagner, *Acta Crystallogr., Sect. C*, 1987, **43**, 1089.

12 (*a*) M. Asplund, S. Jagner, and M. Nilsson, *Acta Chem. Scand., Ser. A*, 1982, **36**, 751; (*b*) M. Asplund and S. Jagner, *ibid.*, 1984, **38**, 297; (*c*) *ibid.*, 1984, **38**, 411; (*d*) H. Hartl, I. Brüdgam, and F. Mahdjour-Hassan-Abadi, *Z. Naturforsch., Teil B*, 1985, **40**, 1032; (*e*) F. Mahdjour-Hassan-Abadi, H. Hartl, and J. Fuchs, *Angew. Chem.*, 1984, **96**, 497.

13 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.

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

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

16 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.

17 C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Tennessee, 1965.

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

19 M. Asplund and S. Jagner, *Acta Chem. Scand., Ser. A*, 1985, **39**, 47.

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