Group 11 Metal(I) Complexes with Low Co-ordination Numbers: The Crystal Structures of $[PPh_3Me]_2[CuBr_3]$, $[PPh_3Me]_2[CuBr_2]Br$, and $[PPh_3Me]_2[AgI_3]$ †

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The crystal structures of $[PPh_3Me]_2[CuBr_3]$, $[PPh_3Me]_2[CuBr_2]Br$, and $[PPh_3Me]_2[AgI_3]$ have been determined by single-crystal *X*-ray diffraction methods at 295 K. The salt $[PPh_3Me]_2[CuBr_3]$ contains a planar, almost perfectly trigonal tribromocuprate (I) ion $[CuBr_3]^{2-}$. The exact symmetry of the ion in the crystal is C_{2v}, with Cu–Br bond lengths of 2.353(3) (twice) and 2.358(6) Å and Br–Cu–Br angles of 118.9(1) (twice) and 122.2(2)°. The salt $[PPh_3Me]_2[CuBr_2]Br$ contains $[CuBr_2]^-$ ions and separate Br^- ions at distances greater than 6.8 Å from the nearest copper atom. The structure of the $[CuBr_2]^-$ ion is almost linear, with Cu–Br bond lengths of 2.228(1) and 2.233(1) Å and a Br–Cu–Br angle of 175.29(4)°. The salt $[PPh_3Me]_2[AgI_3]$ contains a planar tri-iodoargentate(I) ion $[AgI_3]^-$ with approximate trigonal symmetry. The Ag–I bond lengths are 2.742(1), 2.746(1), and 2.755(1) Å and the I–Ag–I angles are 115.90(3), 119.38(4), and 124.67(3)°. This appears to be one of very few examples of a mononuclear, trigonally co-ordinated silver(I) complex. The possible relevance of this structure to the mechanism of conductivity in iodoargentate(I) solid-state electrolytes is discussed.

In the solid state the stereochemistry of copper(I) and silver(I) complexes is dominated by four-co-ordination.[1,2] However, a significant number of two- and three-co-ordinate complexes of copper(I) are known,[1] the simplest of which are the homoleptic, mononuclear halogenocuprates(I) $[CuX_2]^-$ and $[CuX_3]^{2-}$ which have been characterized in the solid state by vibrational spectroscopy[3,4] and *X*-ray crystallography.[4–6] In contrast to this, very few solids containing simple two- or three-co-ordinate mononuclear silver(I) complexes have been reported. The two-co-ordinate $[AgX_2]^-$ species have been characterized by vibrational spectroscopy in tri-n-butyl phosphate solution,[7] but only one solid compound containing such an ion, $[Au(Bu^n{}_2NCS_2)_2][AgBr_2]$, has been reported to date.[8] However, in this compound the anion lies near to the sulphur atoms of the cation, with a relatively short Ag $\cdots$ S distance of 3.16 Å. It has recently been shown that discrete $[Ag_2X_4]^{2-}$ species, with three-co-ordinate silver(I), exist in $[PPh_4]_2[Ag_2X_4]$ (X = Cl or Br).[9] In all other known compounds with $[AgX_2]^-$ stoicheiometry the anions are present as infinite chains of distorted AgX_4 tetrahedra which are linked by sharing edges.[10] Several compounds of the general composition M_2AgX_3 are known, but in all cases where crystal structures have been reported these compounds contain infinite chains of distorted AgI_4 tetrahedra which are linked by sharing corners.[11–14]

We have previously shown that several compounds with the general formula $[PPh_3Me]_2[MX_3]$ (M = Cu or Ag) can be prepared and that their far-i.r. spectra suggest the presence of discrete, trigonal-planar, three-co-ordinate $[MX_3]^{2-}$ ions. This was verified by *X*-ray crystallography in the case of the compound $[PPh_3Me]_2[CuI_3]$, which was shown to contain a slightly distorted planar $[CuI_3]^{2-}$ ion with Cu–I bond lengths of 2.537(2), 2.559(2), and 2.566(2) Å and I–Cu–I bond angles of 116.55(7), 120.54(6), and 122.90(7)°.[4] The structure of the corresponding silver compound $[PPh_3Me]_2[AgI_3]$ has not yet been reported. In view of the fact that very few mononuclear three-co-ordinate silver(I) complexes have been fully characterized structurally to date, we have determined the structure of this compound in the present study. The structure of the corresponding bromocuprate(I) complex $[PPh_3Me]_2[CuBr_3]$ has also not been reported, although the existence of the $[CuBr_3]^{2-}$ ion in the solid state has since been established by the determination of the crystal structure of $[PMe_4]_2[CuBr_3]$, which contains a $[CuBr_3]^{2-}$ ion with exact D_{3h} symmetry.[6] However, the compound $[PPh_3Me]_2[CuBr_3]$ shows an additional interesting feature, namely that it can be prepared in two distinct crystalline forms, the far-i.r. spectra of which suggest that one contains a trigonal $[CuBr_3]^{2-}$ unit, while the other contains separate $[CuBr_2]^-$ and Br^- units. The crystal structures of both these compounds have been determined in this work in order to verify the above conclusions and to determine whether there is any interaction between the $[CuBr_2]^-$ and Br^- ions in the second compound.

Experimental

Preparation of Compounds.—These were prepared according to previously described methods.[4]

Structure Determinations.—Unique data sets were measured at *ca.* 295 K within the limit $2\theta_{max.} = 50°$ using four-circle diffractometers (2θ—θ scan mode; monochromatic Mo-K_α radiation, $\lambda = 0.71069$ Å). N Independent reflections were measured, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement after absorption

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† Bis(methyltriphenylphosphonium) tribromocuprate(I), bis(methyltriphenylphosphonium) dibromocuprate(I) bromide, and bis(methyltriphenylphosphonium) tri-iodoargentate(I).

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

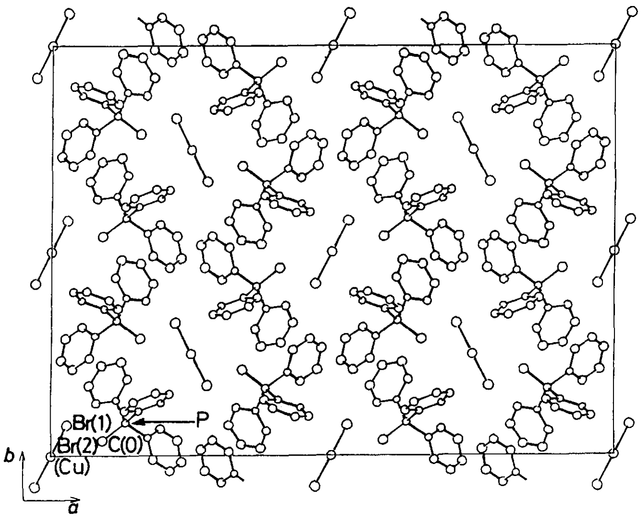

Figure 1. Unit-cell contents of $[PPh_3Me]_2[CuBr_3]$, projection axis *c*, arbitrary thermal ellipsoid envelopes. The anion is projected down Br(2)–Cu, coincident with a two-fold axis normal to the plane of the paper

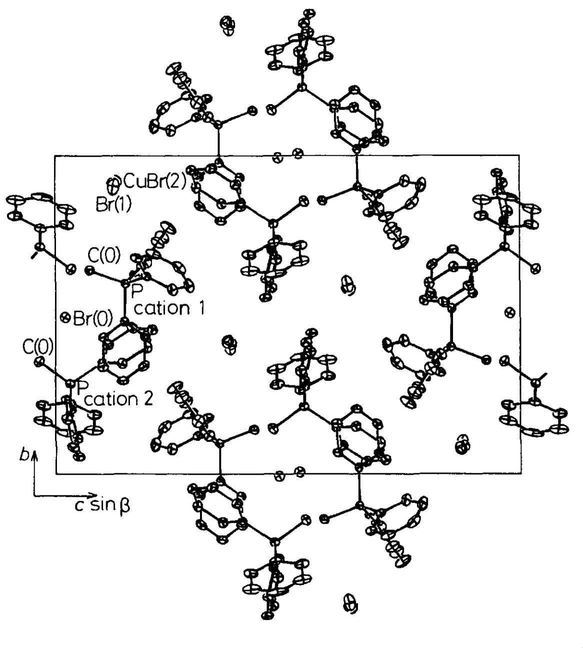

Figure 2. Unit-cell contents of $[PPh_3Me]_2[CuBr_2]Br$, projection axis *a*. 20% Probability amplitude thermal ellipsoids are shown for the non-hydrogen atoms

correction. For the compound $[PPh_3Me]_2[CuBr_3]$, data were limited and the heavy atoms only were refined with anisotropic thermal parameters, the isotropic form being refined for carbon; for the other two compounds, all non-hydrogen thermal parameters were refined with the anisotropic form. Values of $(x, y, z, U_{iso})_H$ for all three structures were constrained at estimated values. Conventional *R*, *R'* on *F* at convergence are quoted; statistical weights derivative of $\sigma^2(I) = \sigma^2(I)_{diff} + n_w\sigma^4\ (I)_{diff}$ were used. Neutral atom complex scattering factors were employed,[15] computation using the XTAL 2.4 program system implemented by S. R. Hall.[16] Atom co-ordinates are given in the Tables; Figures 1—3 display the unit-cell contents of the three compounds, while Figure 4 gives the anion geometries.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

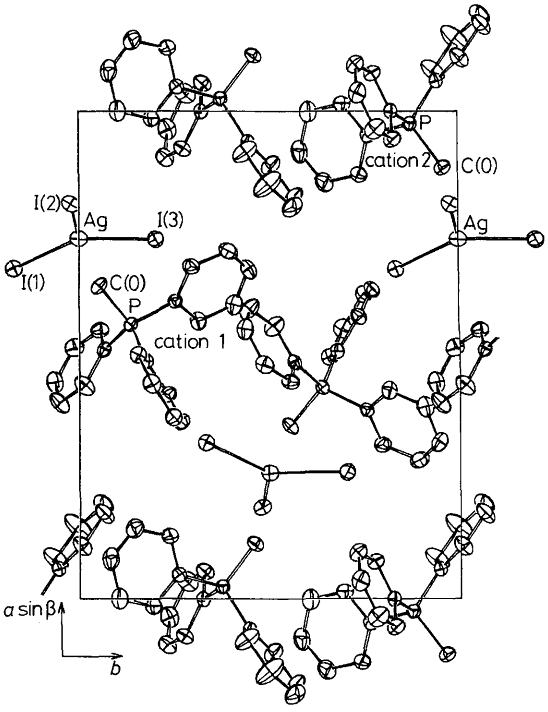

Figure 3. Unit-cell contents of $[PPh_3Me]_2[AgI_3]$, projection axis *c*. 20% Probability amplitude thermal ellipsoids are shown for the non-hydrogen atoms

Crystal and refinement data. $[PPh_3Me]_2[CuBr_3]$. $C_{38}H_{36}Br_3CuP_2$, $M = 857.9$, orthorhombic, space group *Fdd*2 (C_{2v},[17] no. 43), $a = 32.65(2)$, $b = 23.96(1)$, $c = 9.196(3)$ Å, $U = 7\,191(7)$ Å^3, $Z = 8$, $D_c = 1.58$ g cm^{-3}, $F(000) = 3\,424$, $\mu = 39.4$ cm^{-1}, specimen, $0.060 \times 0.30 \times 0.18$ mm (capillary), $A^*_{\text{min.,max.}}$(analytical correction) 1.26, 2.01, $N = 1\,697$, $N_o = 627$, $R = 0.044$, $R' = 0.032$ (preferred hand), $n_w = 2 \times 10^{-4}$, Syntex $P2_1$ diffractometer.

$[PPh_3Me]_2[CuBr_2]Br$. $C_{38}H_{36}Br_3CuP_2$, $M = 857.9$, monoclinic, space group $P2_1/c$ (C_{2h},[5] no. 14), $a = 11.439(2)$, $b = 14.862(5)$, $c = 21.659(4)$ Å, $\beta = 91.56(1)°$, $U = 3\,680.6$ Å^3, $Z = 4$, $D_c = 1.55$ g cm^{-3}, $F(000) = 1\,712$, $\mu = 38.6$ cm^{-1}, specimen, $0.32 \times 0.23 \times 0.25$ mm (capillary), $A^*_{\text{min.,max.}}$(Gaussian correction) 1.77, 2.25, $N = 6\,456$, $N_o = 3\,965$, $R = 0.039$, $R' = 0.038$, $n_w = 5 \times 10^{-4}$, Enraf–Nonius CAD-4 diffractometer.

$[PPh_3Me]_2[AgI_3]$. $C_{38}H_{36}AgI_3P_2$, $M = 1\,043.2$, monoclinic, space group $P2_1$ (C_2,[2] no. 4), $a = 16.469(5)$, $b = 12.514(2)$, $c = 9.673(2)$ Å, $\beta = 103.64(3)°$, $U = 1\,937(1)$ Å^3, $Z = 2$, $D_c = 1.79$ g cm^{-3}, $F(000) = 1\,000$, $\mu = 28.3$ cm^{-1}, specimen, $0.23 \times 0.40 \times 0.46$ mm (capillary), $A^*_{\text{min.,max.}}$(Gaussian correction) 1.73, 2.39, $N = 3\,392$, $N_o = 3\,261$, $R = 0.030$, $R' = 0.037$ (preferred hand), $n_w = 5 \times 10^{-4}$, Enraf–Nonius CAD-4 diffractometer.

Results and Discussion

Bis(methyltriphenylphosphonium) Tribromocuprate(I), $[PPh_3Me]_2[CuBr_3]$.—The non-hydrogen atom co-ordinates for this complex are listed in Table 1, and the structure of the $[CuBr_3]^{2-}$ anion is shown in Figure 4(*a*). The asymmetric unit contains half a formula unit and the anion lies on a two-fold crystallogaphic axis (Figure 1). The anion is necessarily planar, and so has a local symmetry of C_{2v}. However, the distortions from ideal D_{3h} trigonal planar symmetry are small. The mean Cu–Br bond

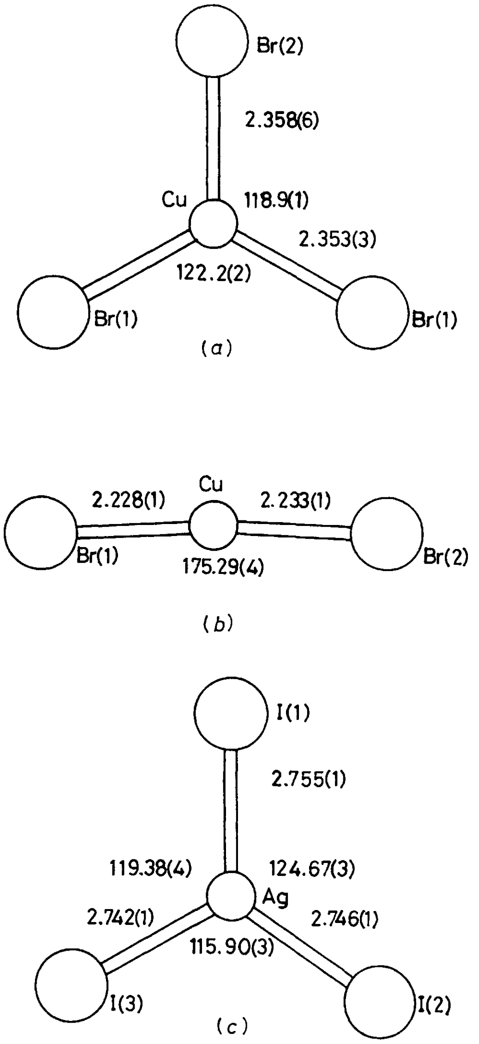

Figure 4. Schematic representation, with dimensions (distances in Å, angles in °), of the complex ions (*a*) $[CuBr_3]^{2-}$ (lying on a two-fold crystallographic axis), (*b*) $[CuBr_2]^-$, and (*c*) $[AgI_3]^{2-}$

length of 2.355(4) Å is only slightly less than the value 2.365(3) Å found for the D_{3h} $[CuBr_3]^{2-}$ ion in $[PMe_4]_2[CuBr_3]$.[6]

Bis(methyltriphenylphosphonium) Dibromocuprate(I) *Bromide*, $[PPh_3Me]_2[CuBr_2]Br$.—The non-hydrogen atom co-ordinates for this complex are listed in Table 2. The solid contains well separated $[CuBr_2]^-$ and Br^- ions (Figure 2). The shortest distance between a copper atom and a non-bonded Br^- ion is 6.811 Å. The structure of the $[CuBr_2]^-$ anion is shown in Figure 4(*b*). This ion has no crystallographically imposed symmetry and is slightly but significantly non-linear, with a Br–Cu–Br angle of 175.29(4)°. The Cu–Br bond lengths [2.228(1) and 2.233(1) Å] lie at the high end of the range 2.207—2.232 Å found for the same ion in a range of other dibromocuprate(I) complexes.[5]

It has been pointed out that the co-ordination number of copper(I) in solid bromocuprate(I) complexes is dependent upon the total bromide concentration in the solid. This concentration can be altered by changing the size of the counter ion in the complex and this effect has been investigated for a number of bromocuprate(I) complexes with symmetrically substituted ammonium and phosphonium cations.[6] It was found that higher copper co-ordination numbers are associated with higher bromide concentrations in the solid. The results of the present study, together with the previously published results for $[PPh_3Me]_2[Cu_2Br_4]$,[17] allow further examination of this effect with a single unsymmetrically substituted cation, $[PPh_3Me]^+$. The total solid-state bromide concentrations in these compounds are: $[PPh_3Me]_2[CuBr_2]Br$, 5.41; $[PPh_3Me]_2[CuBr_3]$, 5.54; and $[PPh_3Me]_2[Cu_2Br_4]$, 6.75 mol dm^{-3}. The fact that one Br^- is not co-ordinated to copper in $[PPh_3Me]_2[CuBr_2]Br$ necessarily increases the molar volume and therefore reduces the total bromide concentration relative to that in $[PPh_3Me]_2[CuBr_3]$. However, despite the structural differences between these two compounds, the total bromide concentrations in both are quite similar, and the existence of both compounds suggests that the 1:3 Cu:Br stoicheiometry results in a situation which is on the borderline between a preference for two- and three-co-ordination for copper. Thus, the critical total bromide concentration for the change from two- to three-co-ordination in the case of the $[PPh_3Me]Br$–CuBr system appears to be about 5.5 mol dm^{-3}. The crystal structure of $[PPh_3Me]_2[Cu_2Br_4]$ shows that it contains binuclear $[Cu_2Br_4]^{2-}$, rather than the two-co-ordinate $[CuBr_2]^-$ species which is the simplest structure which might have been expected on the basis of the 1:2 Cu:Br stoicheiometry alone. However it is clear that the bromide concentration in this compound is well above the value 5.5 mol dm^{-3} which corresponds to the transition from two- to three-co-ordination, and so the binuclear, three-co-ordinate structure of the anion is preferred.

Bis(methyltriphenylphosphonium) Tri-iodoargentate(I), $[PPh_3Me]_2[AgI_3]$.—The non-hydrogen atom co-ordinates for this complex are listed in Table 3, and the structure of the $[AgI_3]^{2-}$ anion is shown in Figure 4(*c*). The asymmetric unit contains one formula unit and the anion has no crystallographically imposed symmetry. However, the anion is almost exactly planar, with the silver atom lying only 0.036 Å out of the plane of the three co-ordinated iodine atoms. The distortion of the anion from ideal D_{3h} symmetry is only slightly greater than that found previously for the corresponding iodocuprate(I) complex $[PPh_3Me]_2$-

Table 1. Non-hydrogen atom co-ordinates for $[PPh_3Me]_2[CuBr_3]$

Atom	*x*	*y*	*z*
Cation			
P	0.133 2(2)	0.083 4(2)	0.605 2(6)
C(0)	0.091 5(6)	0.038 2(7)	0.645(2)
C(11)	0.172 0(4)	0.044 8(6)	0.512(2)
C(12)	0.181 7(5)	—0.010 4(7)	0.560(2)
C(13)	0.211 7(5)	—0.038 2(7)	0.482(2)
C(14)	0.232 2(5)	−0.015 7(8)	0.376(2)
C(15)	0.224 8(6)	0.038 1(8)	0.331(2)
C(16)	0.194 5(6)	0.066 8(7)	0.399(2)
C(21)	0.155 6(5)	0.111 0(6)	0.770(2)
C(22)	0.131 3(6)	0.111 7(7)	0.896(2)
C(23)	0.146 7(5)	0.132 5(7)	1.023(2)
C(24)	0.186 3(5)	0.154 0(6)	1.023(2)
C(25)	0.210 1(5)	0.152 4(7)	0.900(2)
C(26)	0.195 3(5)	0.131 1(6)	0.773(2)
C(31)	0.115 9(5)	0.137 9(6)	0.492(2)
C(32)	0.080 9(5)	0.130 7(7)	0.399(2)
C(33)	0.068 2(5)	0.173 1(8)	0.312(2)
C(34)	0.090 0(6)	0.221 5(7)	0.308(2)
C(35)	0.124 9(6)	0.231 0(7)	0.393(2)
C(36)	0.135 6(5)	0.188 5(7)	0.486(2)
Anion			
Cu	0	0	0.123 6(5)
Br(1)	0.028 50(6)	0.076 72(8)	0
Br(2)	0	0	0.380 0(4)

Table 2. Non-hydrogen atom co-ordinates for $[PPh_3Me]_2[CuBr_2]Br$

	Section 1			Section 2		
Atom	x	y	z	x	y	z
Cation						
C(0)	−0.012 1(4)	0.641 8(3)	0.073 6(2)	0.488 3(4)	0.355 5(3)	−0.033 9(2)
P	0.009 13(10)	0.598 94(8)	0.149 65(5)	0.507 80(10)	0.285 75(8)	0.032 00(6)
C(11)	0.136 2(4)	0.652 0(3)	0.184 1(2)	0.510 2(4)	0.352 8(3)	0.101 1(2)
C(12)	0.246 8(4)	0.622 6(3)	0.170 5(2)	0.605 3(4)	0.408 5(3)	0.112 2(2)
C(13)	0.343 3(5)	0.668 1(4)	0.194 0(3)	0.610 7(5)	0.459 8(3)	0.165 0(2)
C(14)	0.328 6(5)	0.743 6(4)	0.229 6(3)	0.523 3(4)	0.455 1(3)	0.207 6(2)
C(15)	0.220 0(5)	0.773 4(4)	0.243 5(3)	0.429 2(4)	0.400 1(3)	0.196 5(2)
C(16)	0.122 1(4)	0.727 7(4)	0.220 4(3)	0.422 0(4)	0.348 8(3)	0.143 2(2)
C(21)	0.026 9(4)	0.479 1(3)	0.147 7(2)	0.644 2(4)	0.227 7(3)	0.030 0(2)
C(22)	−0.036 3(4)	0.431 5(3)	0.103 1(2)	0.700 8(5)	0.217 2(3)	−0.025 3(3)
C(23)	−0.028 3(5)	0.338 9(3)	0.102 3(2)	0.805 8(5)	0.168 5(4)	−0.025 9(3)
C(24)	0.040 5(5)	0.294 6(3)	0.144 6(2)	0.849 2(5)	0.130 2(4)	0.026 7(4)
C(25)	0.101 0(4)	0.351 5(3)	0.189 7(2)	0.792 9(5)	0.139 9(4)	0.081 7(4)
C(26)	0.095 3(4)	0.434 8(3)	0.191 8(2)	0.690 9(4)	0.189 0(3)	0.083 4(3)
C(31)	−0.117 0(4)	0.622 1(3)	0.195 1(2)	0.390 8(4)	0.205 9(3)	0.034 7(2)
C(32)	−0.204 9(4)	0.678 8(3)	0.174 4(2)	0.277 2(4)	0.235 3(3)	0.023 8(2)
C(33)	−0.301 8(4)	0.692 0(3)	0.211 2(3)	0.185 8(4)	0.174 5(3)	0.026 0(2)
C(34)	−0.310 4(5)	0.649 2(4)	0.266 4(3)	0.207 3(4)	0.085 7(3)	0.037 2(2)
C(35)	−0.223 9(5)	0.593 7(4)	0.286 8(3)	0.319 3(4)	0.055 6(4)	0.049 0(2)
C(36)	−0.126 0(4)	0.579 8(4)	0.251 4(2)	0.412 5(4)	0.115 4(3)	0.047 2(2)
Anions						
Br(0)	0.241 37(4)	0.493 74(3)	0.021 65(2)			
Cu	0.758 38(7)	0.912 25(5)	0.124 23(3)			
Br	0.564 21(6)	0.901 61(6)	0.125 86(3)	0.953 44(5)	0.917 77(4)	0.130 31(3)

Table 3. Non-hydrogen atom co-ordinates for $[PPh_3Me]_2[AgI_3]$

	Cation 1			Cation 2		
Atom	x	y	z	x	y	z
P	0.564 5(1)	0.137 2(2)	0.060 2(2)	0.974 4(1)	0.873 4(1)	0.057 2(2)
C(0)	0.643 3(5)	0.053 6(7)	0.017 2(8)	0.885 9(5)	0.960 7(7)	0.011 7(9)
C(11)	0.611 1(5)	0.254 2(6)	0.149 0(7)	1.000 1(5)	0.823 8(6)	−0.101 5(7)
C(12)	0.682 7(6)	0.295 9(8)	0.119 3(10)	0.942 9(6)	0.827 5(9)	−0.232 3(9)
C(13)	0.714 2(7)	0.392 2(10)	0.179 7(14)	0.963 4(8)	0.782 0(11)	−0.349 2(10)
C(14)	0.677 2(8)	0.445 4(8)	0.269 3(11)	1.037 6(8)	0.734 9(9)	−0.340 5(10)
C(15)	0.604 4(8)	0.407 8(9)	0.293 0(10)	1.095 1(7)	0.729 0(8)	−0.210 8(10)
C(16)	0.570 9(6)	0.314 0(7)	0.234 1(9)	1.076 9(6)	0.774 8(8)	−0.091 0(9)
C(21)	0.512 7(5)	0.065 4(6)	0.173 7(7)	1.061 9(5)	0.944 6(6)	0.158 9(9)
C(22)	0.439 2(7)	0.013 1(9)	0.119 6(9)	1.109 3(7)	1.906 1(9)	0.094 4(10)
C(23)	0.404 0(8)	−0.051 3(10)	0.206 8(11)	1.175 7(8)	1.063 8(10)	0.171 9(13)
C(24)	0.445 6(8)	−0.063 7(8)	0.348 7(10)	1.195 2(8)	1.060 7(11)	0.314 3(13)
C(25)	0.517 2(6)	−0.012 9(10)	0.402 3(9)	1.148 2(11)	0.995 4(15)	0.380 0(13)
C(26)	0.552 3(6)	0.054 1(8)	0.317 4(9)	1.082 5(9)	0.937 0(13)	0.307 8(11)
C(31)	0.489 8(5)	0.177 0(6)	−0.098 4(7)	0.950 6(5)	0.760 7(6)	0.155 8(8)
C(32)	0.502 4(6)	0.155 8(7)	−0.230 8(8)	0.870 7(6)	0.737 1(8)	0.159 0(12)
C(33)	0.443 7(7)	0.190 9(9)	−0.352 9(9)	0.854 7(8)	0.644 6(11)	0.226 0(16)
C(34)	0.373 8(7)	0.248 6(8)	−0.336 6(10)	0.917 6(9)	0.580 9(10)	0.292 5(13)
C(35)	0.364 1(6)	0.270 1(8)	−0.206 4(10)	0.998 9(8)	0.604 3(9)	0.293 2(10)
C(36)	0.420 0(6)	0.234 3(7)	−0.085 0(9)	1.015 0(5)	0.693 0(8)	0.223 3(9)
Anion						
Ag	0.739 73(4)	0*	0.619 56(6)			
I(1)	0.678 06(3)	−0.166 86(7)	0.750 08(5)			
I(2)	0.810 41(4)	−0.021 04(8)	0.390 70(5)			
I(3)	0.738 43(4)	0.202 57(8)	0.726 93(7)			

* Defines origin.

$[CuI_3]$,[4] and the compound can be considered to contain essentially trigonal planar $[AgI_3]^{2-}$ units, as deduced previously from the far-i.r. spectra.[4] The nature of the distortion of these units from ideal D_{3h} symmetry is such that the longest Ag–I bond length is opposite the smallest I–Ag–I bond angle, and *vice versa*. It is not clear whether this is a requirement of the intramolecular bonding in the complex, but it can be noted that the same kind of relationship is observed in the slightly distorted

$[CuI_3]^{2-}$ in $[PPh_3Me]_2[CuI_3]$,[4] as well as in species such as CO_3^{2-} and NO_3^-. The mean Ag–I bond length in $[AgI_3]^{2-}$ is 2.748(1) Å, which is significantly shorter than the values found for K_2AgI_3[13] and Rb_2AgI_3,[14] which lie in the range 2.81—2.88 Å.

A number of other compounds of $[cation]_2[AgI_3]$ stoicheiometry have been reported.[4,18] However the low-wavenumber vibrational spectra of these indicate that they do not contain discrete $[AgI_3]^{2-}$ species.[4] Thus the present compound appears to be the only one examined to date which contains such a species. There appear to be very few other examples of mononuclear silver(I) complexes with trigonal-planar co-ordination. One compound which appears to be in this category is tris(3,5-dimethyl-1-phenylpyrazole)silver(I) nitrate. The crystal structure of this compound shows that it contains a silver atom trigonally co-ordinated to three pyrazole nitrogen atoms.[19] The nitrate anions in this structure lie between the silver ions, but the minimum silver(I)–nitrate oxygen atom separation of 5.46 Å is unusually large, so that the nitrate ion should not be co-ordinated to the silver.[2] However, the nitrate ion in this structure is severely distorted from D_{3h} symmetry, suggesting that there is at least some interaction with the silver atom.[19]

A number of iodoargentates(I) exhibit very high Ag^+ conductivity in the solid state. A typical example is $RbAg_4I_5$, which contains a three-dimensional array of Rb^+ and I^- ions with Ag^+ ions statistically occupying a proportion of tetrahedral sites surrounded by four I^- ions.[20] It has been postulated that part of the reason for the high silver ion mobility in these compounds is the relatively small resistance to movement of the silver atom away from the centre of the AgI_4 tetrahedron to an essentially three-co-ordinate site at the centre of one of the faces of the tetrahedron.[21] This is supported by the observation of a very low frequency Raman band in $RbAg_4I_5$ at 20 cm^{-1} which is assigned to the asymmetric Ag–I stretching mode of the AgI_4 units in the structure.[22] This mode corresponds essentially to movement of the Ag^+ ions away from the centre of the tetrahedra towards the triangular faces. The results of the present study show that the three-co-ordinate state is relatively stable, and should not present a large energy barrier to movement of the Ag^+ ion.

Conclusion

Further examples of the unusual case of mononuclear three-co-ordination for complexes of the Group 11 metals with the d^{10} electron configuration have been characterized in this work. While examples of this type of co-ordination are now known for trihalogenocuprates(I), $[CuX_3]^{2-}$, with X = Cl, Br, or I,[4,6] the tri-iodoargentate(I) ion is the only known example for silver(I). For the series of bromocuprates(I) $[PPh_3Me]_2[CuBr_2]Br$, $[PPh_3Me]_2[CuBr_3]$, and $[PPh_3Me]_2[Cu_2Br_4]$, it is shown that the total solid-state bromide concentration, and not the Cu:Br stoicheiometry, is the important factor in determining the copper co-ordination number.

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