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Structural and spectroscopic characterization of silver(I) tribenzylphosphane complexes including chloro and bromo derivatives with unusual stoichiometries and an iodo complex with a Ag$_{13}$I$_{13}$ cluster core

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The reaction of tribenzylphosphane (PBn$_3$) with silver(I) halides, AgX (X = Cl, Br and I), afforded the cluster compound, [Ag$_{13}$I$_{13}$(PBn$_3$)$_6$] (**1**), a low-yielding ionic salt, [Ag(PBn$_3$)$_2$]$_8$[AgCl$_3$]Cl$_6$·6H$_2$O (**2**), and a non-stoichiometric compound, Ag$_{\sim 11.5}$Br$_{\sim 11.5}$(PBn$_3$)$_{16}$·~5.5H$_2$O (**3**). As well, reactions with the appropriate Ag salt and PBn$_3$ in a 1:2 M ratio yielded [Ag(PBn$_3$)$_2$]PF$_6$ (**4**), [Ag(PBn$_3$)$_2$]BF$_4$ (**5**) and [Ag(PBn$_3$)$_2$Cl]·0.33CHCl$_3$ (**6**) while [Ag(PBn$_3$)$_2$I] (**7**) was obtained when the ratio was 4:1. The iodo-cluster **1** has an onion-like structure with an iodide ion at its center surrounded trigonal-prismatically by an inner core of six silver ions. These silver ions are tetrahedrally coordinated to the innermost iodide ion and by six iodides that bridge to an outer layer of six silver ions which themselves are tetrahedrally coordinated by six bridging iodides and capped by the six PBn$_3$ ligands. The top of the onion features a silver ion with three iodo ligands arranged in a near-planar trigonal arrangement around it. Single crystal X-ray crystallography shows the complexes **2** and **3** to contain columns of discrete [Ag(PBn$_3$)$_2$]$^+$ cations with a linear P–Ag–P coordination, as also observed in the simple salts, **4** and **5**, where the anion is [PF$_6$]$^-$ and [BF$_4$]$^-$. The phenyl groups of PBn$_3$ swing back over the silver to generate a sixfold phenyl embrace. However, in **3**, although the PBn$_3$ sites are fully occupied, about a quarter of the sixfold phenyl embraces are devoid of the object of their attention, the encapsulated silver ion. For **2**, the [AgCl$_3$]$^{2-}$ anions are trigonal-planar, three-coordinated. For **3**, the AgBr$_3$$^{2-}$ appear as motifs in an approximately 25% silver-deficient Ag$_4$Br$_6$$^{2-}$ cluster. The crystal structures of the three-coordinate halides, **6** and **7**, show that the geometry around the silver is close to a T-shape, with the chloride and iodide ions bound. The far-IR and ^{31}P CP MAS NMR spectra of a selection of the new complexes confirm aspects of their symmetry as deduced from the crystallographic studies.

1. Introduction

Tribenzylphosphane (PBn$_3$) is an easily oxidized bulky ligand with a Tolman cone angle of 165° compared to 145° for PPh$_3$ and it is also more basic with the pK_a of its conjugate acid being 2.7 compared to ~6.0 for PPh$_3$ [1]. The conformationally flexible benzyl groups are also be expected to influence the coordination chemistry of PBn$_3$. This has been observed for complexes of copper(I), where, instead of neutral [Cu(PR$_3$)X]$_n$ phosphane complexes (n = 1, 2 or 4 depending on the steric bulk of the PR$_3$ ligands) [2], rearrangement occurs, so that ionic compounds of the form [Cu(PBn$_3$)$_2$][CuX$_2$] (X = Cl and Br) are obtained in the solid state with linear [Cu(PBn$_3$)$_2$]$^+$ cations [3]. For gold(I), the two-coordinate neutral monomeric complexes [Au(PBn$_3$)X] (X = Cl and Br) are obtained, but parallel attempts to prepare the iodo analog resulted in the isolation of the oxide, Bn$_3$PO [4]. However, the monomeric ionic complex [Au(PBn$_3$)$_2$]I could be isolated, as well as the related [Au(PBn$_3$)$_2$]X (X = Cl and BF$_4$) compounds, all of which contain linear [Au(PBn$_3$)$_2$]$^+$ cations with non-coordinated anions. The driving force for the formation of ionic adducts has been ascribed to interligand 'embraces' within the linear two-coordinate cation, which prevents secondary coordination of the counterion to the metal ion [3b,4].

We were interested in extending our work with PBn$_3$ to study the nature of the complexes formed with the third member of the triad, namely silver(I). This report describes the synthesis and structural characterization of a series of compounds showing the structural flexibility of silver leading to a variety of new compound types. For example, from the reaction of tribenzylphosphane with

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AgI in an approximately 1:2 M ratio an unusual onion-like cluster, $[Ag_{13}I_{13}(PBn_3)_6]$ (**1**), crystallizes from the reaction. It is well known that in the presence of phosphanes, silver(I) salts, AgX (X = halide or pseudohalide), readily form a range of clusters. Some of the smaller ones contain, for example, Ag_5 [5], Ag_6 [6], Ag_7 [7], Ag_8 [6a,8], Ag_9 and Ag_{10} [9] and Ag_{12} [10] and there other larger units, for example in the anion $[Ag_{50}S_7(SC_6H_4Bu^t\text{-}4)_{40}]^{4-}$ [11], but a 'stand-alone' Ag_{13} unit has not been reported previously, although, in the presence of CO, an Ag_{13} unit is found in the bimetallic tetra-anion, $[Ag_{13}Fe_8(CO)_{32}]^{4-}$, which features a centered cuboctahedral stereogeometry [12] that resembles a fragment of the cubic face-centered structure of the bulk metal. In other studies, semi-empirical and *ab initio* calculations on a Ag_{13} nanoparticle favor a buckled biplanar structure [13], whereas in the polymeric structure of the $\{[Ag_{13}(\mu\text{-}SC_5H_9NHMe)_{16}]^{3-}\}_n$ cation, $Ag_{10}S_{16}$ units are linked by three silver atoms [14]. Coordination-based self-assembly is an effective way to prepare clusters with unusual structures, and steric bulk can be exploited to produce stable cores, protected by a shell of ligands from self aggregation. The geometry of the Ag_{13} core in $[Ag_{13}I_{13}(PBn_3)_6]$ (**1**) is different from the previous cases, and consists of a non-centered distorted threefold axially symmetric capped prismane-like structure that illustrates the plasticity of not only the silver but also the iodo coordination. No complexes of the type $[Ag(PR_3)X]_4$ (X = Cl, Br or I) were isolated [15], instead the preferences were for the following stoichiometries: $[Ag(PBn_3)_2]_8[AgCl_3]Cl_6{\cdot}6H_2O$ (**2**), the non-stoichiometric complex $Ag_{\sim11.5}Br_{\sim11.5}(PBn_3)_{16}{\cdot}{\sim}5.5H_2O$ (**3**) – for which only the tribenzylphosphane sites are fully occupied – as well as the monometallic species, $[Ag(PBn_3)_2]X$ [X = BF_4 (**4**) and PF_6 (**5**)] and $[Ag(PBn_3)_2X]$ [X = Cl (**6**) and I (**7**)]. All have been crystallographically characterized, **1**, **2** and **3** proving particularly complex. The $[Ag(PBn_3)_2X]$ complexes display distorted T-shaped coordination spheres whereas the $[Ag(PBn_3)_2)]X$ species, as well as $[Ag(PBn_3)_2]_8[AgCl_3]Cl_6{\cdot}6H_2O$ and $Ag_{\sim11.5}Br_{\sim11.5}(PBn_3)_{16}{\cdot}{\sim}5.5H_2O$, all feature linearly or near-linearly coordinated $[Ag(PBn_3)_2)]^+$ cations similar to those found for copper and gold [3,4]. The structures of **2** and **3** contain $[AgCl_3]^{2-}$ and $[AgBr_3]^{2-}$ anions respectively, along with water and the appropriate ionic halide (to balance charge) in the lattice. The far-IR and ^{31}P CP MAS NMR spectra are also reported for several compounds and discussed in relation to their structure and bonding.

2. Experimental

2.1. General

Analytical grade solvents were used without purification. Tribenzylphosphane (Bn_3P) and the silver halide salts were obtained from the Sigma–Aldrich Co. and $[Ag(MeCN)_4]PF_6$ was prepared using the method [16] described for the analogous copper(I) complex. Although all reactions were carried out under an atmosphere of dinitrogen, the presence of adventitious water or oxygen during the crystallization of **2** and **3** resulted in the inclusion of H_2O molecules in the lattice and in the case of **3**, some oxidation of the tribenzylphosphane. All the new compounds were soluble in chloroform. Microanalyses were performed by the Campbell Microanalytical Laboratory, University of Otago. Compounds **2** and **3** were characterized crystallographically since they could only be obtained in low yield along with other reaction products.

2.2. Compound preparation

2.2.1. Triskaidekaiodohexa(tribenzylphosphane)triskaidekasilver(I), $[Ag_{13}I_{13}(PBn_3)_6]$ (1)

Tribenzylphosphane (0.1 g, 0.33 mmol) and AgI (0.17 g, 0.71 mmol) were refluxed in 10 cm^3 chloroform for 1.5 h. The cooled solution was filtered to remove unreacted AgI. Slow diffusion of pentane vapor into the filtrate afforded colorless crystals suitable for X-ray analysis. Yield: 69 mg, 26%. Mp 200–203 °C dec. *Anal.* Calc. for $C_{126}H_{126}Ag_{13}I_{13}P_6$: C, 31.00; H, 2.60. Found: C, 31.73; H, 2.57%.

2.2.2. Octa{bis(tribenzylphosphane)silver(I)} trichloroargentate(I) chloride hexahydrate, $[Ag(PBn_3)_2]_8[AgCl_3]Cl_6{\cdot}6H_2O$ (2)

Tribenzylphosphane (0.10 g, 0.33 mmol) and AgCl (0.475 g, 3.31 mmol) were refluxed in 5 cm^3 chloroform for 1 h. The cooled solution was filtered to remove unreacted AgCl and the filtrate was transferred to a vial and sealed in a jar with pentane. The jar was stored in the dark overnight and small cubic colorless crystals as well as clumps and needles formed around the side of the vial. The product was a mixture and the near cubic crystals were analyzed by X-ray crystallography.

2.2.3. $Ag_{\sim11.5}Br_{\sim11.5}(PBn_3)_{16}{\cdot}{\sim}5.5H_2O$ (3)

Tribenzylphosphane (0.40 g, 1.31 mmol) and AgBr (0.124 g, 0.66 mmol) were refluxed in 20 cm^3 chloroform for 30 min. The cooled solution was filtered to remove unreacted AgBr and the filtrate reduced in volume by half under reduced pressure, then hexane was added until the solution just went cloudy. The flask was allowed to stand overnight in the dark to yield 0.35 g of colorless crystals. Slow diffusion of hexane vapor into a chloroform solution afforded colorless chunky crystals suitable for X-ray analysis. The precipitate also contained crystals of tribenzylphosphane oxide.

2.2.4. Bis(tribenzylphosphane)silver(I) hexafluorophosphate, $[Ag(PBn_3)_2](PF_6)$ (4)

Tribenzylphosphane (0.3 g, 0.99 mmol) and $[Ag(CH_3CN)_4]PF_6$ (0.206 g, 0.49 mmol) were refluxed in 20 cm^3 chloroform for 15 min and a white product was filtered from the cooled reaction mixture and washed well with acetonitrile. The crude product was recrystallized from nitromethane to give colorless crystals suitable for X-ray analysis. Yield: 34 mg, 8%. The crystals start to darken about 280 °C and decomposed at 330–340 °C. *Anal.* Calc. for $C_{42}H_{42}AgF_6P_3$: C, 58.53; H, 4.92. Found: C, 58.21; H 4.97%.

2.2.5. Bis(tribenzylphosphane)silver(I) tetrafluoroborate, $[Ag(PBn_3)_2](BF_4)$ (5)

Tribenzylphosphane (0.4 g, 1.31 mmol) and $AgBF_4$ (0.128 g, 0.66 mmol) were refluxed in 20 cm^3 chloroform for 1 h and the white product filtered from the cooled reaction mixture. The crude product was recrystallized from nitromethane to give colorless crystals suitable for X-ray analysis. Yield: 87 mg, 16%. The crystals start to darken about 280 °C and decomposed at 330–340 °C. *Anal.* Calc. for $C_{42}H_{42}AgBF_4P_2$: C, 62.75; H, 5.27. Found: C, 62.04; H, 5.38%.

2.2.6. Chlorobis(tribenzylphosphane)silver(I) 0.33chloroform, $[Ag(PBn_3)_2Cl]{\cdot}0.33CHCl_3$ (6)

Tribenzylphosphane (0.40 g, 1.31 mmol) and AgCl (0.094 g, 0.66 mmol) were refluxed in 20 cm^3 of chloroform under nitrogen for one hour. The cooled solution was filtered to remove unreacted AgCl and the filtrate reduced in volume by half under reduced pressure then hexane added until the solution just went cloudy. After standing overnight, the product was obtained as fine white needles. Yield: 0.342 g, 66%. Mp 173–180 °C. *Anal.* Calc. for $C_{42}H_{42}AgClP_2{\cdot}0.33CHCl_3$: C, 64.22; H, 5.40. Found: C, 64.23; H, 5.80%. Slow diffusion of hexane vapor into a chloroform solution afforded white needles suitable for X-ray analysis. The discrepancy between the analytical data and the X-ray structure indicates the lattice $CHCl_3$ is readily lost.

2.2.7. *Iodobis(tribenzylphosphane)silver(I), [Ag(PBn$_3$)$_2$I] (**7**)*

PBn_3 (0.1 g, 0.33 mmol) and AgI (0.34 g, 1.45 mmol) were refluxed in 3 cm^3 chloroform under nitrogen for 6 h. The cooled solution was filtered to remove unreacted AgI. Slow diffusion of pentane vapor into the filtrate afforded colorless elongated crystals suitable for X-ray analysis. Yield: 18 mg, 13%. Mp 155–160° dec. *Anal.* Calc. for $C_{42}H_{42}AgIP_2$: C, 59.78; H, 5.02. Found: C, 59.19; H, 5.04%.

2.3. *X-ray data collection and refinement*

The X-ray data were collected on a Siemens P4 four-circle diffractometer, using a Siemens SMART 1K CCD area detector. The crystals were mounted in an inert oil and irradiated with graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) X-rays. The data were collected by the SMART program and processed with SAINT to apply Lorentz and polarization corrections to the diffraction spots (integrated 3 dimensionally). Crystal data are given Table 1. The structures of **4**–**7** were solved by direct methods and refined using the SHELXTL program [17].

2.3.1. *[Ag$_{13}$I$_{13}$(PBn$_3$)$_6$] (**1**)*

The Ag–PBn_3 moiety was readily decipherable from the top direct methods' solution; however, the cluster of 6 large peaks at and around the -3 (S_6) site was not so readily interpretable. Constraining all peaks to have a common isotropic displacement parameter and assigning to each peak a free variable describing the fractional occupancy, x_j, by atom I_j, with fractional occupancy of atom Ag_j constrained to $1 - x_j$, yielded an unambiguous assignment of each peak as either silver or iodine atoms, as well as the total occupancy of the site. Identity of atom and fractional occupancy of these sites were also substantiated in refinements in which the atomic displacement parameter at each site was subject only to the constraint that it was equal for each Ag/I pair. With two Ag atoms being unacceptably close and occupying general positions with only half occupancy, it was concluded that the structure was disordered about the –3 (S_6) center. Assuming 3 (C_3) symmetry and inversion disorder on the AgI cluster led to the novel but chemically sensible cluster $(PBn_3)_6(AgI)_{13}$. Refinement converged very cleanly to a value for R_1 (observed data) of 0.0318. Although residual electron density is concentrated within the cluster near the I and Ag sites, indicating that, perhaps, overall symmetry is lower than 3 (C_3), refinements in space group $R\bar{1}$ (both with and without twinning) did not improve the model.

2.3.2. *[Ag(PBn$_3$)$_2$]$_8$[AgCl$_3$]Cl$_6$·6H$_2$O (**2**)*

The diffraction data could be merged with acceptable statistics into crystals systems cubic and lower, although there was a small but significant difference in one axis compared to the other two. Ignoring the numerous systematic absence violations, refinements in space group *Pnnn* died at $R_1 \sim 0.21$ (even allowing for trilling). (*Note*: *Pnnn* was the initially chosen space group of the bromide (**3**) for which the unit cell is almost identical to that for this chloride derivative.) Structure elucidation was then pursued in space group $P2_12_12$, again ignoring systematic absence violations, but similarly to attempts in space group *Pnnn*, the benzyl moieties were not discernable in electron density maps. To facilitate comparison with the bromide analog, successful structure solution and refinement were conducted in a non-standard setting of *P*222. Stable refinement was achieved in space group *P*222 with pseudo-merohedral trilling [twin law 0 1 0/0 0 1/1 0 0, and final refinement of twin components giving 0.147(58), 0.260(60), 0.184(64), 0.229(58), 0.103 (60) and 0.076, the high errors the result of allowing for inversion twinning]. As for the bromide, a disordered $AgCl_3^{2-}$ cluster disports itself about a 222 site, but yields an apparent X_4Y_6 cluster, where the Y species, sitting on crystallographic twofold axes, are present, each in half occupancy, and the Ag^+ ion, sitting in a general position is present in quarter occupancy. At other 2 and 222 sites chloride ions are found. These together with a chloride ion in a general position, give an overall Ag:Cl:P ratio of 9:9:16. Because of high correlation among parameters resulting from the intrinsic tetragonal pseudo-symmetry and

Table 1
Crystal and refinement data for the complexes.

Compound	$[Ag_{13}I_{13}(PBn_3)_6]$ (**1**)	$[Ag(PBn_3)_2]_8[AgCl_3]Cl_6 \cdot 6H_2O$ (**2**)	$Ag_{\sim 11.5}Br_{\sim 11.5}(PBn_3)_{16} \cdot {\sim}5.5H_2O$ (**3**)	$[Ag(PBn_3)_2]PF_6$ (**4**)	$[Ag(PBn_3)_2]BF_4$ (**5**)	$[Ag(PBn_3)_2Cl] \cdot CHCl_3$ (**6**)
Molecular formula	$C_{126}H_{126}Ag_{13}I_{13}P_6$	$C_{336}H_{348}Ag_9Cl_9O_6P_{16}$	$C_{336}H_{347}Ag_{11.5}Br_{11.5}O_{5.5}P_{16}$	$C_{42}H_{42}AgF_6P_3$	$C_{42}H_{42}AgBF_4P_2$	$C_{43}H_{43}AgCl_4P_2$
Molecular weight	4878.12	6267.52	7117.04	861.54	803.38	871.38
T (K)	200(2)	200(2)	200(2)	203(2)	203(2)	203(2)
Crystal system	rhombohedral	orthorhombic	tetragonal	monoclinic	monoclinic	monoclinic
Space group	$R\bar{3}$	*P*222	*P*4/*nnc*	*C*2/*c*	*C*2/*c*	$P2_1/c$
a (Å)	17.4433(4)	19.722(4)	19.647(3)	14.68490(10)	14.1182(4)	9.8401(2)
b (Å)	17.4433(4)	19.722(4)	19.647(3)	13.6436(2)	13.6580(3)	20.7137(5)
c (Å)	39.8703(13)	19.738(4)	19.745(4)	19.6266(2)	19.5086(5)	20.3865(3)
α (°)	90	90	90	90	90	90
β (°)	90	90	90	90.5370(10)	92.4340(10)	91.6780(10)
γ (°)	120	90	90	90	90	90
V (Å^3)	10506.0(5)	7677(3)	7622(2)	3932.11(8)	3758.38(17)	4153.49(14)
Z	3	1	1	4	4	4
μ (Mo Kα) (mm^{-1})	4.750	0.779	2.369	0.693	0.671	0.849
ρ_{calc} (g cm^{-3})	2.313	1.356	1.551	1.455	1.420	1.393
2*θ* max (°)	50	50.16	49.42	55	54.84	54.84
No. of unique reflections	5235	13,490	3395	4332	4120	9131
Data/restraints/ parameters	5235/0/249	13,490/1461/882	3395/0/229	4332/0/237	4120/47/244	9131/36/479
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0313$, $wR_2 = 0.0783$	$R_1 = 0.0697$, $wR_2 = 0.1590$	$R_1 = 0.0616$, $wR_2 = 0.1640$	$R_1 = 0.0246$, $wR_2 = 0.0661$	$R_1 = 0.0289$, $wR_2 = 0.0709$	$R_1 = 0.0289$, $wR_2 = 0.0709$
R indices (all data)	$R_1 = 0.0435$, $wR_2 = 0.0837$	$R_1 = 0.1273$, $wR_2 = 0.1901$	$R_1 = 0.0982$, $wR_2 = 0.1952$	$R_1 = 0.0279$, $wR_2 = 0.0677$	$R_1 = 0.0353$, $wR_2 = 0.0743$	$R_1 = 0.0624$, $wR_2 = 0.0983$
Goodness of fit on F^2	1.041	1.123	1.014	1.052	1.028	1.128

exacerbated by the trilling into cubic pseudo-symmetry, mild damping and moderate restraints on atomic displacement parameters had to be employed to achieve stable non-oscillatory convergence. In addition, benzyl moieties were restrained to standard geometry. The final R_1(observed data) of 0.0697 is commensurate with the intrinsic quality of the diffraction data.

2.3.3. $Ag_{\sim 11.5}Br_{\sim 11.5}(PBn_3)_{16}\cdot{\sim}5.5H_2O$ (**3**)

In addition to systematic absences consistent with space group *Pnnn*, there is considerable pseudo-symmetry apparent in the cell metric with *a* and *b* axes indistinguishably different, and the *c* axis being only 0.1 Å (~0.5%) longer than the *a* and *b* axes. Moreover, the diffraction data show considerable pseudo-symmetry, with barely unacceptable statistics for merging of data into tetragonal *P*4/*mmm* or cubic $Pm\bar{3}m$ Laue groups ($R_{int} = 0.086$ and 0.092, respectively, compared to 0.072 for merging into *Pmmm*). Finally, reflections $h + k + l = 2n + 1$ are systematically much weaker than average and reflections *hhl*, *hkh* and *hll* are only weakly observed. In either orthorhombic, tetragonal (*P*4/*nnc*) or cubic ($Pn\bar{3}m$) space groups, the $[Ag(PBn_3)_2]^+$ moiety was readily discerned. A Y_8X_6 cluster, where the eight Y sites form the vertices of a cuboid and the six X sites cap each face, was also apparent and defied facile interpretation. Electron density maps and subsequent refinement allowed X to be identified as Br. Requirements of electroneutrality dictated that site Y contained silver, possibly an $[Ag_4Br_6]^{2-}$ cluster, with Ag^+ occupying alternate corners of the cube, and with Ag^+ then disordered about a 222 site, leading to $[Ag(PBn_3)_2]_2[Ag_4Br_6]$. However, this species was (i) inconsistent with crystal packing, which had eight $[Ag(PBn_3)_2]$ units per cell, requiring tetra-anionic species at the two anion sites per cell, (ii) had unnaturally acute bridging Ag–Br–Ag angles of ~60°, and (iii) on refinement led to values for R_1 (observed data) of more than 0.13 for models assuming no twinning, twinning into pseudo-tetragonality (*hkl* and *khl* superimposed) or twinning into pseudo-cubicity (*hkl*, *lhk* and *klh* superimposed) with substantial residual electron density, both positive and negative in the vicinity of Ag and Br sites, and at the other three sites of 222 point symmetry. Refinement of occupancies of all Ag and Br sites, with tight restraints on electroneutrality, led to considerable improvement in the value for R_1 to 0.093 for the cubic "trilling", with the Y_8X_6 cluster being made up of a pair of disordered triangular $AgBr_3{}^{2-}$ moieties (lying on the body diagonal of the Ag cuboid, and then disordered by crystallographic 222 symmetry). At this stage it was becoming increasingly apparent that one of the other sites of 222 symmetry was only partially occupied by Br^- and another was occupied by water, with the remaining 222 site occupied by the apparent cluster. In addition, considerable negative electron density was concentrated at the Ag^+ sites of the $[Ag(PBn_3)_2]^+$ moieties, located on inversion centers, indicating that these Ag^+ sites might not be fully occupied. Final refinement assigned free variables to the (i) occupancy of Ag^+ in the two sites with –1 point symmetry, (ii) occupancy of the two independent Ag^+ sites in the apparent X_8Y_6 cluster of point symmetry 222 (the two crystallographically independent Ag^+ ions on general positions assigned occupancy of 0.25 based on electron density), (iii) occupancy of the three independent Br^- sites (located on the twofold axes) in the apparent X_8Y_6 cluster, and (iv) occupancy of Br^- on a site of 222 symmetry, with the overall restraint of a net charge balance of zero for the Ag^+ and Br^- ions. The prior refinement established that there was equal occupancy of Ag^+ in each pair of Ag^+ sites and of Br^- in the trio of Br^- sites. Thus, overall the compound is non-stoichiometric. This is summarized in the following expression in which the first term is the charge on the ion, the second term is the number of independent sites, the third term is the maximum occupancy of that site and the fourth term is the refined value of fractional occupancy, with its estimated standard deviation in parentheses:

$$\begin{aligned} 0 = {} & (+1)(2)(0.5)(0.765(3))\ [\mathrm{Ag^+\ in\ Ag(PBn_3)_2}]^+ \\ & (+1)(2)(0.25)(1.354(10))\ [\mathrm{Ag^+\ in\ X_8Y_6\ moiety}]^+ \\ & (-1)(3)(0.5)(0.932(4))\ [\mathrm{Br^-\ in\ X_8Y_6\ moiety}]^+ \\ & (-1)(1)(0.25)(0.178(11))\ [\mathrm{Br^-\ at\ 222\ site}]. \end{aligned}$$

There are eight $[Ag_{0.765}(PBzn)_2]^{+0.765}$ moieties per cell and approximately two pairs of pairs of $AgBr_3{}^{2-}$ moieties with disordered Ag^+ ions per cell. Full occupancy of this site would lead to 12 Br^- and 4 Ag^+ per cell; 11.16 Br^- are observed and 5.42 Ag^+. Immediately adjacent cation sites (X) of the apparent X_8Y_6 moiety are separated by only 2.0 Å and cannot, therefore, be simultaneously occupied. The excess Ag^+ ions, however, requires that in addition to the pairs of body-diagonally related Ag^+ ions there is also a significant fraction of face-diagonally related Ag^+ ions in the cluster. The final ratio of Ag:Br:P is 11.55:11.55:16. Forcing whole-number stoichiometric ratios (e.g. 12:12:16) led to higher values for R_1, as well as patterns of positive and negative peaks consistent with deficits and surpluses of electron density. The final difference Fourier map was flat and featureless. Because of the high degree of pseudo-merohedral twinning (twin law 0 1 0/0 0 1/1 0 0 with refined twin components of 0.219(4) and 0.316(2) and 0.465), false/ghost atoms appeared at special positions in early electron density maps and changes in atomic displacement parameters were often highly correlated, especially for atoms on special positions. Stability of refinement was improved when the geometry of the benzyl groups was restrained by use of free variables. Once the disorder model for the disordered $AgBr_3{}^{2-}$ cluster, for the partly occupied lone Br^- site and for the incomplete occupancy of the Ag^+ site of the $[Ag(PBn_3)_2]$ moiety was deciphered, final refinements converged smoothly. The final value for R_1 (observed data) is 0.0707. The crystal packing of this material is distinctly different to the chloride analog, which is in the subgroup *P*222 of *Pnnn*. Although the arrangement of the $[Ag(PBn_3)_2]$ moieties is essentially identical, the bromide features two disordered $AgBr_3{}^{2-}$ ions per cell and a partially occupied Br^- site, giving a $(AgBr)_{11.55}$ stoichiometry. In contrast, the chloride analog (**2**) has exact stoichiometry Ag:Cl:P of 9:9:16. However, close metrical relationships among atoms led to final refinements being performed in the higher symmetry tetragonal space group *P*4/*nnc* with the empirical formula simplified (within estimated standard deviations) to $Ag_{\sim 11.5}Br_{\sim 11.5}(PBn_{23})_{16}\cdot{\sim}5.5H_2O$ and chemical entities distributed as 0.375/0.50 Ag^+ in the $Ag(PBnz_3)_2$ site of –1 symmetry, 0.34375/1.00 Ag^+ in a general position in the $AgBr_3{}^{2-}$ cluster for which the Br^- occupancies are 0.21875/0.25 for the site of fourfold symmetry and 0.46875/0.50 for the site with twofold [0 1 0] symmetry (numbers after the slash are fractional site multiplicities); stoichiometric balance is achieved by 0.03125/0.125 occupancy by Br^- of the isolated H_2O site of 422 symmetry. A site of 222 symmetry is fully occupied by another H_2O. The final value for R_1 (observed data) is 0.0616, significantly lower than that for the orthorhombic refinement, and the permutative cubic twin law (0 1 0/0 0 1/1 0 0) had final refined components of 0.270(5) and 0.260(5) and 0.530.

2.4. Infrared spectroscopy

Far-infrared spectra were recorded at 4 cm^{-1} resolution on samples suspended in polythene disks using a Nicolet 8700 FT-IR spectrometer or a Perkin Elmer Spectrum 400 FT-IR spectrometer.

2.5. NMR spectroscopy

The ^{31}P cross-polarization, magic-angle-spinning (CPMAS) NMR spectra of compounds **4**, **5** and **7** were recorded at 7.0 T on a Varian Infinity Plus-300 spectrometer operating at a ^{31}P frequency of 121.47 MHz. All spectra were obtained with conventional cross-polarization (CP) methods and a MAS frequency of ~10 kHz using a Bruker 4 mm double-air-bearing probe. The typical pulse parameters employed were: a ^{1}H $\pi/2$ pulse time of 3.5 μs, a Hartmann-Hahn contact period of 10 ms, a recycle delay of 20 s, and a ^{1}H decoupling field strength during acquisition of ~80 kHz. All data were referenced to 85% H_3PO_4 via an external reference of $(NH_4)(H_2PO_4)$ (δ 1.0 ppm), which was also used to set the Hartmann–Hahn match condition. The CPMAS NMR spectrum of 1 was recorded at 9.4 T on a Varian INOVA spectrometer operating at a ^{31}P frequency of 161.92 MHz. Spectra were obtained with conventional CP methods and a MAS frequency of ~5 kHz using a Varian 7 mm CPMAS probe. Two thousand transients were collected using a ^{1}H $\pi/2$ pulse time of 8 μs, a Hartmann–Hahn contact period of 4 ms, an acquisition time of 50 ms and a recycle delay of 15 s. The ^{1}H decoupling field strength during acquisition was ~60 kHz. Spectra were zero filled to 4096 data points and a 20 Hz line broadening applied prior to FT. The ^{31}P chemical shift was referenced to 85% H_3PO_4 via an external reference of triphenylphosphane (δ −9.9 ppm).

3. Results and discussion

3.1. Synthesis

Efforts to prepare complexes of 1:1 stoichiometry from the reaction of one molar equivalent of AgX (X = Cl, Br or I) with PBn_3 were unsuccessful. Instead, the cluster $[Ag_{13}I_{13}(PBn_3)_6]$ (**1**) was isolated when the AgI:PBn_3 ratio was ~2:1, but when the initial molar ratio was 4:1 the complex $[Ag(PBn_3)_2I]$ (**7**) crystallized. The main difference in these two reactions, since unreacted AgI is removed from both, lies in the concentration of PBn_3 which is higher for the latter reaction. For the chloride, when the ratio of AgCl:PBn_3 was 10:1, a compound of stoichiometry $[Ag(PBn_3)_2]_8[AgCl_3]Cl_6$ $6H_2O$ (**2**) was isolated but when the ratio was 1:2 $[Ag(PBn_3)_2Cl]$ (**6**) resulted. In the above reaction from which **2** was isolated, it appeared that **6** was also crystallizing from the solution, which meant the yield of a pure product was very low. For the bromide, tribenzylphosphane oxide, from adventitious oxygen, formed when the AgBr:PBn_3 ratio was 1:1, but when the ratio was 1:2 both the non-stoichiometric species, $Ag_{\sim11.5}Br_{\sim11.5}(PBn_3)_{16}\cdot{\sim}5.5H_2O$ (**3**) and phosphane oxide were isolated. Overall, the variety and complexity of the formulations for these silver(I) compounds indicates that crystal growth occurs from a solution containing a mixture of halide and silver ions and the phosphane ligand. With weakly coordinating anions BF_4^- and PF_6^-, the reactions afforded the compounds $[Ag(PBn_3)_2]X$ [X = PF_6 (**4**) and BF_4 (**5**)].

In contrast to these silver complexes, with gold well defined 1:1 and 1:2 compounds of the type $[Au(PBn_3)X]$ (X = Cl and Br) and $[Au(PBn_3)_2]X\cdot nH_2O$ (X = Cl, n = 1 or 2; X = I, n = 0), respectively, were isolated. Unusually with the latter 1:2 complexes, the halide groups are ionic in contrast to the silver analogs [4].

Interestingly, when AgF was refluxed with PBn_3 in a 1:1 M ratio in $CHCl_3$ the complex $[Ag(PBn_3)_2Cl]\cdot0.33CHCl_3$ was formed presumably accordingly to the equation:

$$AgF + 2PBn_3 + 2CHCl_3 \rightarrow [Ag(PBn_3)_2Cl]\cdot CHCl_3 + CHCl_2F$$

The probable halide exchange reaction of $CHCl_3$ with AgF under mild conditions may have been promoted by the complexation of AgF with the basic PBn_3 which then produces a stronger fluoro nucleophile. Similarly, it has been reported [18] that a halide exchange reaction occurs when 7,7-dichloro-2,5-diphenylbenzocyclopropene reacts with excess AgF in MeCN for 24 h at room temperature. The presence of a coordinating solvent may speed up what is otherwise a slow reaction.

3.2. Crystal structures

Table 2 summarizes the bond lengths and angles for the new compounds. The cluster $[Ag_{13}I_{13}(PBn_3)_6]$ (**1**) has an onion-like structure with overall C_3 symmetry (Fig. 1). At the center is an iodide ion on a special position with C_3 symmetry surrounded trigonal-prismatically by an inner core of six silver ions. These silver ions are arranged with C_3 symmetry and are tetrahedrally coordinated by the innermost iodide ion and by six iodides that bridge to an outer layer of six silver ions. In this outer layer the silver ions are also tetrahedrally coordinated by six bridging iodides and capped by the six PBn_3 ligands, together arranged with S_6 symmetry. The top of the onion features a silver ion lying on the unique threefold axis and capping the cluster with three iodo ligands arranged in a near-planar trigonal arrangement around this silver ion. The inner core of silver ions and iodo ligands, which have C_3 symmetry, are disordered by the crystallographic center of inversion of space group $R\bar{3}$.

The crystal structures of **2**–**5** confirm that the complexes all contain the linear $[Ag(PBn_3)_2]^+$ cation (Fig. 2), as has been observed previously for other d^{10} species, namely Cu(I) [3], Au(I) [4] and Hg(II) [19]. Like these complexes, the Ag(I) also resides within a 'sextuple phenyl embrace' [20] – an array of intramolecular π···H–C interactions between the benzyl groups on different ligands as they encapsulate the metal center.

For $[Ag(PBn_3)_2]_8[AgCl_3]Cl_6\cdot6H_2O$ (**2**) and $Ag_{\sim11.5}Br_{\sim11.5}(PBn_3)_{16}\cdot{\sim}5.5H_2O$ (**3**), the trihalo-anion $[AgX_3]^{2-}$ is disordered, unlike the case for copper(I) where $[CuX_2]^-$ (X = Cl or Br) is found in $[Cu(PBn_3)_2][CuX_2]$ [3]. Both **2** and **3** contain the $[Ag(PBn_3)_2]^+$ cation along with halide ions and water in the lattice, but the bromo complex contains also uncoordinated pairs of PBn_3 molecules (still embracing each other in a sixfold phenyl embrace in the absence of an encapsulated silver ion), non-stoichiometric $AgBr_3^{2-}$ moieties, as well as partially occupied free bromide sites. Although the PBn_3 sites are fully occupied, about a quarter of the encapsulated silver sites are vacant. The $AgBr_3^{2-}$ species appear as motifs in approximately 25% silver-deficient apparent $Ag_4Br_6^{2-}$ clusters.

Table 2
Selected bond lengths (Å) and angles (°) for the silver-tribenzylphosphane compounds **1**–**7**.[a]

Compound	Ag–P	Ag–X	P–Ag–P	P–Ag–X
1	2.458(1)	2.6974(4)–3.0777(5)[b]		121.89(5)–100.20(3)[b]
2	2.377(3)–2.389(3)	2.620(12)–2.714(13)[c]	179.3(2), 178.7(2)	
3	2.402(3)	2.599(5)–2.702(7)[d]	180	
4	2.3742(4)		180	
5	2.3762(5)		180	
6	2.4064(7), 2.4820(8)	2.5508(8)[c]	142.89(3)	125.81(3), 90.58(3)[c]
7	2.4228(7), 2.4335(7)	2.8063(3)[b]	140.00(2)	120.26(2), 99.33(2)[b]

[a] Tables of bond lengths and angles are given in more detail in Supporting Information.
[b] X = I.
[c] X = Cl.
[d] X = Br.

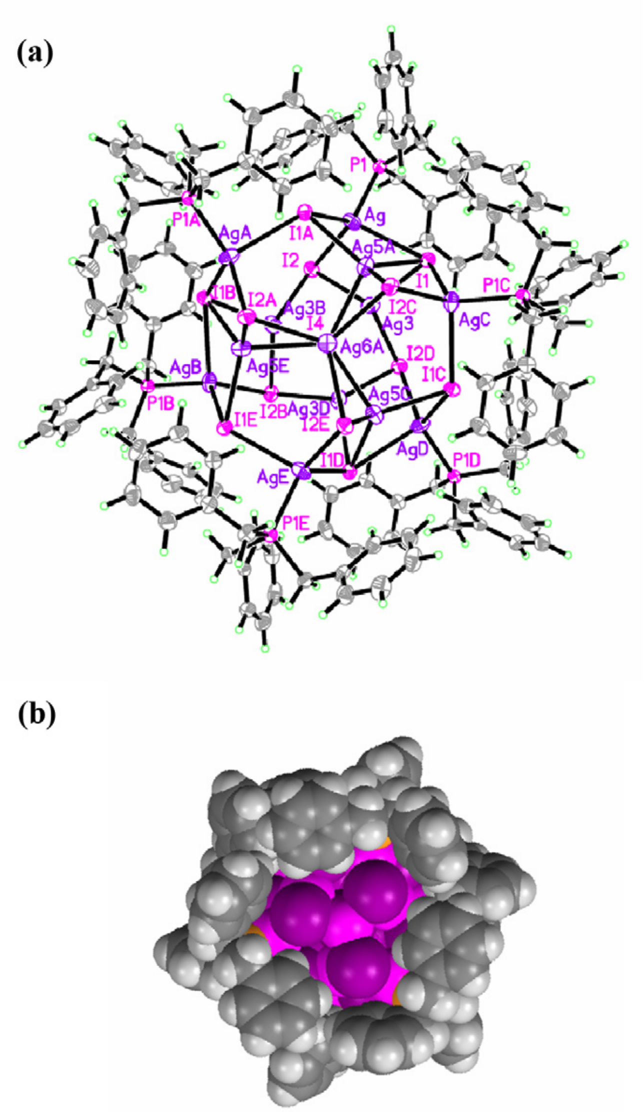

Fig. 1. (a) The structure of $[Ag_{13}I_{13}(PBn_3)_6]$ (**1**) viewed along the unique threefold, Ag6A-I4 axis. Ag6A is bound to I2A, I2C and I2E. The inner iodide ion, I4, is bound to Ag3, Ag3B, Ag3E, Ag5A, Ag5 and Ag5E. Ag, AgA, AgB, AgC, AgD and AgE form the outer layer of silver ions. (b) A space-filling representation of **1** viewed along the Ag6A-I4 threefold axis.

The final refinement (see Experimental Section) indicates the empirical formula can be simplified to $Ag_{\sim 11.5}Br_{\sim 11.5}(PBn_3)_{16}\cdot{\sim}5.5H_2O$. The complex $[Ag(PBn_3)_2]_8[AgCl_3]Cl_6\cdot 6H_2O$ (**2**) appears to be stoichiometric, with two silver ions present in full occupancy in general positions within two pairs of sixfold phenyl embraces of the tribenzylphosphane ligands. Within each $[Ag(PBn_3)_2]^+$ complex the two P–Ag–P bond angles are slightly but significantly distorted from linearity [178.7(2)° and 179.3(2)°]. The $AgCl_3{}^{2-}$ moiety is disordered about a site of 222 symmetry, creating the illusion of an $Ag_4Cl_6^{2-}$ cluster; however, the silver ions occupy general sites with partial 25% occupancy. Isolated non-disordered chloride ions and water molecules complete the crystal structure.

For **2** the four unique Ag–P distances range from 2.377(3) to 2.389(3) Å; for **3** the Ag–P distance is marginally longer at 2.402(3) Å, possibly indicative of a slightly less close approach of PBn_3 moieties in a silver-free phenyl embrace. For **2**, the three AgCl bonds in the $AgCl_3{}^{2-}$ species are 2.620(13), 2.667(13) and 2.714(13) Å and the Cl–Ag–Cl bond angles are 118.5(2)°, 120.0(2)° and 121.4(3)°; for **3** the six unique Ag–Br bonds in the highly disordered $[Ag_{4-z}Br_6]$ cluster range from 2.599(5) to 2.702(7) Å and the Br–Ag–Br bond angles range from 117.4(2)° to 123.8(2)°. There are only a few structurally characterized $AgX_3{}^{2-}$ (X = Cl, Br or I) anions in the literature. For example, discrete slightly distorted $AgI_3{}^{2-}$ ions are found in $[PPh_3Me](AgI_3)$ [21a], but in $[Hg_7As_4](AgI_3)_2$ the anions have an off-plane geometry giving them C_{3v} symmetry [21b]. In contrast $AgCl_3{}^{2-}$ and $AgBr_3{}^{2-}$, which have been isolated as guests in their (dibenzo-18-crown-6)potassium and -rubidium salts, have regular D_{3h} symmetry

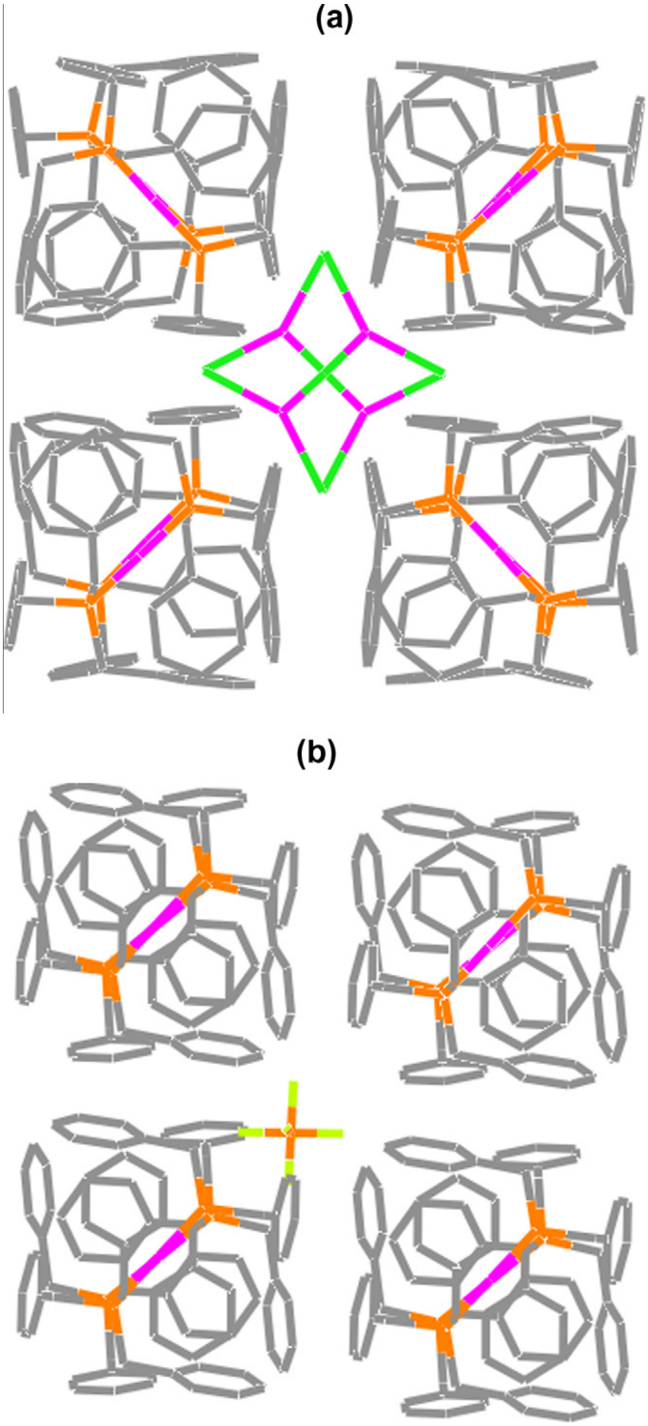

Fig. 2. The packing arrangement of eight $[Ag(PBn_3)_2]^+$ cations. (a) In **3** showing the formation of the anion-containing holes. (b) A similar view of **4**. The packing arrangements for **2** and **5** are also similar.

[21c]. The compound formulated as $[Hg_6As_4](AgCl_3)_2$ contains one-dimensional anionic chains, not discrete $AgCl_3^{2-}$ anions [21d].

In the two-coordinate compounds, **4** and **5**, which contain the non-coordinating anions, PF_6^- and BF_4^- (Fig. 3(a)), the Ag(I) atom lies on a center of symmetry with the P–Ag–P angles necessarily constrained to 180°. Ag–P lengths observed here are 2.3742(4) and 2.3762(5) Å compared with 2.205(3) and 2.2977(8) Å in the analogous $CuPF_6$ and $AuBF_4$ adducts, which like the silver complexes also crystallize in the monoclinic *C*2/*c* space group [3,4]. These observations reinforce the view that relativistic effects are particularly pronounced for gold, making its covalent radius smaller than that of silver regardless of its coordination environment [22]. It should be noted, presumably because of the attractive effect of the intramolecular 'sextuple phenyl embrace', the M–P distances are slightly shorter for the PBn_3 complexes than those observed for another series of linear, two-coordinate coinage metal compounds, $[M(PMes_3)_2]BF_4$ ($PMes_3$ = trimesitylphosphane) with Cu–P, Ag–P and Au–P Å being 2.242(2), 2.4409(9) and 2.3525(10) Å, respectively [22e].

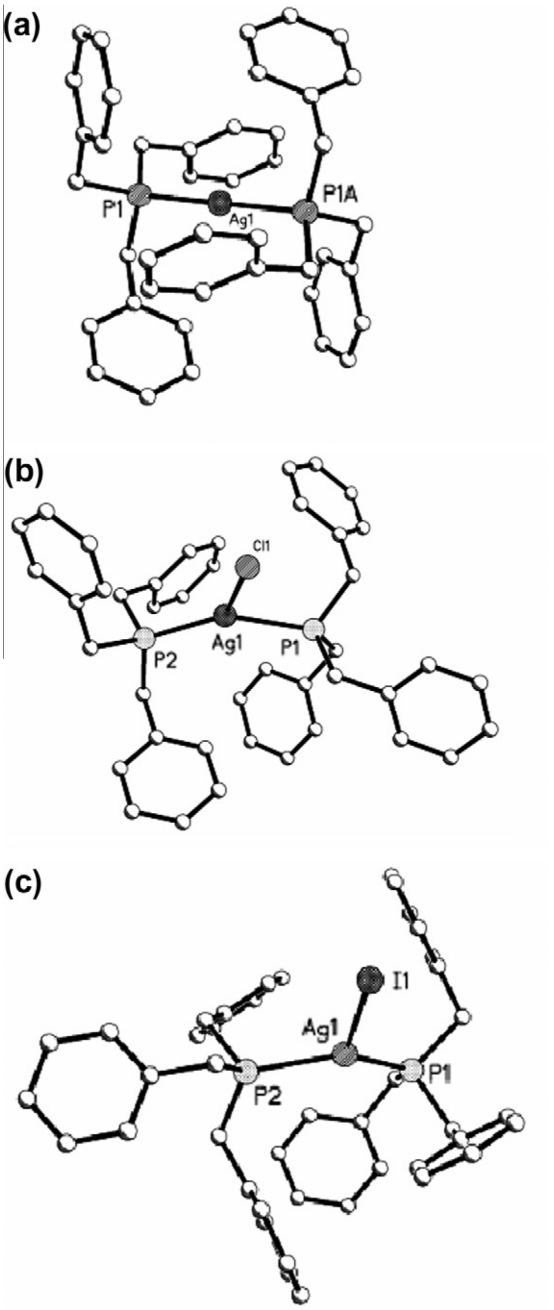

Fig. 3. (a) The linear $[Ag(PBn_3)_2]^+$ cation in the crystal structure of **4**. The structure of the cation in **5** is almost identical. (b) The structure of $[Ag(PBn_3)_2Cl]$ in **6**. (c) The structure of $[Ag(PBn_3)_2I]$ (**7**).

Despite the slightly chaotic nature of the speciation in the compounds **2** and **3**, the packing motifs present in the four crystal structures **2**–**5** are very similar. The six phenyl rings of the 'embrace' in the $Ag(PBn_3)_2$ or '$(PBn_3)_2$' pairs are spatially disposed to approximate as six corners of a cube, with the phosphorus atoms diagonally opposing and sitting on the two remaining corners (Fig. 2). In **2** and **3**, the cubes pack together face-to-face in a regular manner such that a hole is left in the array, approximately where the phosphorus atoms from adjacent molecules are the closest (Fig. 2(a)). Close contacts between phenyl and benzyl hydrogen atoms and the aromatic rings of adjacent molecules cement together these cubic blocks. The spaces that are generated in the lattice near the phosphorus atoms contain the remaining components of the crystal, where further stabilizing hydrogen bonding interactions can occur between the halogen or oxygen atoms and benzyl or aromatic hydrogen atoms. Unlike **2** and **3**, in **4** and **5** all the cubes are lined up in the same direction which means that the

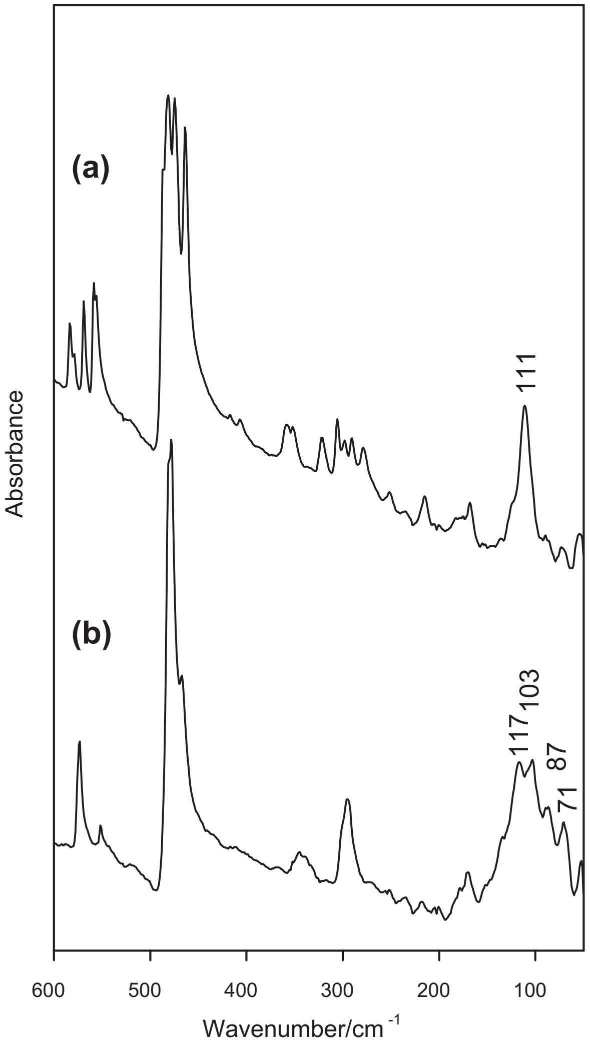

Fig. 4. Far-IR spectra of (a) $[Ag(PBn_3)_2I]$ (**7**); (b) $[Ag_{13}I_{13}(PBn_3)_6]$ (**1**). Bands assigned as *ν*(AgI) are labeled with their wave numbers.

holes that are generated have only half of the cubes with P–Ag–P axes orientated towards the hole (Fig. 2(b)). The PF_6^- counter-ions have a well-defined orientation in the holes that involve C–H···F hydrogen bonding with three of the six fluorine atoms per anion, although some disorder exists in the BF_4^- species. However, in **2** and **3** the holes are much larger, in order to accommodate the disordered orientations of the AgX_3^{2-} anions or the remaining halide ions and water molecules.

The $[Ag(PBn_3)_2X]$ (X = Cl and I) complexes, **6** and **7** (Fig. 3(b) and (c)) contain three-coordinate Ag(I) centers with 'P_2X' donor sets, which are best described as distorted T-shaped. The Ag–P bonds are 2.4064(7) and 2.4820(8) Å for **6** and 2.4228(7) and 2.4335(7) Å for **7**, whereas the bond Ag–Cl is 2.5508(8) Å and Ag–I 2.8063(3) Å. The angles around the coordination plane in both complexes are quite varied, ranging between 90.58(3)° and 142.89(3)° in the chloro complex and 99.33(2)° and 140.00(2)° in the iodo complex.

In both complexes a similar conformational change in one of the PBn_3 ligands (in comparison with $[Ag(PBn_3)_2]^+$) allows coordination of the halide ligand. One ligand of the pair retains approximate C_3 symmetry whereas in the other ligand, rotation about the P–CH_2 bond pins back one of the phenyl rings to make room for the three-coordinate geometry. A partial 'embrace' of intramolecular close contacts is maintained by the other phenyl rings. In **6**, a weak hydrogen bond is formed between the hydrogen atom of the disordered chloroform solvate and the chloride ligand. Similar conformations and coordination geometries have been observed in the $[Cu(PBn_3)_2X]$ (X = Cl, Br and I) complexes [3b].

3.3. Spectroscopic measurements

The far-IR spectrum of $[Ag(PBn_3)_2I]$ (**7**) shows a single ν(Ag–I) band at 111 cm^{-1}, whereas the cluster $[Ag_{13}I_{13}(PBn_3)_6]$ (1) displays a complex set of partially resolved bands from about 120 to 70 cm^{-1} (Fig. 4). The single band for the former complex is consistent with the monomer structure, the ν(Ag–I) frequency being slightly less than the value 121 cm^{-1} found for $[Ag(PCy_3)_2I]$ (PCy_3 = tricyclohexylphosphane) [23]. This is in keeping with the Ag–I bond being longer (2.806 vs. 2.778 Å) and the P–Ag bonds being shorter (2.423 and 2.433 vs. 2.478 Å) in the PBn_3 complex. The ν(Ag–I) range for 1 is similar to that found for $[\{Ag(PCy_3)I\}_4]$ [24] but the band structure is more complex due to the lower symmetry and more complex structure of the former compound.

The ^{31}P CP MAS NMR spectra for **4** and **5** are shown in Fig. 5. The naturally occurring isotopes of silver (^{107}Ag, 51.82% natural abundance; ^{109}Ag, 48.18%) both have nuclear spin $I = ½$, and their magnetogyric ratios are similar in magnitude. The ^{31}P NMR spectra of complexes of silver(I) with phosphorus-donor ligands normally show splitting due to ^1J(P–Ag) coupling but in the solid state separate splitting due to the ^{107}Ag and ^{109}Ag nuclei, which is usually observed in solution, is not normally resolved due to the greater line widths ($\Delta\nu \sim 40$ Hz) that occur under these conditions. The spectrum of the coordinated phosphane thus consists of a doublet with a weighted average ^{31}P–$^{107,109}Ag$ splitting $^1J(^{31}P$–Ag) [23,24].

The solid-state ^{31}P CP MAS NMR spectrum for the iodo-cluster **1** shows a doublet at −4.9 ppm with $^1J(^{31}P$–Ag) = 525 Hz, these parameters being similar to those observed for $[\{Ag(PCy_3)I\}_4]$ [24] which also contains a '$AgPI_3$' coordination sphere. The observation of a single doublet is consistent with the crystallographic equivalence of the six phosphane ligands in the complex (see above). The spectra of $[Ag(PBn_3)_2]PF_6$ (**4**) and $[Ag(PBn_3)_2]BF_4$ (**5**) show doublets for the PBn_3 phosphorus atoms at 42.0 and 44.9 ppm with $^1J(^{31}P$–Ag) = 535 and 522 Hz, respectively (Fig. 5). The spectrum of **4** also shows a signal due to the PF_6^- counterion at −142.5 ppm with $^1J(^{31}P$–Ag) = 717 Hz. The $^1J(^{31}P$–Ag) for the coordinated PBn_3 are similar to those in the related complexes $[Ag(tmpp)_2]ClO_4$ (tmpp = tris(2,4,6-trimethoxyphenylphosphane; 622 Hz) [25], and $[Ag(PCy_3)_2)]ClO_4$ (*ca.* 500 Hz) [23]. The observation of single doublets for the phosphane P atoms in 4 and 5 is consistent with their centrosymmetric structures.

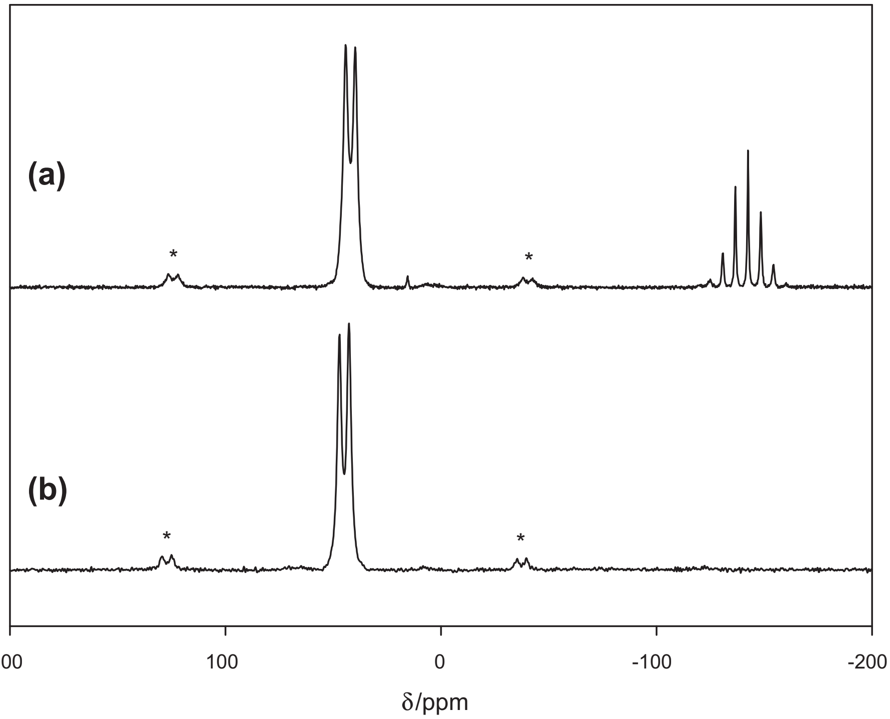

Fig. 5. ^{31}P CP MAS NMR spectra at $B = 7.0$ T of (a) $[Ag(PBn_3)_2]PF_6$ (**4**); (b) $[Ag(PBn_3)_2]BF_4$ (**5**). Peaks marked ∗ are spinning sidebands.

4. Conclusions

The chemistry of the silver(I)–tribenzylphosphane system is considerably more varied than that observed for the copper(I) or gold(I) analogs, resulting in the formation of the unique iodo cluster, $[Ag_{13}I_{13}(PBn_3)_6]$ (**1**), and the identification of the unusual chloro and bromo derivatives, $[Ag(PBn_3)_2]_8[AgCl_3]Cl_6{\cdot}6H_2O$ (**2**), and $Ag_{\sim 11.5}Br_{\sim 11.5}(PBn_3)_{16}{\cdot}{\sim}5.5H_2O$ (**3**) in the presence of coordinating anions. The formation of $[Ag(PBn_3)_2]^+$ in **2** and **3**, and also in the presence of non-coordinating anions PF_6^- and BF_4^-, reinforces the propensity for tribenzylphosphane to readily form linear two-coordinate cations owing to the driving force of the 'sextuple phenyl embrace' [20]. In this respect Ag(I) resembles the other d^{10} metals, Cu(I), Au(I) and Hg(II).

Acknowledgments

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Appendix A. Supplementary material

CCDC 787379, 787380, 787381, 787382, 787383, 787384 and 787385 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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