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Spectroscopic and structural studies on 1 : 1 adducts of silver(I) salts with tricyclohexylarsine

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Adducts of a number of silver(I) salts, AgX, with tricyclohexylarsine, of 1 : 1 AgX : $As(C_6H_{11})_3$ stoichiometry have been synthesized for X = Cl, Br, I, NO_3, NCO or CN and subjected to room temperature single crystal X-ray determinations and studies of their low frequency vibrational spectra. The chloride is binuclear $[\{(C_6H_{11})_3As\}Ag(\mu\text{-}Cl)_2Ag\{As(C_6H_{11})_3\}]$, isomorphous with its previously recorded $P(C_6H_{11})_3$, X = Cl, Br counterparts, the silver environment being quasi-planar, trigonal $AsAg(\mu\text{-}Cl)_2$; the nitrate is isomorphous, with a central planar $Ag(\mu\text{-}O)_2Ag$ array, a pair of oxygen atoms, one from each of a pair of symmetry-related nitrate groups, bridging the two silver atoms. The present bromide, unlike its $P(C_6H_{11})_3$ counterpart, is not a dimer, but, like the iodide, a 'cubane' tetramer; the iodide is isomorphous with its $P(C_6H_{11})_3$ analogue, a crystallographic 2 axis passing through a pair of opposed faces of the tetramer, but the bromide is of a new type, rhombohedral space group $R\bar{3}$. Remarkably, the cyanate is also of the cubane form, the first recorded (other than an organometallic) incorporating a first-row atom, obtained unsolvated and bis(pyridine) solvated. The cyanide is a linear polymer . . . $\{(C_6H_{11})_3As\}_2AgNCAgCN\{As(C_6H_{11})_3\}_2AgNC$ . . . ('α' phase, from 2-methylpyridine); a second 'β' phase was obtained from 2,4,6-trimethylpyridine, of similar form, while from pyridine, a solvate of 3 : 4 : 2 AgCN : $As(C_6H_{11})_3$: py stoichiometry $[\{Ag[As(C_6H_{11})_3]_2(py)\}_2(CN)][Ag(CN)_2]$ was obtained. The structure of the E = P*x* = CN unsolvated 1 : 1 analogue was also determined, also being a linear polymeric array like its E = As counterpart. The far-IR spectra of the halide complexes exhibit bands due to ν(AgX) vibrational modes at 229, 148 cm^{-1} (X = Cl), 167, 151, 125, 109 cm^{-1} (X = Br) and at 111, 86 cm^{-1} (X = I). These spectra were interpreted in terms of idealised C_{2h} Ag_2Cl_2 and T_d Ag_4X_4 structures of the silver halide cores.

In the preceding paper[1] we have recorded the results of synthetic, structural (room-temperature, single crystal X-ray) and low-frequency vibrational spectroscopic studies on adducts of silver(I) salts, AgX, with tricyclohexylarsine, of 1 : 2 stoichiometry, accessing and defining an extensive novel, mononuclear array of As_2AgX environments, paralleling those found similarly with tricyclohexylphosphine.[2] With $P(C_6H_{11})_3$ a family of 1 : 1 adducts has also been defined, the chloride and bromide being binuclear and the iodide tetranuclear,[3] contrasting with the linear two-co-ordinate array found in AuCl : $P(C_6H_{11})_3$ (1 : 1),[4] paralleled in many more AuX : $P(C_6H_{11})_3$ (1 : 1) species with more complex X. In the present report we describe the results of a counterpart study of the parallel 1 : 1 array, specifically for X = Cl, Br, I, NO_3 or NCO; while, unsurprisingly, the halides and nitrate are $Ag(\mu\text{-}X)_2Ag$ or Ag_4X_4 binuclear or tetranuclear 'cubane' arrays, the cyanate, remarkably, is also a cubane tetramer, obtained in two forms, as is the cyanide, a linear polymer. We have also obtained the 1 : 1 $P(C_6H_{11})_3$: CN analogue of the arsenic complex described above; as with many of the cyanide arrays described here and in other studies,[5] the joint objectives of obtaining nicely crystalline material suitable for X-ray work and substantial pure homogeneous bulk sample for elemental analysis and spectroscopy become increasingly difficult of simultaneous achievement, some complexes being loosely solvated while others appear to provide crystals in an ill defined matrix of, presumably, various polymer forms, which the cyanides are prone to form, and where characterisation depends heavily on the X-ray work. Caveats concerning the latter are described at length in ref. 1.

Experimental

Syntheses

All compounds were obtained by the dissolution of the appropriate silver(I) salt (1 mmol) with tricyclohexylarsine (1 mmol) in pyridine (5 cm^3) [exceptions: the nitrate (methanol) and the cyanide (2-methyl- or 2,4,6-trimethyl-pyridine)] with warming, followed by cooling and standing, whereupon colourless crystals deposited. X = Cl: m.p. 208–211 °C (Found: C, 46.3; H, 7.10. Calc. for $C_{36}H_{66}Ag_2As_2Cl_2$: C, 46.23; H, 7.11%). X = Br: m.p. >203 °C (Found: C, 42.4; H, 6.3. Calc. for $C_{72}H_{132}Ag_4As_4Br_4$: C, 42.21; H, 6.49%). X = I: m.p. >199 °C (decomp.) (Found: C, 38.8; H, 6.1. Calc. for $C_{72}H_{132}Ag_4As_4I_4$: C, 38.67; H, 5.95%). X = NO_3: m.p. > 112 °C (Found: C, 43.6; H, 6.9; N, 3.0. Calc. for $C_{36}H_{66}Ag_2As_2N_2O_6$: C, 43.74; H, 6.73; N, 2.83%). X = NCO: m.p. >211 °C (decomp,), no satisfactory analysis obtained. X = CN (Found: C, 50.1; H, 7.2; N, 3.1. Calc. for $C_{38}H_{66}Ag_2As_2N_2$: C, 49.8; H, 7.26; N, 3.06%). The 1 : 1 AgCN : $P(C_6H_{11})_3$ adduct was obtained similarly from pyridine, m.p. 136–138 °C (Found: C, 54.7; H, 7.7; N, 4.5. Calc. for $C_{19}H_{33}AgNP$: C, 55.08; H, 8.03; N, 3.38%).

Structure determinations

The general procedure is given in the preceding paper;[1] specific details are as follows.

(***a***) Triclinic, space group $P\bar{1}$ (C_i^1, no. 2), $Z = 1$ dimer. (*i*) **X = Cl.** $C_{36}H_{66}Ag_2As_2Cl_2$, $M = 935.4$, $a = 8.827(2)$, $b = 9.451(2)$, $c = 13.338(2)$ Å, $\alpha = 99.41(3)$, $\beta = 93.66(2)$, $\gamma = 114.96(2)°$, $U = 984.1$ Å^3, $D_c = 1.57_8$ g cm^{-3}, $F(000) = 476$, $\mu_{Mo} = 28.2$ cm^{-1}, specimen 0.13 × 0.30 × 0.20 mm; $A^*_{min,max} = 1.53, 1.90$, $2\theta_{max} = 55°$, $N = 4519$, $N_o = 3121$, $R = 0.036$, $R' = 0.039$.

(*ii*) **X = NO$_3$.** $C_{36}H_{66}Ag_2As_2N_2O_6$, $M = 988.5$, $a = 9.244(3)$, $b = 9.628(3)$, $c = 13.343(2)$ Å, $\alpha = 96.77(2)$, $\beta = 90.72(2)$, $\gamma = 117.32(3)°$, $U = 1044._8$ Å^3, $D_c = 1.57_1$ g cm^{-3}, $F(000) = 504$, $\mu_{Mo} = 25.5$ cm^{-1}, specimen 0.42 × 0.26 × 0.18 mm, $A^*_{min,max} = 1.51, 1.89$, $2\theta_{max} = 50°$, $N = 3669$, $N_o = 2809$, $R = 0.040$, $R' = 0.047$.

Variata. The cell and coordinate setting follows that previously defined for the isomorphous chloride $P(C_6H_{11})_3$ counterpart.[3] For the chloride, $(x, y, z, U_{iso})_H$ were refined. In the nitrate high 'thermal motion' on two of the rings suggests unresolved disorder.

(*b*) X = Br. $C_{72}H_{132}Ag_4As_4Br_4$, $M = 2048.7$, rhombohedral, space group $R\bar{3}$ (C^2_{3i}, no. 148), $a = 22.482(5)$, $c = 28.35(2)$ Å, $U = 12\,413$ Å^3 (hexagonal setting), D_c ($Z = 6$ tetramers) $= 1.64_5$ g cm^{-3}, $F(000) = 6144$, $\mu_{Mo} = 44.9$ cm^{-1}, specimen $0.12 \times 0.15 \times 0.21$ mm, $A^*_{min,max} = 1.75$, 3.73 (analytical correction), $2\theta_{max} = 50°$, $N = 4857$, $N_o = 1471$, $R = 0.057$, $R' = 0.049$.

Variata. The three rings of ligand 1 were modelled as disordered over two sites, occupancy 0.5, with isotropic thermal parameter forms.

(*c*) X = I. $C_{72}H_{132}Ag_4As_4I_4$, $M = 2236.7$, monoclinic, space group $C2/c$ (C^6_{2h}, no. 15), $a = 15.660(7)$, $b = 29.284(9)$, $c = 19.312(6)$ Å, $\beta = 108.67(3)°$, $U = 8390$ Å^3, D_c ($Z = 4$ tetramers) $= 1.77_0$ g cm^{-3}, $F(000) = 4384$, $\mu_{Mo} = 39.9$ cm^{-1}, specimen $0.28 \times 0.56 \times 0.38$ mm, $A^*_{min,max} = 2.60$, 3.45 (analytical correction), $2\theta_{max} = 50°$, $N = 7378$, $N_o = 3736$, $R = 0.046$, $R' = 0.045$.

Variata. The compound is isomorphous with its $P(C_6H_{11})_3$ counterpart[3] and was refined in that cell and coordinate setting. 'High thermal motion' appears a foil for widespread disorder, resolved in ring 22.

(*d*) X = NCO. This compound was obtained, unsolvated from MeCN, and as a bis(pyridine) solvate from pyridine, the structures of both having been determined. The latter, being the more precise, is recorded in detail here, further details for the unsolvated form being deposited.

(*i*) *Unsolvated.* $C_{76}H_{132}Ag_4As_4N_4O_4$, $M = 1897.1$, rhombohedral, space group $R3$ (C^4_3, no. 146), $a = 24.181(4)$, $c = 12.615(2)$ Å, $U = 6379$ Å^3 (hexagonal setting), D_c ($Z = 3$ tetramers) $= 1.47_9$ g cm^{-3}, $F(000) = 2904$, $\mu_{Mo} = 24.9$ cm^{-1}, specimen $0.32 \times 0.12 \times 0.41$ mm, $A^*_{min,max} = 1.35$, 1.74, $2\theta_{max} = 55°$; $N = 3254$, $N_o = 1352$; $R = 0.058$, $R' = 0.058$ (preferred hand).

(*ii*) Bis(pyridine) solvate. $C_{76}H_{132}Ag_4As_4N_4O_4 \cdot 2C_5H_5N$, $M = 2055.3$, monoclinic, space group $C2/c$ (C^6_{2h}, no. 15), $a = 27.536(9)$, $b = 14.667(7)$, $c = 24.008(9)$ Å, $\beta = 106.51(3)°$, $U = 9297$ Å^3, D_c ($Z = 4$ tetramers) $= 1.46_8$ g cm^{-3}, $F(000) = 4208$, $\mu_{Mo} = 22.9$ cm^{-1}, specimen $0.44 \times 0.07 \times 0.32$ mm, $A^*_{min,max} = 1,18$, 2.31, $2\theta_{max} = 50°$, $N = 7841$, $N_o = 2506$, $R = 0.050$, $R' = 0.042$.

Variata. For the unsolvated specimen, data although extensive were weak, and, in the context of a non-centrosymmetric space group and disorder in the axial ligand substituents, as well as the axial cyanate which inclines to the axis from its point of attachment, would support meaningful anisotropic thermal parameter refinement for Ag, As only, with some further constraints in ligand and anion geometries. High 'thermal motion' was also evident in certain of the rings of the solvated form, modelled as such in the context of the inability meaningfully to deconvolute any disordered components. For both forms, the assignment of anion atoms was problematic, favouring N coordination, but with some dubiousness occasioned by occurrences such as a need to refine the central carbon of anion 2 in the solvated form with an isotropic thermal parameter and in the unsolvated form to constrain components of the anion geometry.

(*e*) X = CN. $C_{38}H_{66}Ag_2As_2N_2$, $M = 916.6$.

α *Phase.* Monoclinic, space group $P2_1/n$ (C^5_{2h}, no. 14, variant), $a = 10.140(4)$, $b = 25.542(9)$, $c = 15.520(4)$ Å, $\beta = 90.63(3)°$, $U = 4020$ Å^3, D_c ($Z = 4$) $= 1.51_4$ g cm^{-3}, $F(000) = 1872$, $\mu_{Mo} = 26.3$ cm^{-1}, specimen $0.27 \times 0.08 \times 0.05$ mm, $A^*_{min,max} = 1.12$, 1.26, $2\theta_{max} = 48°$, $N = 6309$, $N_o = 2858$; $R = 0.058$, $R' = 0.058$.

Variata. Assignment of the cyanide C, N components, made on the basis of refinement behaviour and consistent with the usual NCAgCN component norm, should, none the less, be taken with a grain of salt in consequence of a rather weak body of data, consistent with small crystal size.

β *Phase.* Monoclinic, space group $P2_1/c$ (C^5_{2h}, no. 14), $a = 9.815(3)$, $b = 17.829(7)$, $c = 24.216(8)$ Å, $\beta = 103.63(3)°$, $U = 4118$ Å^3, D_c ($Z = 4$) $= 1.47_8$ g cm^{-3}, $F(000) = 1872$, $\mu_{Mo} = 25.7$ cm^{-1}, specimen $0.50 \times 0.28 \times 0.13$ mm, $A^*_{min,max} = 1.34$, 1.79, $2\theta_{max} = 50°$, $N = 7248$, $N_o = 3704$, $R = 0.053$, $R' = 0.051$.

Variata. This material was obtained by crystallisation from 2,4,6-trimethylpyrdine. A similar caveat to the above applies in respect of cyanide C, N assignment. High thermal motion on rings 21, 23 is probably a foil for unresolved disorder.

(*f*) $[\{Ag[As(C_6H_{11})_3]_2(py)\}_2(CN)][Ag(CN)_2]$. Crystallization of the cyanide from pyridine yielded small crystals of an adduct of 3 : 4 : 2 AgCN : $As(C_6H_{11})_3$: py stoichiometry (Found: C, 55.2; H, 7.6; N, 3.5. $C_{85}H_{142}Ag_3As_4N_5$ requires C, 54.97; H, 7.71; N, 3.77%), also the subject of a rather imprecise albeit useful determination: $C_{85}H_{142}Ag_3As_4N_5$, $M = 1857.4$, monoclinic, space group $P2_1$ (C^2_2, no. 4), $a = 14.887(6)$, $b = 14.429(3)$, $c = 20.636(7)$ Å, $\beta = 97.79(3)°$, $U = 4392$ Å^3, D_c ($Z = 2$) $= 1.40_4$ g cm^{-3}, specimen $0.21 \times 0.33 \times 0.12$ mm, $A^*_{min,max}$ 1.24, 1.64, $2\theta_{max} = 50°$, $N = 8040$, $N_o = 2839$, $R = 0.075$, $R' = 0.070$ (preferred hand).

Variata. The cyanide C, N assignment caveat applies, atoms in the cation being modelled as composites and in the anion as C-bound. Data were weak and limited in scope, supporting, in the context of a non-centrosymmetric space group, meaningful anisotropic thermal parameter refinement for Ag, As only.

(*g*) X = CN, E = P. This is similar in unit cell to the β form of the arsine derivative (*e*) above but is triclinic: $C_{38}H_{66}Ag_2N_2P_2$, $M = 828.7$, triclinic, space group $P\bar{1}$ (C^1_i, no. 2), $a = 23.063(9)$, $b = 17.557(6)$, $c = 10.17(1)$ Å, $\alpha = 90.02(5)$, $\beta = 94.88(6)$, $\gamma = 101.06(3)°$, $U = 4027$ Å^3, D_c ($Z = 4$) $= 1.36_7$ g cm^{-3}, $F(000) = 1728$, $\mu_{Mo} = 9.8$ cm^{-1}, specimen $0.30 \times 0.14 \times 0.52$ mm, $A^*_{min,max} = 1.14$, 1.33, $2\theta_{max} = 50°$, $N = 12\,235$, $N_o = 6647$; $R = 0.069$, $R' = 0.073$.

Variata. Cyanide groups within the NCAgCN array were modelled as C-bound, albeit undefinitively.

CCDC reference number 186/984.

See http://www.rsc.org/suppdata/dt/1998/2131/ for crystallographic files in .cif format.

Spectroscopy

Far-infrared spectra were recorded at 4 cm^{-1} resolution at room temperature as Polythene discs on a Digilab FTS-60 Fourier transform infrared spectrometer employing an FTS-60V vacuum optical bench with a 6.25 µm mylar film beam splitter, a mercury lamp source and a pyroelectric triglycine sulfate detector.

Discussion

Crystal structures

Crystallization of a variety of silver(I) salts, AgX (X = Cl, Br, I or NO_3), with tricyclohexylarsine in 1 : 1 stoichiometric ratio from acetonitrile results in the production of a number of colourless crystalline complexes; the results of room-temperature single crystal X-ray determinations, coupled with elemental analysis, are consistent with the stoichiometry and connectivity implied in the AgX : $As(C_6H_{11})_3$ (1 : 1) formulation. The structures of a selection of the compounds studied are shown in Figs. 1–4. The chloride is isomorphous with its $P(C_6H_{11})_3$ counterpart, [and the AgBr : $P(C_6H_{11})_3$ (1 : 1) adduct] crystallizing in a triclinic $P\bar{1}$ cell which contains one centrosymmetric dimer of the form $[\{(C_6H_{11})_3E\}Ag(\mu\text{-}X)_2Ag\{E(C_6H_{11})_3\}]$, one half of which comprises the asymmetric unit of the structure. Geometries of the systems are compared in Table 1, together with that of a counterpart nitrate adduct, also isomorphous, and isolated with the present array; there appear to be no other structurally characterised oxyanion counterparts hitherto described for any AgX : P$(C_6H_{11})_3$ (1 : 1) system. By contrast, $AgNO_3$: EPh_3 (1 : 1) (E = P,[6] As[7] or Sb[8]) have all been defined as one-dimensional polymers, rather than the present dimeric type. The form of the present nitrate is of interest, the anion bridging by way of a single oxygen atom, rather than various alternatives. The silver–silver distance is much longer than in the chloride, but the two Ag · · · O distances may be regarded as unsymmetrical here also, as also are the As–Ag–O angles. The nitrate itself is also unsymmetrically disposed *vis-à-vis* the two silver atoms, so that O(2), O(3) · · · Ag, Ag′ distances are unsymmetrical, with O(2) displaying a semichelate interaction. The nitrate plane is tilted relative to the Ag(μ-O)$_2$Ag plane, the dihedral angle being 44.3(3)°.

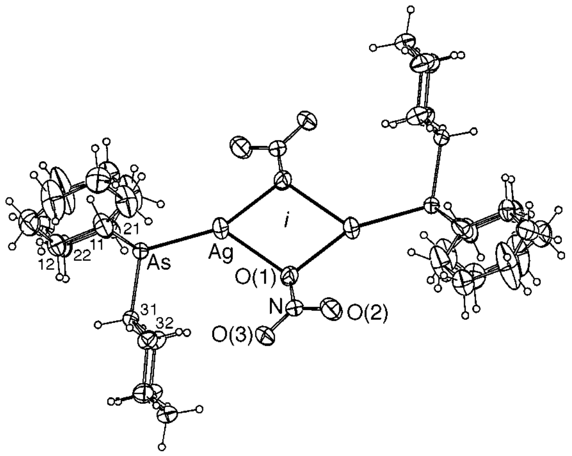

Fig. 1 Projection of the binuclear nitrate, normal to the Ag(μ-O)$_2$Ag plane; 20% thermal envelopes are shown for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å

Table 1 Dimer core geometries in [{[$(C_6H_{11})_3$E]AgX}$_2$]. Distances in Å, angles in °; primed atoms are centrosymmetrically related

	E/X		
	P/Cl	As/Cl	As/ONO$_2$
Ag–X	2.640(3)	2.643(2)	2.428(6)
Ag–X′	2.454(2)	2.456(1)	2.269(5)
Ag–E	2.354(2)	2.4519(9)	2.4198(8)
Ag · · · Ag′	3.488(2)	3.3809(9)	3.807(1)
X · · · X	3.718(3)	3.822(2)	2.757(7)
Ag–X–Ag′	86.33(6)	82.97(4)	108.2(2)
X–Ag–X′	93.67(7)	97.03(5)	71.8(2)
E–Ag–X	118.85(6)	115.76(4)	130.0(1)
E–Ag–X′	147.48(6)	147.21(4)	158.3(1)

In the nitrate Ag · · · O(2′) is 2.792(5) Å; N–O(1,2,3) are 1.245(6), 1.197(8), 1.225(9) Å, with angles opposed being 121.3(5), 121.8(6), 116.9(5)°.

The iodide is also isomorphous with its P$(C_6H_{11})_3$ counterpart, being a tetramer of the 'cubane' type, lying disposed about a crystallographic 2 axis in monoclinic space group *C*2/*c* (the axis passing through the midpoints of an opposed pair of Ag_2I_2 faces); geometries are compared in Table 2. The bromide, unlike its P$(C_6H_{11})_3$ analogue which is a dimer, is also a tetramer of the cubane form, but not isomorphous with the iodide, crystallising in rhombohedral space group $R\bar{3}$, a crystallographic 3 axis passing through bromide, silver and arsenic sequence disposed along a cube body diagonal; the core geometry is given in Table 3. The crystal packing is of some interest here, the molecules being disposed in layers normal to the 3 axis, the axial ligands projecting and plugging into cavities in the adjacent layers (Fig. 3).

The cyanate, also a tetramer, obtained in both unsolvated and bis(pyridine) solvated forms is remarkable; although cubane types are well known among coinage metal(I) salt : Group V unidentate base adducts of 1 : 1 stoichiometry, their occurrence is hitherto restricted to halides X = Cl, Br or I, with the 'step' form as a less frequent alternative. The present is the first recorded occurrence of a pseudohalogen example, the anion participating by co-ordination of one of its termini within the cube, the remaining linearly disposed atoms projected outwards along the putative 3 axis. Which end of the anion coordinates is not definitively established by the X-ray work here, crystals of both forms being deficient in respect of the precision achievable within the determination; for the present, in lieu of a better experiment, we accept indication on the basis of the refinement that it is the nitrogen atom, as might be expected on the basis of previous studies.[2,9–11] The present complex is the first example of an $L_4M_4X_4$ 'cubane' structure in which X = pseudohalide. Other examples of such structures in which the anion component X is a first row atom donor ligand are known, including organometallic compounds (*e.g.* [Cu_4{P(C_6H_4Me-*p*)$_3$}$_4$(μ_3-η^1-C≡CPh)$_4$]),[12] and further examples may prove to be achievable (there being no recorded fluoride examples) with species such as azide. The 'cube' in the present form is the

Table 2 Tetramer core geometries in cubane [{[$(C_6H_{11})_3$E]AgX}$_4$]. Distances in Å, angles in °; primed atoms are related by the internal 2 axis. The two values in each entry are for E = P, As respectively for X = I, followed by X = NCO

Ag(1)–X(1)	2.889(2), 2.897(2); 2.46(1)	Ag(2)–X(1)	2.848(2), 2.839(1); 2.39(1)
Ag(1)–X(2)	2.902(2), 2.900(2); 2.36(1)	Ag(2)–X(2)	3.095(2), 3.050(2); 2.41(1)
Ag(1)–X(1′)	2.975(2), 2.933(1); 2.50(1)	Ag(2)–X(2′)	2.861(2), 2.851(2); 2.48(2)
Ag(1)–E(1)	2.470(4), 2.560(2); 2.461(2)	Ag(2)–E(2)	2.435(2), 2.536(1); 2.467(2)
Ag(1) · · · Ag(1′)	3.555(2), 3.341(2); 3.554(2)	X(1) · · · X(1′)	4.602(2), 4.699(2); 3.46(2)
Ag(1) · · · Ag(2′)	3.749(2), 3.551(2); 3.510(2)	X(1) · · · X(2′)	4.226(1), 4.290(2); 3.36(2)
Ag(1) · · · Ag(2)	3.356(2), 3.203(2); 3.360(2)	X(1) · · · X(2)	4.811(2), 4.884(2); 3.44(2)
Ag(2) · · · Ag(2′)	3.818(2), 3.589(2); 3.465(2)	X(2) · · · X(2′)	4.512(2), 4.601(2); 3.46(2)
Ag(1) · · · X(2′)	4.879(2), 4.820(2); 4.22(1)	Ag(2) · · · X(1′)	5.040(2), 4.964(2); 4.20(1)
X(1)–Ag(1)–X(2)	112.38(5), 114.82(4); 91.1(4)	X(1)–Ag(2)–X(2)	108.02(5), 112.00(4); 91.4(4)
X(1)–Ag(1)–X(1′)	103.41(6), 107.43(5); 88.4(4)	X(1)–Ag(2)–X(2′)	95.50(4), 97.85(4); 87.3(5)
X(2)–Ag(1)–X(1′)	91.95(4), 94.69(3); 87.8(5)	X(2)–Ag(2)–X(2′)	98.45(4), 102.40(4); 89.9(5)
E(1)–Ag(1)–X(1)	110.4(1), 107.25(5); 124.8(3)	E(2)–Ag(2)–X(1)	122.07(9), 117.91(5); 127.4(3)
E(1)–Ag(1)–X(2)	124.4(1), 121.38(6); 133.3(3)	E(2)–Ag(2)–X(2)	100.9(1), 100.12(5); 124.0(3)
E(1)–Ag(1)–X(1′)	110.3(1), 109.83(5); 118.6(3)	E(2)–Ag(2)–X(2′)	128.7(1), 125.77(5); 125.5(3)
Ag(1)–X(1)–Ag(2)	71.60(5), 67.88(4); 87.6(4)	Ag(1)–X(2)–Ag(2)	67.97(4), 65.08(3); 89.6(4)
Ag(1)–X(1)–Ag(1′)	74.63(5), 69.94(4); 91.6(4)	Ag(1)–X(2)–Ag(2′)	81.7(4), 76.25(3); 93.0(5)
Ag(2)–X(1)–Ag(1′)	80.12(4), 75.91(3); 91.8(4)	Ag(2)–X(2)–Ag(2′)	79.62(5), 74.82(4); 90.1(5)

In the cyanate N–C, C–O for anions 1 and 2 are 0.81(2), 1.39(2) and 1.06(2), 1.24(2) Å; N–C–O are 176(2) and 177(2)°. Ag(1,1′,2)–N–C are 123(1), 125(2), 128(2) (anion 1) and Ag(2,2′,1)–N–C are 125(1), 125(1), 124(1)° (anion 2).

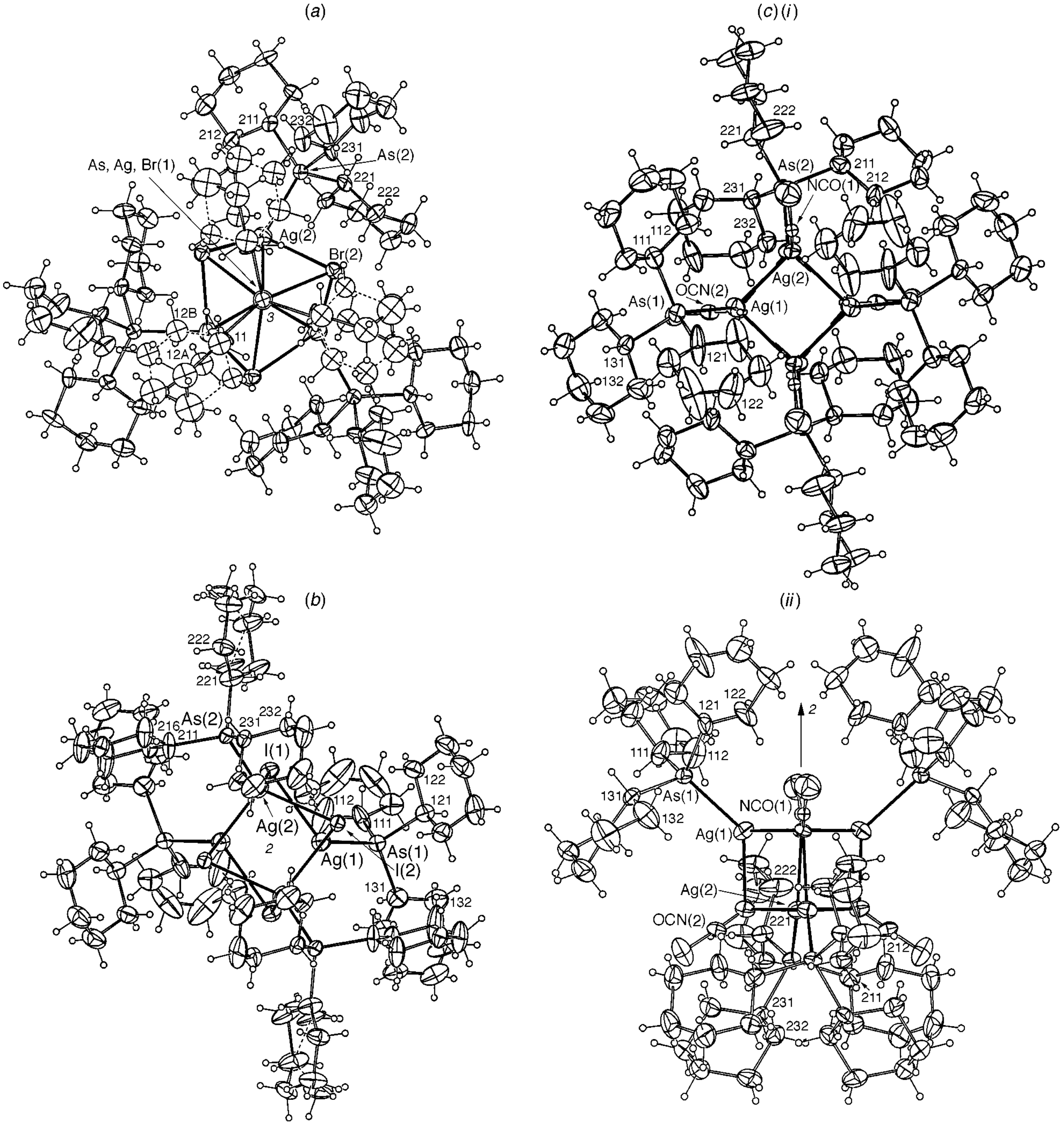

Fig. 2 (*a*), (*b*) The bromide and iodide 'cubane' structures, projected down their 3 and 2 axes respectively. (*c*) The cyanate [bis(pyridine) solvate form], projected (*i*) down and (*ii*) normal to the 2 axis

most nearly 'cubic' example, angles at the silver and nitrogen atoms within the array lying closer to 90° than in any other systems hitherto recorded.

The cyanide, by contrast, is a polymer, found so far, in two phases, α and β, depending on the crystallisation solvent, and of similar type, taking the form of a 1:2 complex with the complex ion $[Ag(CN)_2]^-$ as the counter ion which then bridges successive $Ag\{As(C_6H_{11})_3\}_2$ units in the manner of the 1:2 thiocyanate complex described in the previous paper:[1] $\cdots\{(C_6H_{11})_3As\}_2Ag(NCAgCN)\{(C_6H_{11})_3\}_2Ag\cdots$ [Fig. 4(*a*)], assignment of the C, N components of the anion being tentatively made on the basis of refinement behaviour in the context of weak data and consistent with C-bound cyanide within the anionic (NCAgCN) component. One $\cdots\{(C_6H_{11})_3As\}_2Ag(NCAgCN)\cdots$ unit comprises the asymmetric unit of the polymer which is generated by the unit *a* translation in the α form and the 2_1 screw of the monoclinic space group $P2_1/c$ in the β form. Selected structural parameters are listed in Table 4. The geometry of the linear NCAgCN anionic component is unremarkable, being comparable to those of the numerous examples of it as a discrete entity. About the 'cationic' silver, Ag(1), in an As_2AgN_2 environment, we find that the As–Ag–As angle is considerably enlarged here [144.20(8), 137.20(6)°, *cf.* the thiocyanate[1] 121.84(7), 122.11(9)°], as is N–Ag–N, *cf.* N–Ag–S 108.3(5), 104.0(4) *vs.* 94.2(5), 96.8(4)°. The Ag–As distances are only slightly shorter here 2.539(2), 2.568(2), 2.576(1), 2.545(2) Å, *cf.* 2.573(1)–2.581(2) Å, while Ag–N are intermediate [2.43(1), 2.51(2); 2.41(1), 2.38(1) Å] *cf.* 2.33(1), 2.36(2) (Ag–N) and 2.602(5), 2.602(5) (Ag–S) of the thiocyanate. An interesting feature of both phases is the non-linear co-ordination of one of the anionic cyanides to the cationic silver [Ag–N–C 134(1), 145(1)°]. The E = P analogue, whose characterisation rests on the single crystal X-ray study, is similar in nature, crystallising in a derivative triclinic cell, wherein a pair of independent pseudo-symmetrically related strands of polymer lying parallel to *a* each contribute one repeat unit to the asymmetric unit of

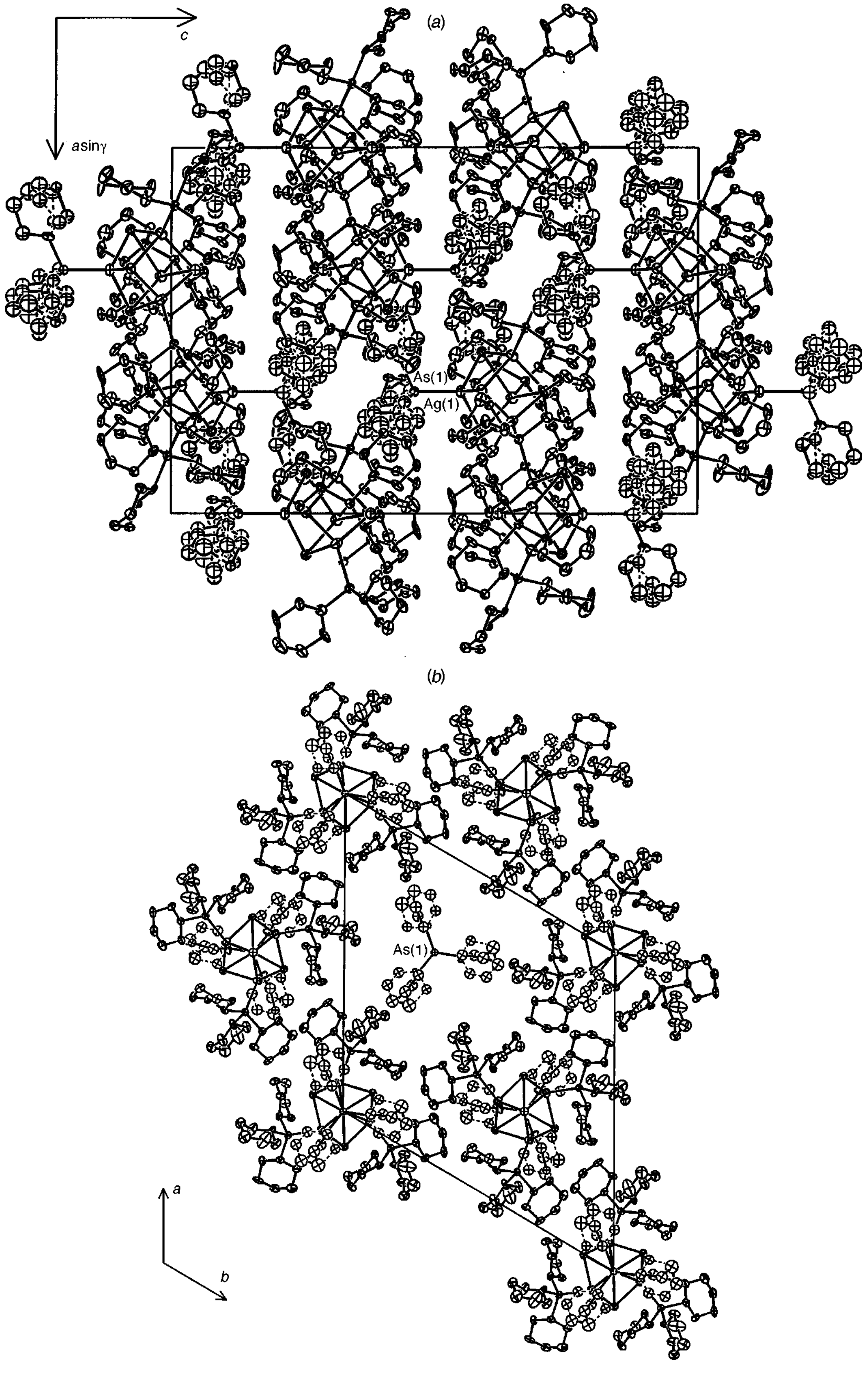

Fig. 3 The bromide structure projected normal to (*a*) and down (*b*) (one sheet only) the 3 axis, showing the disposition of the tetramers in sheets, with axial ligands interlocking adjacent sheets

the structure, the strands being similar in aspect to those of their E = As counterparts. The geometry differs significantly however (Table 4); the non-linear co-ordination of one end of the NCAgCN unit to the 'cationic' silver atom, noted above in the E = As analogue, is now exacerbated [Ag–N(2′)–C(2′) 119(1), 121(1)°] with a marked disparity of *ca.* 0.5 Å now evident in the Ag–N(1,2′) distances, *i.e.* N(2′) is now incipiently dissociating and the $P_2AgN(1)$ angle sums now (*ca.* 356°) approaching planarity closely.

Crystallisation of the E = As reaction mixture from pyridine, rather than 2-methyl- or 2,4,6-trimethyl-pyridine, results in solvation of the cationic silver atoms, displacing some of the co-ordinated anions, to yield an interesting adduct of 3 : 4 : 2 AgCN : $As(C_6H_{11})_3$: py stoichiometry. The general nature of the

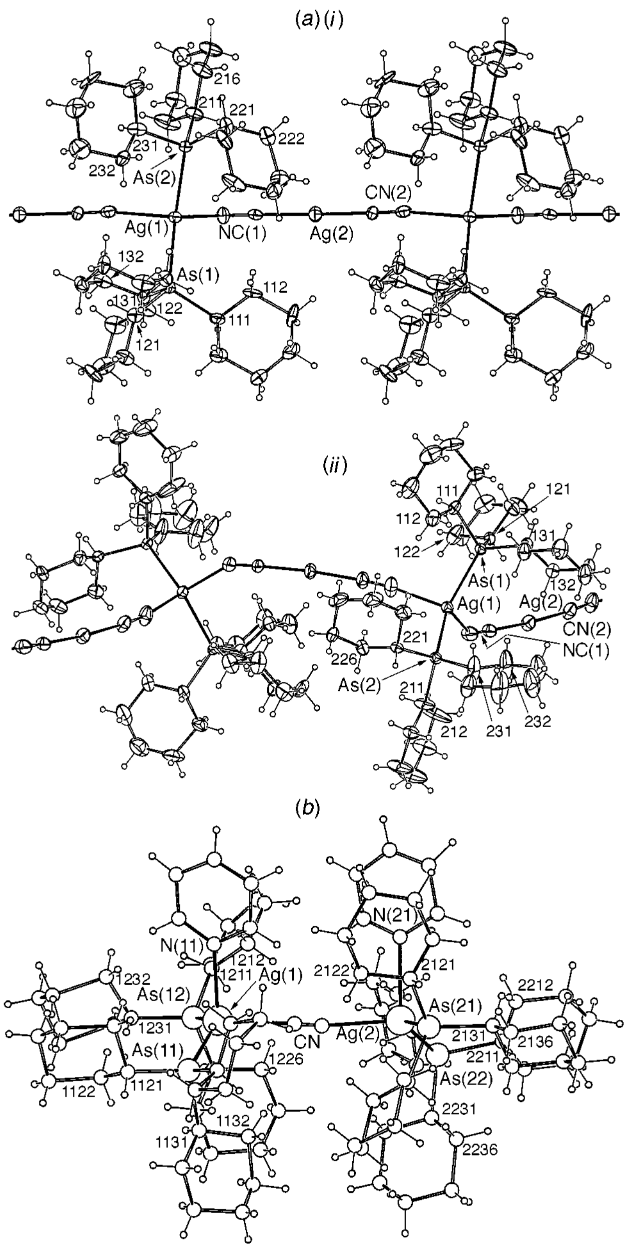

Fig. 4 (*a*) A single strand of the cyanide polymer in the α (*i*) and β form (*ii*). (*b*) The $[\{Ag[As(C_6H_{11})_3]_2(py)\}_2(CN)]^+$ cation of the 3 : 4 : 2 AgCN : $As(C_6H_{11})_3$: py adduct

Table 3 'Cubane' core geometry in $[\{[(C_6H_{11})_3As]AgBr\}_4]$. Distances in Å, angles in °; singly and doubly primed atoms are generated by $1 - x, x - y, z$ and $1 - x + y, 1 - x, z$ respectively

Ag(1)–As(1)	2.497(5)	Ag(2)–As(2)	2.494(4)
Ag(1)–Br(2)	2.726(3)	Ag(2)–Br(1)	2.747(4)
		Ag(2)–Br(2)	3.035(3)
		Ag(2)–Br(2″)	2.616(5)
Ag(1) ··· Ag(2)	3.448(4)	Br(1) ··· Br(2)	4.268(5)
Ag(2) ··· Ag(2′)	3.553(4)	Br(2) ··· Br(2′)	4.300(5)
Ag(1) ··· Br(1)	4.599(6)	Ag(2) ··· Br(2′)	4.813(5)
As(1)–Ag(1)–Br(2)	114.43(8)	As(2)–Ag(2)–Br(1)	115.2(1)
		As(2)–Ag(2)–Br(2)	95.0(1)
		As(2)–Ag(2)–Br(2″)	135.5(1)
Br(2)–Ag(1)–Br(2′)	104.1(1)	Br(1)–Ag(2)–Br(2)	95.01(8)
		Br(1)–Ag(2)–Br(2″)	105.4(1)
		Br(2)–Ag(2)–Br(2″)	98.8(1)
Ag(2)–Br(1)–Ag(2″)	80.6(1)	Ag(1)–Br(2)–Ag(2)	73.31(9)
		Ag(1)–Br(2)–Ag(2′)	80.4(1)
		Ag(2)–Br(2)–Ag(2′)	77.52(9)

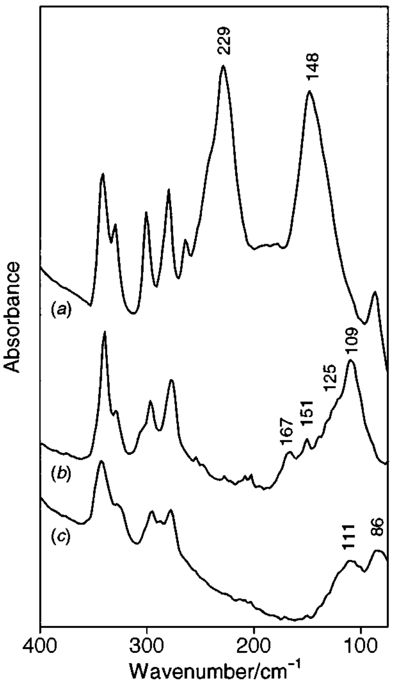

Fig. 5 Far-IR spectra of (*a*) $[\{[As(C_6H_{11})_3]AgCl\}_2]$, (*b*) $[\{[As(C_6H_{11})_3]AgBr\}_4]$, (*c*) $[\{[As(C_6H_{11})_3]AgI\}_4]$. The bands assigned to the ν(AgX) modes are labelled with their wavenumbers

complex is definitively, albeit imprecisely, established by elemental analysis coupled with a single crystal X-ray study as $[\{Ag[As(C_6H_{11})_3]_2(py)\}_2(CN)][Ag(CN)_2]$ [Fig. 4(*b*)], the $[Ag(CN)_2]^-$ counter ion now being discrete, the two cationic silver atoms bridged by a simple linearly co-ordinated cyanide, modelled with C,N scrambled, and with the fourth co-ordination site occupied by pyridines. The imprecise geometries are unexceptional, but it is of interest that the pair of py groups within the cation are aligned so as to be eclipsed relative to the Ag ··· Ag line.

Infrared spectroscopy

The far-IR spectra of $[\{[(C_6H_{11})_3As]AgCl\}_2]$ and $[\{[(C_6H_{11})_3As]AgX\}_4]$ (X = Br or I) are shown in Fig. 5. Strong bands due to the $As(C_6H_{11})_3$ ligand are evident down to about 280 cm^{-1}; ligand bands also occur in the region below this, but these are generally quite weak. Strong bands, the wavenumbers of which are dependent on the nature of X, are also observed in these spectra. For the chloride the two very strong bands at 229 and 148 cm^{-1} are assigned to the ν(AgCl) modes of the Ag_2Cl_2 unit that is present in this complex (see above). The situation is similar to that found previously for the $[\{[P(C_6H_{11})_3]AgX\}_2]$ and $[\{(Ph_3P)_2AgX\}_2]$ (X = Cl or Br) complexes, which contain similar silver halide core units.[3,13] For an Ag_2X_2 unit of D_{2h} symmetry (x parallel to the Ag ··· Ag diagonal, y parallel to the X ··· X diagonal) two IR-active modes of B_{2u} and B_{3u} symmetry are predicted, involving displacement of X and Ag along the positive and negative x directions respectively (B_{3u}) or a similar vibration in the y direction (B_{2u}). For a perfectly square Ag_2X_2 unit these two modes would have the same frequency, and this situation has been observed in the chloroform solvates $[\{(Ph_3P)_2AgX\}_2]\cdot 2CHCl_3$ (X = Cl or Br).[13] A distortion in which two bonds on opposite sides of the square are shortened and the other two are lengthened results in a lowering of the symmetry from D_{2h} to C_{2h}, and the two IR-active ν(AgX) modes both have B_u symmetry. The forms of these modes are such that one mainly involves stretching of the two short Ag–X bonds, the other stretching of the two long Ag–X bonds, so that the two modes should give rise to bands at significantly different wavenumbers. This situation has previously been observed in unsolvated $[\{(Ph_3P)_2AgCl\}_2]$[13] and in $[\{[(C_6H_{11})_3P]AgCl\}_2]$,[3]

Table 4 Selected geometries: cyanide adducts. Distances in Å, angles in °

(a) $AgCN:As(C_6H_{11})_3$ (1 : 1). The two values in each entry are for α,β forms respectively; primed atoms are generated by $x - 1, y, z$ and $2 - x, y - \frac{1}{2}, \frac{1}{2} - z$ respectively

(i) The 'cationic' silver atoms [Ag(1)]

Ag–As(1)	2.539(2), 2.576(1)	Ag–N(1)	2.43(1), 2.41(1)
Ag–As(2)	2.568(2), 2.545(2)	Ag–N(2′)	2.51(2), 2.38(1)
As(1)–Ag–As(2)	144.20(8), 137.20(6)	As(2)–Ag–N(2′)	100.3(4), 105.3(3)
As(1)–Ag–N(1)	107.6(4), 99.8(3)	N(1)–Ag–N(2′)	108.3(5), 104.0(4)
As(1)–Ag–N(2′)	97.1(4), 99.5(3)	Ag–N(1)–C(1)	134(1), 145(1)
As(2)–Ag–N(1)	96.4(4), 107.2(2)	Ag–N(2′)–C(2′)	163(2), 168(1)

(ii) The 'anionic' silver atoms [Ag(2)]

Ag–C(1)	2.08(2), 2.04(1)	C(1)–N(1)	1.11(2), 1.12(2)
Ag–C(2)	2.02(2), 2.04(1)	C(2)–N(2)	1.08(2), 1.12(2)
C(1)–Ag–C(2)	177.5(7), 174.4(6)	Ag–C(1)–N(1)	171(2), 175(1)
		Ag–C(2)–N(2)	178(2), 177(1)

(b) $AgCN:P(C_6H_{11})_3$ (1 : 1); primed atoms are generated by the unit *a* translation, the two values in each entry being for strands 1,2 respectively

(i) The 'cationic' silver atoms [Ag(1)]

Ag–P(1)	2.420(4), 2.429(4)	Ag–N(1)	2.41(1), 2.44(1)
Ag–P(2)	2.414(3), 2.413(3)	Ag–N(2′)	2.97(1), 2.92(1)
P(1)–Ag–P(2)	147.9(1), 149.4(1)	P(2)–Ag–N(2′)	93.5(3), 94.3(3)
P(1)–Ag–N(1)	99.6(3), 98.4(3)	N(1)–Ag–N(2′)	99.8(5), 99.9(4)
P(1)–Ag–N(2′)	97.0(3), 94.8(2)	Ag–N(1)–C(1)	168(1), 171(1)
P(2)–Ag–N(1)	108.3(3), 108.7(3)	Ag–N(2′)–C(2′)	119(1), 121(1)

(ii) The 'anionic' silver atoms [Ag(2)]

Ag–C(1)	2.04(1), 2.06(1)	C(1)–N(1)	1.17(2), 1.12(2)
Ag–C(2)	2.10(1), 2.09(1)	C(2)–N(2)	1.16(2), 1.18(2)
C(1)–Ag–C(2)	174.5(6), 176.0(6)	Ag–C(1)–N(1)	167(1), 169(1)
		Ag–C(2)–N(2)	177(1), 176(1)

(c) $AgCN:As(C_6H_{11})_3:py$ (3 : 4 : 2)

(i) The cation: the two values for each entry are for moieties 1,2

Ag–As(1)	2.54(5), 2.57(2)	Ag–C/N	2.34(5), 2.40(5)
Ag–As(2)	2.55(2), 2.55(3)	C–N	0.84(6)
Ag–N(1)	2.49(3), 2.58(4)		
As(1)–Ag–As(2)	128(1), 124.1(6)	As(2)–Ag–C/N	108(2), 112.6(9)
As(1)–Ag–N(1)	107(1), 104.1(9)	N(1)–Ag–C/N	95(2), 93(1)
As(1)–Ag–C/N	108(1), 112(2)	Ag–C/N–N/C	170(4), 166(3)
As(2)–Ag–N(1)	106(1), 106(2)		

(ii) The anion

Ag–C	1.94(7), 2.04(6)	C–N	1.21(8), 1.06(7)
C(1)–Ag–C(2)	177(2)	Ag–C–N	165(5), 172(5)

and is the reason for the large separation between the two ν(AgX) bands observed for $[\{[(C_6H_{11})_3As]AgCl\}_2]$ (Fig. 5). It has previously been shown that the wavenumbers of the ν(MX) modes of Group 11 metal halide complexes are sensitive to the strength of the M–X bonds. Thus, the ν(MX) wavenumbers have been empirically correlated with the M–X bond length *r via* relationship (1) where *b* and *m* are constants.[14,15] Somewhat

$$\nu/\mathrm{cm}^{-1} = b(r/\text{Å})^{-m} \qquad (1)$$

surprisingly, this relationship appears to be valid for vibrations involving both terminal and bridging halogen atoms X.[3,15,16] The most likely reason for this is that the M–X–M angles in the bridged complexes are close to 90°, so that the vibrations of the M–X bonds involved in the bridge are essentially uncoupled, and so are independent of each other. The angles in the Ag_2Cl_2 unit in $[\{[(C_6H_{11})_3As]AgCl\}_2]$ are close to 90° (Table 1), so the frequencies of the ν(AgCl) modes should fit the previously established correlation (1) for AgCl complexes. Fig. 6 shows that this is indeed the case. The spectra of the cubane tetramers $[\{[(C_6H_{11})_3As]AgX\}_4]$ (X = Br or I) show ν(AgX) bands below 200 cm^{-1}. For an Ag_4X_4 unit of T_d symmetry two IR-active ν(AgX) modes of T_2 symmetry are predicted.[17–19] Thus, the two bands at 111 and 86 cm^{-1} for the X = I complex (Fig. 5) can be assigned to these modes. The positions of these bands are quite similar to those of the corresponding $P(C_6H_{11})_3$ complex (113, 83 cm^{-1}).[3] The situation for the X = Br complex is less straightforward; four partially resolved bands are observed at 167, 151, 125 and 109 cm^{-1} (Fig. 5). A possible reason for this is the significant distortion of the Ag_4Br_4 core from T_d symmetry that is observed in this complex. The Ag–Br bond lengths range from about 2.6 to 3.0 Å (Table 3), compared with a range 2.8 to 3.0 Å for the Ag–I bond lengths in the iodide (Table 2). The recently established correlation between the ν(AgX)

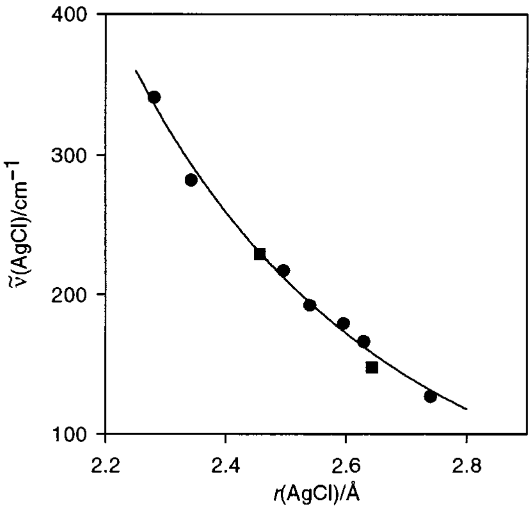

Fig. 6 Plot of wavenumber of the ν(AgCl) band against Ag–Cl bond length. The data (●) and the best fit curve using equation (1) are from ref. 15. The data (■) are for $[\{[(C_6H_{11})_3As]AgCl\}_2]$

wavenumbers and the Ag–X bond lengths[15] suggests that the ν(AgBr) bands of the bromide tetramer should lie in the range 100 to 160 cm^{-1}, which agrees well with the observed spectrum. The reduction in the symmetry of the Ag_4Br_4 core from T_d to C_{3v} would result in the two T_2 modes being split into four components. This is the most likely explanation for the relatively complex pattern of bands observed in the far-IR spectrum of the bromide.

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