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Spectroscopic and structural studies on 1:2 adducts of silver(I) salts with tricyclohexylarsine

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A series of mononuclear complexes $[Ag\{As(C_6H_{11})_3\}_2X]$ (X = Cl, Br, I, CN, NCO, $OClO_3$, O_2NO or O_2CCF_3) have been synthesized and characterised by room temperature single crystal X-ray determinations and low-frequency vibrational spectroscopy. For X = Cl, Br, I or $OClO_3$ the crystal structures are isomorphous with a number of their previously recorded $P(C_6H_{11})_3$ counterparts, crystallising in the familiar monoclinic $C2/c$ array with the Ag–X bond lying on a crystallographic 2 axis (the perchlorate is disordered) which also relates the pair of $As(C_6H_{11})_3$ ligands. The silver environment in all is planar three-co-ordinate $XAgAs_2$. For X = CN, NCO or O_2NO the derivative lower-symmetry triclinic $P\bar{1}$ array, also common among the $P(C_6H_{11})_3$ analogues is found. The trifluoroacetate, resembling the nitrate in that the anion behaves as a small 'bite' bidentate ligand, $[Ag\{As(C_6H_{11})_3\}_2(O_2CCF_3)]$, is monoclinic space group $P2_1/n$. The thiocyanate by contrast, utilising the ambidentate capacity of the SCN ligand, remarkably, is a linear polymer, $\cdots\{As(C_6H_{11})_3\}_2Ag(SCN)Ag(SCN)\cdots$, triclinic, space group $P1$, in which the silver atom environment is four-co-ordinate, $NSAgAs_2$. Far-IR spectra of the halide and pseudo-halide complexes in the series exhibit single bands due to ν(AgX) vibrational modes at 230, 165, 139, 262 and 311 cm^{-1} for X = Cl, Br, I, NCO and CN respectively. These are all higher than the values for the corresponding $P(C_6H_{11})_3$ complexes, suggesting that the Ag–X bonding is stronger in the $As(C_6H_{11})_3$ complexes, this being the result of weakened Ag–L bonding in going from L = $P(C_6H_{11})_3$ to $As(C_6H_{11})_3$.

In recent years single crystal X-ray determinations in concert with low frequency vibrational spectroscopic studies have defined isomeric forms and their bonding characteristics for a wide spectrum of adducts of coinage metal(I) salts, MX, with unidentate Group V bases. Whereas for donor atoms E = N a variety of stereochemical and electronic characteristics may be employed, linear RCN, trigonal planar pyridine derivatives, tertiary NR_3, *etc*., extensive essays with heavier E = P, As, Sb tend to be largely restricted to tertiary ER_3, adducts $MX:ER_3$ (1:*n*) for R = Ph being commonly defined for *n* = 4 as the ionic form $[M(EPh_3)_4]^+X^-$ for X = ClO_4 or NO_3,[1] for *n* = 3 as mononuclear $[M(EPh_3)_3X]$ (diverse X),[2] for *n* = 2 as mononuclear $[M(EPh_3)_2X]$ [small M, E (= Cu, P) only] or binuclear $[(Ph_3E)_2M(\mu\text{-}X)_2M(EPh_3)_2]$,[3] and for *n* = 1 as 'step' or 'cubane' tetramers $[\{(Ph_3E)MX\}_4]$ (E = P or As only),[4] all except $[M(EPh_3)_2X]$ having tetrahedral metal atom environments. Nevertheless, studies with alternative R substituents of different stereochemical or electronic characteristics have shown that it is possible to prepare extensive series of complexes of a particular structural type with a wide range of X, as shown recently in the arrays of adducts of silver(I) salts with tricyclohexylphosphine, n_{max} being 2 in mononuclear $[Ag\{P(C_6H_{11})_3\}_2X]$,[5] while *n* = 1 forms may be frequently binuclear rather than tetranuclear.[6] In that spirit we now extend our studies of these arrays to encompass adducts of silver(I) salts with tricyclohexylarsine, recording in the present report results obtained for the $AgX:As(C_6H_{11})_3$ (1:2) system, and, in the following,[7] the 1:1 system. We report here syntheses, and structural and spectroscopic characterisation, of $AgX:As(C_6H_{11})_3$ (1:2) for X = Cl, Br, I, CN, NCO, NO_3, ClO_4 or O_2CCF_3 as mononuclear $[Ag\{As(C_6H_{11})_3\}_2X]$ arrays; by contrast, in keeping with the ambidentate nature of the SCN ligand, $AgSCN:As(C_6H_{11})_3$ (1:2) is found to be an infinite one-dimensional polymer with four-co-ordinate silver(I).

Experimental

Syntheses

All compounds were obtained by dissolution of the appropriate silver(I) salt (1 mmol) with tricyclohexylarsine (2 mmol) with warming in acetonitrile (5 cm^3), colourless crystals depositing on cooling and standing. X = Cl: m.p. > 109 °C (decomp.), no satisfactory analysis data obtained. X = Br: m.p. >125 °C (decomp.) (Found: C, 51.7; H, 7.8. Calc. for $C_{36}H_{66}AgAs_2Br$: C, 51.69; H, 7.95%). X = I: m.p. >131 °C (decomp.) (Found: C, 49.1; H, 7.5. Calc. for $C_{36}H_{66}AgAs_2I$: C, 48.94; H, 7.53%). X = CN: m.p. 148–150 °C (Found: C, 56.8; H, 8.7; N, 1.6. Calc. for $C_{37}H_{66}AgAs_2N$: C, 56.78; H, 8.50; N, 1.7%). X = NCO: m.p. >158 °C (decomp.) (Found: C, 55.4; H, 8.4. Calc. for $C_{37}H_{66}AgAs_2NO$: C, 55.64; H, 8.33%). X = NO_3: m.p. >143 °C (decomp.) (Found: C, 52.7; H, 8.0. Calc. for $C_{36}H_{66}AgAs_2NO_3$: C, 52.82; H, 8.13%). X = ClO_4: m.p. >189 °C (decomp.), no satisfactory analysis obtained. X = O_2CCF_3: m.p. 146–148 °C (Found: C, 52.2; H, 7.9. Calc. for $C_{38}H_{66}AgAs_2F_3O_2$: C, 52.48; H, 7.65%). X = SCN: m.p. >171 °C (decomp.) (Found: C, 54.7; H, 7.9. Calc. for $C_{37}H_{66}AgAs_2NS$: C, 54.55; H, 8.17%).

Structure determinations

Unique room-temperature diffractometer data sets were measured (2θ–θ scan mode, $2\theta_{max}$ as specified: monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å, $T \approx 295$ K) yielding *N* independent reflections, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the full matrix least squares refinements after gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ being included at estimated values. Conventional residuals *R*,*R*′ on |*F*| are quoted at convergence, statistical reflection weights being derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$. Neutral atom complex scattering factors were employed, computation using the XTAL 3.2 program system.[8] Abnormal feature/idiosyncrasies/variations in procedure are noted individually below ('variata'). In all figures, 20% thermal envelopes are shown for the non-hydrogen atoms, hydrogen atoms (where shown) having arbitrary radii of 0.1 Å. Ring carbon atoms are labelled *lmn* (*l* = ligand number, *m* = ring number, *n* = atom number).

A general comment is called for in respect of the treatment of cyanate and cyanide moieties in this and accompanying/following papers. In all cases assignment of the atoms concerned was attempted on the basis of crystallographic and chemical considerations during refinement by consideration of the behaviour of residuals, thermal parameters, geometries, *etc*. In a few cases a 'definitive' assignment emerged, but in many cases the result was ambiguous, and that presented should be treated with appropriate circumspection. Thus, all cyanates are treated as N-bonded; in *e.g.* the example presented in the present paper apparent bond length distributions and the behaviour of residuals during refinement support this assignment, but the attachment of the ligand at the nitrogen is non-linear, and 'thermal motion' at the peripheral oxygen is abnormally high. A similar observation may be made in respect of cyanides: the weight of evidence supports the probability that these are C-bound in terminally attached species, or in isolated or bridging $[NCAgCN]^-$ arrays, but are scrambled in situations where they behave as a bridging group between two similar atoms. Individual cases are described in detail, particularly for those few where departure from the above norm is suggested.

Crystal/refinement data for $[AgX\{As(C_6H_{11})_3\}_2] \equiv C_{36}H_{66}AgAs_2X$. (*a*) *Monoclinic*, *space group* $C2/c$ (C^6_{2h}, no. 15), $Z = 4$. (*i*) **X = Cl.** $M = 792.1$, $a = 17.016(3)$, $b = 9.209(3)$, $c = 24.821(5)$ Å, $\beta = 108.07(2)°$, $U = 3698$ Å^3, $D_c = 1.42_3$ g cm^{-3}, $F(000) = 1648$, $\mu_{Mo} = 24.2$ cm^{-1}, specimen 0.23 × 0.40 × 0.11 mm, $A^*_{min,max} = 1.26$, 1.72, $2\theta_{max} = 60°$, $N = 5375$, $N_o = 3466$, $R = 0.050$, $R' = 0.062$.

(ii) **X = Br.** $M = 836.6$, $a = 16.997(7)$, $b = 9.239(2)$, $c = 24.826(8)$ Å, $\beta = 108.20(3)°$, $U = 3704$ Å^3, $D_c = 1.50_0$ g cm^{-3}, $F(000) = 1720$, $\mu_{Mo} = 34.2$ cm^{-1}, specimen 0.19 × 0.34 × 0.17 mm, $A^*_{min,max} = 1.61$, 1.82 (analytical correction), $2\theta_{max} = 55°$, $N = 4056$, $N_o = 2642$, $R = 0.035$, $R' = 0.035$.

(iii) **X = I.** $M = 883.6$, $a = 17.094(2)$, $b = 9.344(6)$, $c = 24.99(1)$ Å, $\beta = 108.67(2)°$, $U = 3781$ Å^3, $D_c = 1.55_2$ g cm^{-3}, $F(000) = 1792$, $\mu_{Mo} = 31.1$ cm^{-1}, specimen 0.58 × 0.44 × 0.10 mm, $A^*_{min,max} = 1.36$, 3.37 (analytical correction), $2\theta_{max} = 60°$, $N = 5490$, $N_o = 3543$, $R = 0.039$, $R' = 0.040$.

(iv) **X = ClO_4.** $M = 856.1$, $a = 17.03(1)$, $b = 9.568(4)$, $c = 25.185(8)$ Å, $\beta = 109.57(4)°$, $U = 3866$ Å^3, $D_c = 1.47_1$ g cm^{-3}, $F(000) = 1776$, $\mu_{Mo} = 23.2$ cm^{-1}, specimen 0.15 × 0.21 × 0.09 mm, $A^*_{min,max} = 1.18$, 1.31 (analytical correction), $2\theta_{max} = 50°$, $N = 3471$, $N_o = 1898$, $R = 0.057$, $R' = 0.058$.

Variata. For the above compounds the cell and coordinate setting previously defined[5] for certain $P(C_6H_{11})_3$ counterparts was adopted. In the perchlorate the chlorine atom is located on the 2 axis, while the unco-ordinated oxygen atoms are necessarily disordered about the twofold axis in the $C2/c$ model; the co-ordinated oxygen atom was also modelled as disordered, lying somewhat off the Ag ··· Cl axis.

(*b*) *Triclinic*, *space group* $P\bar{1}$ (C^1_i, no. 2), $Z = 2$. (i) **X = CN.** $M = 782.7$, $a = 9.205(3)$, $b = 9.759(4)$, $c = 23.673(7)$ Å, $\alpha = 95.13(3)$, $\beta = 97.38(2)$, $\gamma = 117.29(3)°$, $U = 1847$ Å^3, $D_c = 1.40_7$ g cm^{-3}, $F(000) = 816$, $\mu_{Mo} = 23.5$ cm^{-1}, specimen 0.22 × 0.10 × 0.15 mm, $A^*_{min,max} = 1.23$, 1.41, $2\theta_{max} = 50°$, $N = 6527$, $N_o = 2861$, $R = 0.056$, $R' = 0.051$.

(ii) **X = NCO.** $M = 798.7$, $a = 9.327(7)$, $b = 9.816(2)$, $c = 23.692(4)$ Å, $\alpha = 95.54(2)$, $\beta = 96.52(3)$, $\gamma = 117.41(4)°$, $U = 1886$ Å^3, $D_c = 1.40_6$ g cm^{-3}, $F(000) = 832$, $\mu_{Mo} = 23.0$ cm^{-1}, specimen 0.46 × 0.20 × 0.06 mm, $A^*_{min,max} = 1.14$, 1.57, $2\theta_{max} = 50°$, $N = 6447$, $N_o = 4083$, $R = 0.060$, $R' = 0.068$.

(iii) **X = NO_3.** $M = 818.7$, $a = 9.199(2)$, $b = 9.813(3)$, $c = 23.844(5)$ Å, $\alpha = 95.08(2)$, $\beta = 96.13(2)$, $\gamma = 115.16(2)°$, $U = 1915$ Å^3, $D_c = 1.41_9$ g cm^{-3}, $F(000)$ 852, $\mu_{Mo} = 22.7$ cm^{-1}, specimen 0.42 × 0.55 × 0.32 mm, $A^*_{min,max} = 1.27$, 1.83, $2\theta_{max} = 50°$, $N = 6717$, $N_o = 5285$, $R = 0.043$, $R' = 0.050$.

Variata. For the above compounds the cell and coordinate setting previously defined for certain $P(C_6H_{11})_3$ counterparts[5] was adopted. In the cyanate and nitrate various components of various cyclohexyl rings were modelled as disordered over pairs of sites, occupancies set at 0.5 after trial refinement. In the cyanate the thermal parameter refinement of the peripheral component was ill behaved and the isotropic form was adopted, possibly encompassing disorder or isomerism of the potentially ambidentate ligand. Although modelled as C-bound, a C/N, disordered model for the cyanide is indistinguishable on the basis of refinement, a possibility supported by rather aberrant thermal parameters.

(*c*) X = O_2CCF_3. $M = 869.7$, monoclinic, space group $P2_1/n$ [C^5_{2h}, no. 14 (variant)], $a = 10.085(5)$, $b = 24.36(1)$, $c = 16.462(8)$ Å, $\beta = 93.91(4)°$, $U = 4034$ Å^3, D_c ($Z = 4$) $= 1.43_2$ g cm^{-3}, $F(000) = 1800$, $\mu_{Mo} = 21.7$ cm^{-1}, specimen 0.29 × 0.34 × 0.47 mm, $A^*_{min,max} = 1.72$, 2.00, $2\theta_{max} = 50°$, $N = 6838$, $N_o = 4579$, $R = 0.046$, $R' = 0.052$.

Variata. One of the ligand rings was modelled as disordered over two sets of sites, disordered atom occupancy set at 0.5 after trial refinement.

(*d*) X = SCN. $M = 814.8$, triclinic, space group $P1$ (C^1_1, no. 1), $a = 13.767(5)$, $b = 13.589(3)$, $c = 11.952(6)$ Å, $\alpha = 100.23(3)$, $\beta = 90.98(4)$, $\gamma = 118.47(2)°$, $U = 1920$ Å^3, D_c ($Z = 2$) $= 1.40_8$ g cm^{-3}, $F(000) = 848$, $\mu_{Mo} = 23.1$ cm^{-1}, specimen 0.09 × 0.10 × 0.46 mm, $A^*_{min,max} = 1.17$, 1.32, $2\theta_{max} = 50°$, $N = 6749$, $N_o = 5040$, $R = 0.042$, $R' = 0.041$ (preferred hand).

CCDC reference number 186/983.

See http://www.rsc.org/suppdata/dt/1998/2123/ 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

Depending on the nature of the anionic moiety X, species of the type $[M(ER_3)_n]X$ or $[\{(R_3E)_nMX\}_m]$ may be isolated for M = univalent coinage metal, E = P, As or Sb, *n* rising to a maximum of 4 in ionic compounds or 3 in those where X is covalently bound, the ligand substituent being variously alkyl or aryl. With R = cyclohexyl, structurally characterised examples are more limited and characterised by diminished *n*. For simple molecular or ionic adducts, the maximum *n* recorded in structurally characterised examples is 2, and those for E = P, *i.e.* $P(C_6H_{11})_3$, as ligand, only. For M = Cu or Ag, 'simple' X, X interacts with one metal alone in $MX:P(C_6H_{11})_3$ (1 : 2) complexes, all being mononuclear, regardless of whether X is a (pseudo-)halide or oxyanion, $[M\{P(C_6H_{11})_3\}_2X]$ arrays being structurally defined for (a) Cu, X = I,[9] N_3,[10] $OClO_3$,[11] FBF_3[12] (X unidentate) or O_2NO[13] [X (small bite) bidentate], (b) Ag, X = Cl, Br, I, CN, SCN, NCO,[5] $OClO_3$[5,14] (unidentate) or O_2NO[5,14] (small bite bidentate). By contrast, for M = Au (which we shall not consider further), all $AuX:P(C_6H_{11})_3$ (1 : 2) adducts take the form of ionic $[Au\{P(C_6H_{11})_3\}_2]X$ (X = Cl,[15] SCN[16] or PF_6[17]), with a linear two-co-ordinate metal atom in the cation.

The results of the present room-temperature single crystal X-ray studies are consistent in stoichiometry, connectivity and stereochemistry with the complexes being of 1 : 2 $AgX:As(C_6$-

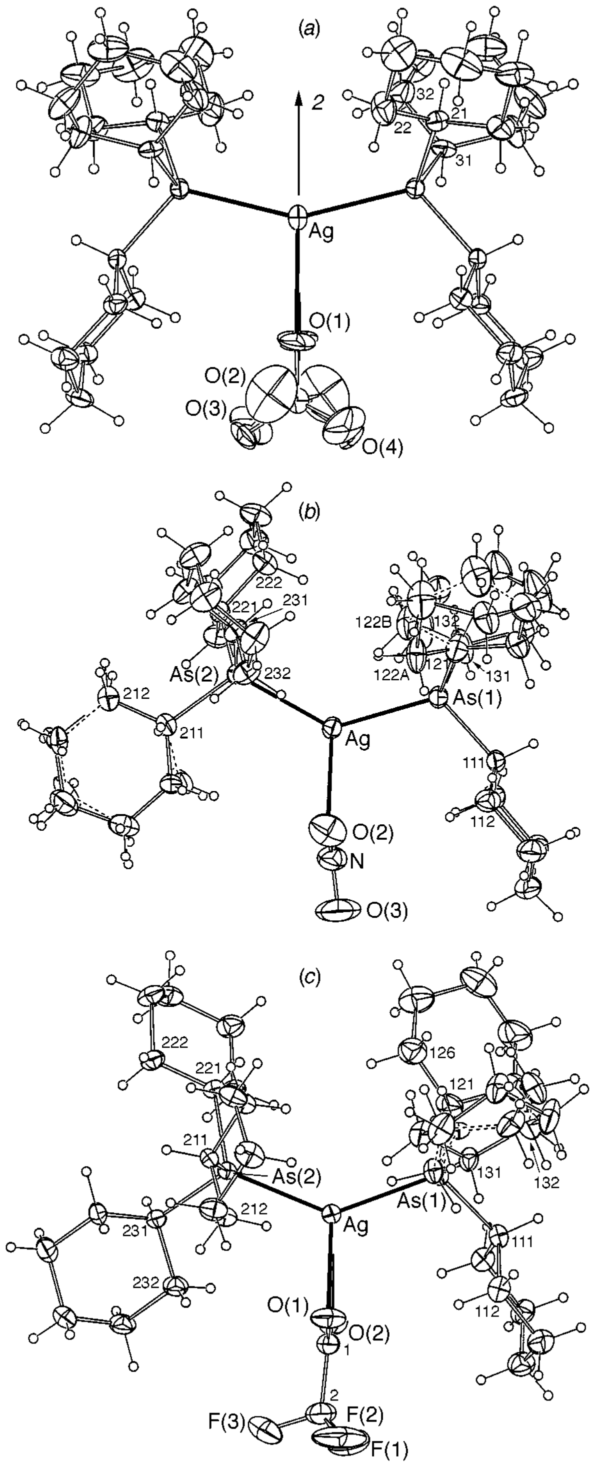

Fig. 1 Molecular projections of (*a*) the perchlorate, (*b*) the nitrate, (*c*) the trifluoroacetate, normal to the As_2Ag plane

$H_{11})_3$ formulation [the first coinage metal $As(C_6H_{11})_3$ complexes so characterised]. The structures of a selection of the compounds studied are shown in Figs. 1 and 2. For X = Cl, Br, I, CN, NCO, $OClO_3$ or O_2NO, all anionic moieties except the nitrate (which is a small bite bidentate) behave as unidentate ligands, so that the metal is (pseudo-)planar three-co-ordinate As_2MX. Like their $P(C_6H_{11})_3$ counterparts,[5] these complexes form a limited number of isomorphous structural systems, arising from a monoclinic $C2/c$ cell, $Z = 4$, in which the M–X bond is disposed on a crystallographic 2 axis which relates the two $E(C_6H_{11})_3$ ligands, only one of which is crystallographically independent, *or* a derivative triclinic $P\bar{1}$ array, $Z = 2$, in which one independent $[M\{E(C_6H_{11})_3\}_2X]$ moiety comprises the asymmetric unit of the structure. In the $P(C_6H_{11})_3$ array the $C2/c$ form was found for the X = Cl, Br, I, CN or SCN adducts (the anionic moiety in the last being disordered); for the present $As(C_6H_{11})_3$ array that form is found for the X = Cl, Br or I adducts, inclusive also of the O-bonded perchlorate complex. In the $P(C_6H_{11})_3$ array the position of the latter was somewhat ambiguous, an earlier determination having described it as in the triclinic $P\bar{1}$ for, but further studies suggested the possibility of the achievement of the higher $C2/c$ symmetry in admixture or as an alternative to it, the difference between the two forms possibly being very slight (dependent on crystallisation conditions?). Here, with $As(C_6H_{11})_3$ as ligand, we find the array unproblematically $C2/c$, although, as modelled in that space group, the perchlorate is necessarily disordered about the two-fold axis; in detail, the silver atom lies on that axis, as does the chlorine, the latter albeit with a thermal parameter slightly higher than *e.g.*, the anionic ligands, but not so high as to suggest gross disorder. By contrast, the co-ordinated oxygen atom is resolvable into a pair of symmetry-related off-axis components 1.31(4) Å apart; the associated geometry should be treated appropriately circumspectly. The ligand components match those of the $P(C_6H_{11})_3$ analogues, with which co-ordination geometries about the metal are compared in Table 1. The alternative form recorded for the remaining $P(C_6H_{11})_3$ complexes of ref. 5 is a triclinic $P\bar{1}$ array derivative of the $C2/c$ form, found for X = NCO, O_2NO (and $OClO_3$), the two $P(C_6H_{11})_3$ ligands now having different conformations with disorder resolvable in ring 21n. This form is also found among the $As(C_6H_{11})_3$ complexes, again for the X = NCO or O_2NO arrays, but also for X = CN, the $CN/P(C_6H_{11})_3$ complex having been found to be $C2/c$. The disorder characteristics among the ligand rings are diverse, affecting rings 12*n* and 21*n* in varying degree [ring 21*n* having been modelled as disordered in the previous $P(C_6H_{11})_3$/nitrate complex], manifested either as exalted thermal motion and/or resolvable disorder in either or both of these rings. In the cyanide and the cyanate (particularly the latter) the behaviour of the anionic moiety is not conducive to definitive assignment of co-ordination of one particular end of that ligand; the 'bent' co-ordination of the cyanate in particular is at variance with the NC assignment supported by the bond length. The Ag–N–C angle [133(1)°] in the present complex is significantly less than the value [151.2(4)°] in the $P(C_6H_{11})_3$ analogue, also modelled as N-bound.[5] Given that in both $P(C_6H_{11})_3$ and $As(C_6H_{11})_3$ adducts the nitrate can co-ordinate as O,O′-bidentate, albeit of small 'bite', it may be that the co-ordination site has a more appropriately spacious ambience (*vis-à-vis* the $C2/c$ form), permitting high 'thermal motion' and/or alternative co-ordination modes more readily. The geometries of these complexes are also compared with those of their $P(C_6H_{11})_3$ counterparts in Table 1.

The trifluoroacetate complex, also mononuclear, crystallizes in a form different to the above, being monoclinic, $P2_1/n$, $Z = 4$, with one $[Ag\{As(C_6H_{11})_3\}_2(O_2CCF_3)]$ molecule, devoid of crystallographic symmetry, comprising the asymmetric unit of the structure. It resembles the nitrate in that the anion behaves as a bidentate ligand of small 'bite', raising the co-ordination number of the silver to four. The ligand conformation, exhibiting disorder in one of the substituent rings, more nearly resembles that of the triclinic $P\bar{1}$ examples than the monoclinic $C2/c$ (which have molecular 2 symmetry). Given the seriously different base strengths of O_2CCF_3 *vs.* O_2NO, it might be expected that this would be reflected in the parameters of the metal atom environment; changes are relatively minor, perhaps the opposite of expectations which would suggest that O_2CCF_3 being a stronger base than O_2NO should co-ordinate more strongly. The Ag–O distances in the O_2CCF_3 are appreciably larger, with Ag–As shorter and As–Ag–As enlarged. A comparison of the relationship between the *d*(Ag–E) bond lengths and the E–Ag–E bond angles for $[Ag\{E(C_6H_{11})_3\}_2X]$ (E = P or As) is shown in Fig. 3. This shows that the longer Ag–E bonds are generally accompanied by smaller E–Ag–E angles, but the

Table 1 Molecular core geometries for mononuclear $[Ag\{E(C_6H_{11})_3\}_2X]$ complexes. Distances in Å, angles in °. Values for E = As are given below those for E = P. Values for the triclinic $P\bar{1}$ phase (rather than the monoclinic $C2/c$ phase) are characterized by the presence of two distance/angle entries

X	Ag–E	Ag–X	E–Ag–E	E–Ag–X
Cl	2.4712(8)	2.489(1)	128.29(3)	115.85(2)
	2.5628(7)	2.481(2)	122.21(4)	118.90(2)
Br	2.4734(9)	2.618(1)	129.42(3)	115.29(2)
	2.5559(7)	2.556(1)	123.39(3)	118.31(2)
I	2.478(1)	2.778(1)	130.75(4)	114.62(3)
	2.5587(8)	2.715(2)	125.48(4)	117.26(2)
CN	2.4803(9)	2.153(6)	124.86(4)	117.57(2)
	2.558(2), 2.568(2)	2.14(2)	120.86(8)	114.7(6), 124.2(6)
$OClO_3$	2.429(1), 2.4323(9)	2.720(7), 3.014(9)	147.34(3)	98.5(1), 113.5(1)
	2.517(1)	2.61(2)	152.40(7)	102.8(5), 103.9(5)
NCO	2.457(1), 2.454(1)	2.205(6)	133.65(4)	111.6(1), 114.5(1)
	2.541(2), 2.540(2)	2.38(1)	127.31(7)	115.5(2), 116.7(2)
O_2NO	2.451(2), 2.440(2)	2.47(1), 2.79(1)	139.14(9)	110.5(2), 109.0(2)
	2.5243(8), 2.5185(8)	2.452(8), 2.553(6)	134.39(3)	106.5(2)–116.6(2)
O_2CCF_3	2.432(2), 2.437(2)	2.531(6), 2.666(6)	141.19(6)	103.5(1)–109.2(1)
	2.506(1), 2.511(1)	2.515(7), 2.585(7)	137.41(4)	105.5(2)–113.2(2)

Data for the E = P array are taken from ref. 5, inclusive of data for the perchlorate from ref. 14. For the present $As(C_6H_{11})_3$ arrays, for the cyanide, 'C–N' is 0.90(3) Å and 'Ag–C–N' 175(2)°; for the cyanate 'C–N,O' are 0.75(2), 1.34(3) Å, and Ag–N–C, N–C–O 133(1), 172(2)° [*cf.* 1.06(1), 1.25(2) Å; 151.2(4), 174.5(6)° for the E = P analogue];[5] for the nitrate Ag–O–N are 101.6(7), 95.2(4)°, and for the perchlorate Ag–O–Cl are 137(2)°. E = P data for the O_2CCF_3 adduct are as yet unpublished; the E = P structure is isomorphous, albeit devoid of disorder. It should be noted that the present monoclinic $C2/c$ array, characteristic of silver(I) complexes, and with $\beta \approx 108°$, is different to that found in some copper(I) analogues where $\beta \approx 96°$, the cyclohexyl ring dispositions differing in the two 'polymorphs'; see ref. 18.

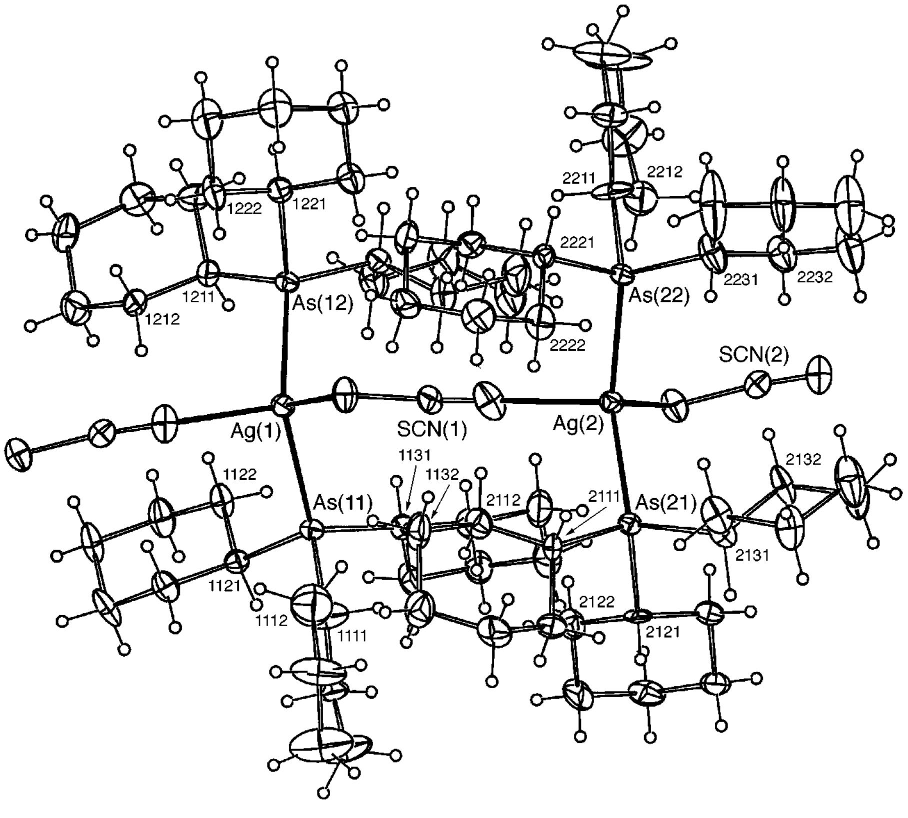

Fig. 2 A single strand of the polymer of the thiocyanate

correlation shows a considerable degree of scatter, particularly in the case of the E = As complexes. It has previously been noted that the P–Ag–P angle in some three- and four-co-ordinate AgX/diphosphine complexes is sensitive to the nature of the Ag–X bonding,[19] and a correlation between increasing *d*(Hg–P) and decreasing θ(P–Hg–P) has been observed for some four-co-ordinate triphenylphosphine mercury(II) complexes $[HgX_2(PPh_3)_2]$.[20] This correlation has been attributed to an effect of the anionic ligand X on both of these structural parameters, as a result of competition for electron density between the M–P and the M–X bonds.[5] The straight lines in Fig. 3 are approximate correlations for $[Ag\{E(C_6H_{11})_3\}_2X]$ with unidentate anionic ligands X, and these show that *d*(Ag–E) is approximately equally sensitive to changes in X for both E = P and As, but that θ(E–Ag–E) is more sensitive to such changes for E = As. This is consistent with the view that $As(C_6H_{11})_3$ is a weaker electron donor than $P(C_6H_{11})_3$, so that the effects of changes in the Ag–X bonding on the As–Ag–As angle are significantly greater. The points for $[Ag\{As(C_6H_{11})_3\}_2X]$ (X = NO_3 or O_2CCF_3) in Fig. 3 are displaced to smaller *d*(Ag–E) and θ(E–Ag–E) relative to the line corresponding to the correlation for the unidentate ligands X = ClO_4, CN, Cl, Br or I. The most

Table 2 Silver environments in AgSCN : $As(C_6H_{11})_3$ (1 : 2). Distances in Å, angles in °. The two values in each entry are for silver (associated ligands) with $n = 1$ or 2 respectively. Primed atoms belong to the adjoining moiety

Ag(*n*)–As(*n*1)	2.573(1), 2.574(3)	As(*n*1)–Ag(*n*)–As(*n*2)	121.84(7), 122.11(9)
Ag(*n*)–As(*n*2)	2.580(2), 2.581(2)	As(*n*1)–Ag(*n*)–S(*n*)	112.1(1), 111.8(1)
Ag(*n*)–S(*n*)	2.602(5), 2.602(5)	As(*n*1)–Ag(*n*)–N(*n*)	103.3(3), 107.6(4)
Ag(*n*)–N(*n*′)	2.33(1), 2.36(2)	As(*n*2)–Ag(*n*)–S(*n*)	111.8(1), 112.6(1)
		As(*n*2)–Ag(*n*)–N(*n*′)	109.5(4), 102.0(3)
S(*n*)–C(*n*)	1.64(2), 1.62(2)	S(*n*)–Ag(*n*)–N(*n*′)	94.2(5), 96.8(4)
N(*n*)–C(*n*)	1.12(2), 1.21(2)	Ag(*n*)–S(*n*)–C(*n*)	98.7(7), 99.6(6)
		S(*n*)–C(*n*)–N(*n*)	178(1), 174(2)
Ag(1) · · · Ag(2,2′)	6.433(3), 6.435(3)	C(*n*)–N(*n*)–Ag(*n*′)	144(2), 139(1)

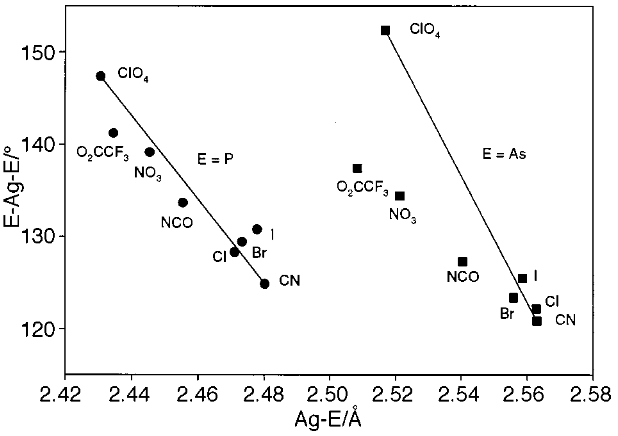

Fig. 3 The *d*(Ag–E) *vs.* θ(E–Ag–E) correlation for $[Ag\{E(C_6H_{11})_3\}_2X]$ [E = P (●) or As (■); data for E = P from ref. 5]. The straight lines are drawn in as *ad hoc* unidentate data

likely reason for this is that NO_3 and O_2CCF_3 act as bidentate ligands in these complexes. This is supported by the observation that the corresponding points for $[Ag\{P(C_6H_{11})_3\}_2X]$ (X = NO_3 or O_2CCF_3) are much closer to the correlation line for unidentate X; NO_3 acts as a unidentate ligand in this case while O_2CCF_3, although formally bidentate in both cases, shows a greater tendency towards unidentate co-ordination (*i.e.* a greater difference between the two Ag–O bond lengths) in the X = P case. As discussed previously for the $[Ag\{P(C_6H_{11})_3\}_2X]$ complexes, the E–Ag–E angle shows an overall decrease as the donor strength of X increases, but the behaviour of the halide complexes is anomalous in this respect, as this angle shows a small increase along the series X = Cl, Br, I, although the donor strength of X^- is expected to increase along this series. The exact reason for this behaviour is not known at present, but we note that the same trend is observed in the present $[Ag\{As(C_6H_{11})_3\}_2X]$ series.

The present work has also defined the nature of the AgSCN : $As(C_6H_{11})_3$ (1 : 2) complex. Whereas the $P(C_6H_{11})_3$ counterpart is relatively unexceptional, being mononuclear and of the monoclinic *C*2/*c* family,[5] here we find a one-dimensional polymer, $\cdots\{As(C_6H_{11})_3\}_2Ag(SCN)\{As(C_6H_{11})_3\}_2Ag(SCN)\cdots$, with four-co-ordinate As_2AgSN silver (Fig. 2); comparison is invited with the structure of AgCN : $As(C_6H_{11})_3$ (1 : 1) in the following paper in the context of potential or actual ambidentate co-ordination by these ligands.[7] The complex crystallises in the rare triclinic space group *P*1 with two formula units comprising the asymmetric unit. The structural parameters that define the silver atom environments are given in Table 2. Whereas the distances within the two silver environments are very similar, there are significant and substantial differences in their angular geometries. The structure overall, however, is of higher pseudo-symmetry, the quasi-screw axis relating the two independent components of the asymmetric unit being clearly evident in Fig. 2. It is of interest that the As–Ag–As angles in the present complexes are not greatly different to the counterpart angles in the mononuclear arrays, suggesting that the possibility of polymer or dimer formation in those arrays may not be energetically very different from that in the monomer.

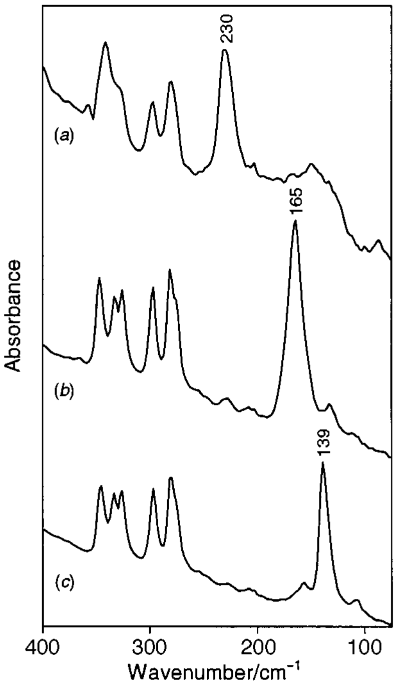

Fig. 4 Far-IR spectra of $[Ag\{As(C_6H_{11})_3\}_2X]$: X = Cl (*a*), Br (*b*) or I (*c*). The bands assigned to the ν(AgX) modes are labelled with their wavenumbers

Infrared spectroscopy

The far-IR spectra of $[Ag\{As(C_6H_{11})_3\}_2X]$ (X = Cl, Br, I, NCO or CN) are shown in Figs. 4 and 5. Strong bands due to $As(C_6H_{11})_3$ ligands 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 the spectra. Thus, for X = Cl, Br or I, strong, halogen-sensitive bands are observed at 230, 165 and 139 cm^{-1} respectively (Fig. 4), and these are assigned as the ν(AgX) modes for these complexes. The wavenumbers of these modes correlate well with those of other AgX complexes. This can be verified by comparison with data for the corresponding $P(C_6H_{11})_3$ complexes,[5] as shown in Table 3, and for other AgX complexes with PPh_3 and $AsPh_3$ ligands.[20] For a range of complexes of the latter type it has been shown that the dependence of ν(AgX) on *r*(AgX) can be represented by the empirical formula (1) where *b* = 22 340, 22 490,

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

41 300 and *m* = 5.09, 5.18, 5.68 for X = Cl, Br, I respectively.[21] These correlations are shown as the continuous lines in Fig. 6, and the data for $[Ag\{E(C_6H_{11})_3\}_2X]$ (E = P or As; X = Cl, Br or

Table 3 Wavenumbers (cm^{-1}) of the ν(AgX) modes in the IR spectra of $[Ag\{E(C_6H_{11})_3\}_2X]$

X	E = P*	E = As
Cl	207	230
Br	149	165
I	121	139
NCO	241	262
CN	288	311

* Ref. 5

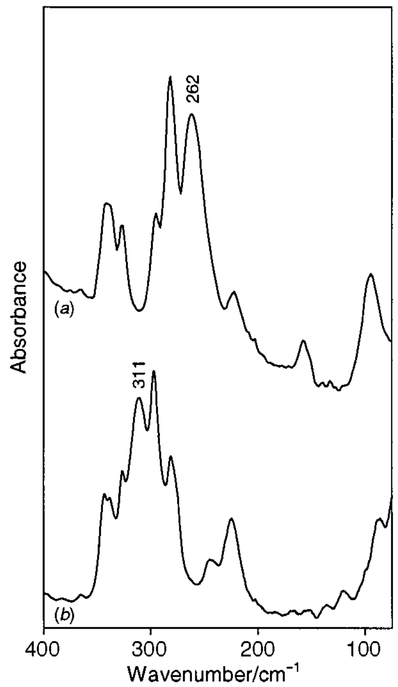

Fig. 5 Far-IR spectra of $[Ag\{As(C_6H_{11})_3\}_2X]$: X = NCO (*a*) or CN (*b*). The bands assigned to the ν(AgX) modes are labelled with their wavenumbers

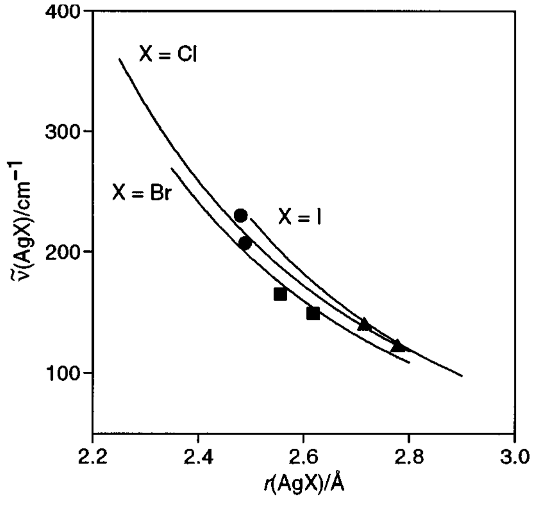

Fig. 6 Plots of ν(AgX) wavenumber against bond length *r*(AgX) from equation (1). Data points are for $[Ag\{E(C_6H_{11})_3\}_2X]$ [X = Cl (●), Br (■) or I (▲); data for E = P from ref. 5 are the points with greater *r*(AgX) and smaller ν(AgX) for each X]

I) are represented as points on this graph. From this it is evident that the data for the $E(C_6H_{11})_3$ compounds lie very close to the correlation lines that were established for the EPh_3 complexes, nearly all of which have structures that are different from those of the $E(C_6H_{11})_3$ complexes.

As is evident from the data in Fig. 6, the $As(C_6H_{11})_3$ compounds show shorter *r*(AgX) and greater ν(AgX) than for the corresponding $P(C_6H_{11})_3$ complexes. A similar observation has been made recently in connection with the data for $[Ag(EPh_3)X]$ (E = P or As; X = Cl, Br or I), and has been attributed to weakened Ag–L bonding in going from $L = PPh_3$ to $AsPh_3$.[22] Possible reasons for this have been given in terms of contributions from steric and electronic effects.[22] The data for $[Ag\{E(C_6H_{11})_3\}_2X]$ are consistent with those for $[Ag(EPh_3)_3X]$, but do not seem to offer any further means of distinguishing between the two possible causes of the observed trends. The assignment of the ν(AgX) modes for $[Ag\{As(C_6H_{11})_3\}_2X]$ (X = NCO or CN) is complicated by the presence of ligand bands in the same region. However, a comparison of the spectra of these two compounds (Fig. 5) suggests ν(AgX) 262 and 311 cm^{-1} for X = NCO and CN respectively. Comparison of these results with those for the corresponding $P(C_6H_{11})_3$ complexes (Table 3) provides strong support for these assignments. In particular, there is an increase in ν(AgX) of about 20 cm^{-1} from the $P(C_6H_{11})_3$ to the corresponding $As(C_6H_{11})_3$ complex, as is also found for the X = Cl, Br or I compounds. The increase in ν(AgX) for the X = NCO complex is somewhat puzzling, however, as the X-ray data suggest an increase in the Ag–X bond length in this case (Table 1), suggesting that the Ag–X bond is weaker in the $As(C_6H_{11})_3$ complex. This is not consistent with the IR result given above, and is contrary to the trend observed in all of the other complexes in Table 1. In this connection, it is relevant that the Ag–As/As–Ag–As data for this complex, as presented in Fig. 3, are also somewhat anomalous, the point for this compound lying well to the left of the correlation line for the other $[Ag\{As(C_6H_{11})_3\}_2X]$ compounds involving unidentate X. The reason for these anomalies is not known at present, although we note that the crystal structure determination for $[Ag\{As(C_6H_{11})_3\}_2(NCO)]$ presented some difficulties (see Experimental section). It would appear that a structure in which Ag–P is greater and Ag–X is smaller than the values given in Table 1 would be more consistent with the spectroscopic data for this compound, and the structural data for the compounds in Table 1.

Acknowledgements

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