DALTON

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

**Graham A. Bowmaker,[a] Effendy,[b,c] Peta J. Harvey,[d] Peter C. Healy,[d] Brian W. Skelton[b] and Allan H. White[b]**

[a] *Department of Chemistry, University of Auckland, Private Bag 92019, Auckland, New Zealand*
[b] *Department of Chemistry, University of Western Australia, Nedlands, Western Australia 6907, Australia*
[c] *Jurusan Pendidikan Kimia, FPMIPA IKIP Malang, Jalan Surabaya 6, Malang 65145, Indonesia*
[d] *Faculty of Science and Technology, Griffith University, Brisbane, Queensland 4111, Australia*

The 1 : 1 adducts of silver(I) halides (AgX; X = Cl, Br or I) with tricyclohexylphosphine have been prepared and their room-temperature single-crystal structures, solid-state cross polarization magic angle spinning (CP MAS) $^{31}$P NMR, solution $^{31}$P NMR and far-IR spectra determined. The solid-state structures of the chloride and bromide complexes recrystallized from pyridine are unsolvated, isomorphous, centrosymmetric dihalide-bridged dimers, $[\{AgX[P(C_6H_{11})_3]\}_2]$, with three-co-ordinate metal centres. Crystals are triclinic, space group $P\bar{1}$, $a \approx 8.8$, $b \approx 9.4$, $c \approx 13.3$ Å, $\alpha \approx 100$, $\beta \approx 92$, $\gamma \approx 115°$. Recrystallization of the iodide complex from pyridine (py) yielded a novel dimer consisting of $[\{AgI(py)_{0.5}[P(C_6H_{11})]_3]\}_2]$ units in which the silver and phosphorus atoms are folded around the I $\cdots$ I vector and towards a bridging pyridine ligand in a 'crevice' co-ordination mode. Recrystallization of the iodide from substituted pyridine bases did not yield further examples of such complexes but rather crystals of an unsolvated 'cubane' tetramer, $[\{AgI[P(C_6H_{11})_3]\}_4]$. The far-IR spectra of the complexes exhibit bands due to ν(AgX) vibrational modes at 225, 143 cm$^{-1}$ for X = Cl, 189, 167, 135. 114 cm$^{-1}$ for X = Br, 113, 83 cm$^{-1}$ for X = I and at 115, 90 cm$^{-1}$ for $[\{AgI(py)_{0.5}[P(C_6H_{11})_3]\}_2]$. These spectra are interpreted in terms of idealized $C_{2h}$ $Ag(\mu\text{-}X)_2Ag$ and $T_d$ $Ag_4I_4$ structures of the silver halide cores. The separation between the bands in the spectra of the dimeric species is a sensitive function of the extent of distortion of the cores from $D_{2h}$ symmetry. The solid-state CP MAS $^{31}$P NMR spectra of the dimers exhibit simple doublets with average $^1J$(P–Ag) coupling constants of 648 Hz for $[\{AgCl[P(C_6H_{11})_3]\}_2]$, 612 Hz for $[\{AgBr[P(C_6H_{11})_3]\}_2]$ and 552 Hz for $[\{AgI(py)_{0.5}[P(C_6H_{11})_3]\}_2]$. Solution $^{31}$P NMR spectra of the chloride and bromide complexes show well resolved sets of doublets due to $^1J$(P–$^{107,109}$Ag) coupling at 25 and 0 °C respectively with average $^1J$(P–Ag) coupling constants of 642 and 627 Hz. The solution spectra of both the tetrameric and crevice iodide complexes are similar, showing broad signals at room temperature and doublets at −60 °C [δ 12, $^1J$(P–Ag) = 544 Hz]. These structural and spectroscopic results are compared with those for other 1 : 1 AgX : phosphine complexes.

Structural studies on complexes formed from the reaction of silver(I) halides with monodentate tertiary phosphines in 1 : 1 stoichiometric ratios show that the majority of the complexes exist as tetrameric 'cubane' clusters of general formula $[\{AgX(PR_3)\}_4]$ in which the silver atoms are surrounded by one phosphine ligand and three halide anions to form a distorted-tetrahedral configuration.[1–6] Exceptions to this include formation of a 'step' tetramer as well as the cubane tetrameric isomer for $[\{AgI(PPh_3)\}_4]$[4] and the adducts of AgCl and AgBr with tris(2,4,6-trimethoxyphenyl)phosphine (tmpp) which form linear two-co-ordinate monomeric complexes, [AgX(tmpp)].[7] No dimeric $[\{AgX(PR_3)\}_2]$ complexes with three-co-ordinate silver atoms have been structurally characterized for this system. The basicity and steric profile of tricyclohexylphosphine suggested to us the possibility that 1 : 1 adducts with AgX would form such dimers and to explore this we recrystallized 1 : 1 stoichiometric ratios of AgX and $P(C_6H_{11})_2$ from pyridine. The results of this work show that the chloride and bromide complexes do indeed form unsolvated $[\{AgX[P(C_6H_{11})_3]\}_2]$ dimers as air-stable crystalline materials. However, the iodide complex yields instead a novel pyridine-bridged dimer, $[\{AgI(py)_{0.5}[P(C_6H_{11})_3]\}_2]$ in which the pyridine molecule is weakly co-ordinated to both silver atoms, while with other pyridine bases a 'normal' unsolvated cubane $[\{AgI[P(C_6H_{11})_3]\}_4]$ tetramer rather than the dimer is formed. We report here these synthetic results together with characterization of the complexes by single-crystal X-ray determinations, far-infrared, solid-state $^{31}$P NMR and solution $^{31}$P NMR spectroscopy.

## Experimental

### Preparations

**$[\{AgX[P(C_6H_{11})_3]\}_2]$ (X = Cl or Br).** The compound AgX (0.25 mmol) and $P(C_6H_{11})_3$ (0.25 mmol) were dissolved in warm pyridine (5 cm$^3$) to give clear solutions which on cooling deposited colourless crystals of the product. X = Cl: m.p. 274–277 °C (decomp.) (Found: C, 51.2; H, 7.9; P, 7.1. Calc. for $C_{36}H_{66}Ag_2Cl_2P_2$: C, 51.0; H, 7.85; P, 7.3%). X = Br: m.p. 247–249 °C (decomp.) (Found: C, 46.3; H, 7.1; P, 6.5. Calc. for $C_{36}H_{66}Ag_2Br_2P_2$: C, 46.2; H, 7.1; P 6.6%).

**$[\{AgI(py)_{0.5}[P(C_6H_{11})_3]\}_2]$.** Silver iodide (0.25 mmol) and $P(C_6H_{11})_3$ (0.25 mmol) were dissolved in warm pyridine (10 cm$^3$) to give a clear solution which on cooling deposited colourless crystals of the product, decomp. > 58 °C (Found: C, 44.3; H, 6.4; N, 1.3; P, 5.4. Calc. for $C_{41}H_{71}Ag_2I_2NP_2$: C, 44.4; H, 6.45; N, 1.25; P, 5.6%).

**$[\{AgI[P(C_6H_{11})_3]\}_4]$.** Silver iodide (0.25 mmol) and $P(C_6H_{11})_3$ (0.25 mmol) were dissolved in warm 2-methylpyridine (10 cm$^3$) to give clear solutions which on cooling deposited colourless crystals, m.p. > 202 °C (decomp.) (Found: C, 42.0; H, 6.3; P, 6.2. Calc. for $C_{36}H_{66}Ag_2I_2P_2$: C, 41.95; H, 6.45; P, 6.0%).

### Crystallography

General procedures are given in ref. 8; specific details are as follows.

**Crystal data.** $[\{AgCl[P(C_6H_{11})_3]\}_2]$, $C_{36}H_{66}Ag_2Cl_2P_2$, $M = 847.5$, triclinic, space group $P\bar{1}$, ($C_i^1$, no. 2), $a = 8.699(8)$, $b = 9.324(6)$, $c = 13.285(3)$ Å, $\alpha = 99.67(4)$, $\beta = 92.85(4)$, $\gamma = 114.69(5)°$, $U = 956$ Å$^3$. $D_c$ ($Z = 1$ dimer) = 1.47 g cm$^{-3}$, $F(000) = 440$, $\mu_{Mo} = 11.6$ cm$^{-1}$, specimen 0.31 × 0.25 × 0.04 mm, $A^*_{min,max} = 1.05, 1.30$, $2\theta_{max} = 50°$, $N = 3352$, $N_o = 2686$, $R = 0.044$, $R' = 0.050$.

$[\{AgBr[P(C_6H_{11})_3]\}_2]$, $C_{36}H_{66}Ag_2Br_2P_2$, $M = 936.4$, triclinic, space group $P\bar{1}$, $a = 8.875(5)$, $b = 9.459(4)$, $c = 13.343(4)$ Å, $\alpha = 99.89(3)$, $\beta = 91.85(4)$, $\gamma = 115.70(3)°$, $U = 987$ Å$^3$, $D_c$ (Z = 1 dimer) = 1.57 g cm$^{-3}$, $F(000) = 476$, $\mu_{Mo} = 30.0$ cm$^{-1}$, specimen 0.31 × 0.25 × 0.11 mm, $A^*_{min,max} = 1.32, 1.74$, $N = 3109$, $N_o = 1882$, $R = 0.043$, $R' = 0.040$.

$[\{AgI(py)_{0.5}[P(C_6H_{11})_3]\}_2]$, $C_{41}H_{71}Ag_2I_2NP_2$, $M = 1109.5$, monoclinic, space group $C2/c$ ($C_{2h}^6$, no. 15), $a = 9.313(7)$, $b = 17.03(3)$, $c = 28.23(1)$ Å, $\beta = 93.17(5)°$, $U = 4470$ Å$^3$, $D_c$ (Z = 4) = 1.65 g cm$^{-3}$, $F(000) = 2216$, $\mu_{Mo} = 21.8$ cm$^{-1}$, specimen 0.30 × 0.46 × 0.05 mm, $A^*_{min,max} = 1.07, 1.65$, $N = 3630$, $N_o = 2074$, $R = 0.047$, $R' = 0.049$.

$[\{AgI[P(C_6H_{11})_3]\}_4]$, $C_{72}H_{132}Ag_4I_4P_4$, $M = 2060.9$, monoclinic, space group $C2/c$, $a = 15.583(5)$, $b = 29.113(3)$, $c = 19.135(7)$ Å, $\beta = 108.86(3)°$, $U = 8214$ Å$^3$, $D_c$ ($Z = 4$ tetramer) = 1.67 g cm$^{-3}$, $F(000) = 4096$, $\mu_{Mo} = 23.7$ cm$^{-1}$, specimen 0.50 × 0.36 × 0.30 mm, $A^*_{min,max} = 1.79, 2.14$, $N = 7239$, $N_o = 3710$, $R = 0.060$, $R' = 0.061$.

Ring C(13*x*) is disordered over two sets of sites, as is ring 22*x*; atoms C(134), C(136), C(224), C(226) were modelled with two components A, B, each with site occupancy 0.5 after consideration of refinement behaviour.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/40.

### Spectroscopy

General procedures for obtaining the solid-state cross polarization magic angle (CP MAS) $^{31}P$ NMR, variable-temperature solution $^{31}P$ ($CH_2Cl_2$–10% $CD_2Cl_2$) and far-infrared spectra for the complexes are given in ref. 8.

## Results and Discussion

### Synthesis and structural data

Recrystallization of 1:1 stoichiometric quantities of AgX and $P(C_6H_{11})_3$ from pyridine for X = Cl or Br gives well formed, analytically pure, unsolvated 1:1 complexes which room-temperature single-crystal X-ray studies show to be isomorphous with each other and with the copper(I) chloride analogue,[9] the setting of which provides the basis for the present structure. The triclinic unit cell contains one centrosymmetric dihalide-bridged dimer $[\{AgX[P(C_6H_{11})_3]\}_2]$, with the $Ag(\mu\text{-}X)_2Ag$ central rhomb necessarily planar (Fig. 1). The $AgX_2P$ silver co-ordination sphere is also planar with the phosphorus atom deviating from the plane by $0.00_8$ (Cl) and $0.03_4$ Å (Br) and the sum of the angles around the silver atom not differing significantly from 360°. Crystallization from pyridine for X = I, however, does not result in the formation of an unsolvated dimer but rather a dimer with one weakly co-ordinated pyridine molecule. The structure as determined by single-crystal X-ray diffraction is shown in Fig. 2 and consists of a dimer disposed about a crystallographic 2 axis passing through the centre of the $AgI_2Ag$ core and the N–C(4) axis of the co-ordinated pyridine molecule. The pyridine lies in the cleft formed by cyclohexyl rings of the ligands and acts as a weakly co-ordinated bridging ligand to both silver atoms with Ag–N 2.76(1) Å. The effect of this mode of co-ordination is to fold the $PAgI_2AgP$ core about the I ··· I axis such that the silver and phosphorus atoms bend toward the pyridine molecule, with the $AgI_2/I_2Ag$ dihedral angle 57.80(6)° (Fig. 2). The pyridine lies almost but not exactly in the I ··· I axis in projection down the 2 axis, being twisted about that axis slightly with a dihedral angle between the $I_2N$ and $C_5N$ planes of 7.5(6)°. The two $AgI_2P$ co-ordination spheres of the dimer are only slightly distorted from planarity with the sum of the P–Ag–I and I–Ag–I angles being 357° and the silver atom 0.6 Å above the $I_2P$ plane. This 'crevice' bridging co-ordination mode of pyridine is very unusual and has, to our knowledge, only been described for the molybdenum complex $[(MoO)_2(C_8H_9PS_2)_4(OS)_2(py)]$.[10] Further experiments aimed at preparing similar crevice complexes with a range of other pyridine bases did not prove successful, chemical analyses on the products obtained being consistent with the formation of unsolvated 1:1 complexes which, somewhat surprisingly, were shown by X-ray determination on crystalline samples not to be dimeric but rather the 'standard' cubane tetramer (Fig. 3).

The geometric parameters for the dimeric complexes are given in Table 1 and the tetrameric $[\{AgI[P(C_6H_{11})_3]\}_4]$ complex in Table 2. Table 3 provides a summary of average distances and angles for the molecular core geometries of structurally characterized $(AgXP)_n$ compounds with $n$ = 1, 2 or 4. For $[\{AgCl[P(C_6H_{11})_3]\}_2]$ the Ag–P bond length of 2.354(2) Å is marginally shorter than ⟨Ag–P⟩ for the chloride 'cubane' tetramers [2.38(1) Å] and is also unexpectedly shorter than that recorded for *d*(Ag–P) in the two-co-ordinate com-

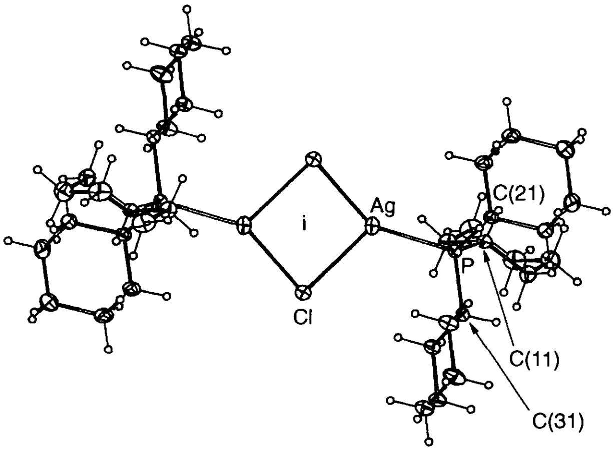


**Fig. 1** Crystal structure of the chloride dimer projected normal to $Ag_2Cl_2$ plane

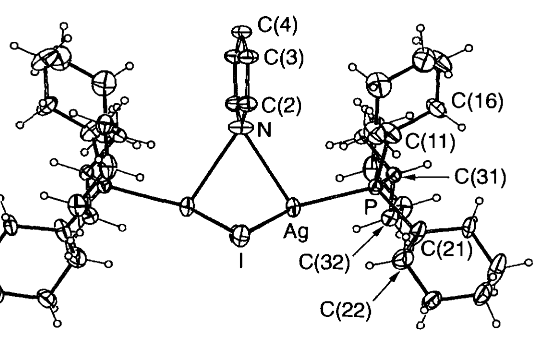


**Fig. 2** Crystal structure of the crevice dimer viewed normal to the 2 axis and to the Ag ··· Ag line

**Table 1** Silver environments [distances in Å, angles in °, L = $P(C_6H_{11})_3$]

| | $[\{AgCl(L)\}_2]$ | $[\{AgBr(L)\}_2]$ | $[\{AgI(py)_{0.5}L]\}_2]$ |
|---|---|---|---|
| Ag–X | 2.640(3) | 2.718(2) | 2.822(1) |
| Ag–X′ | 2.454(2) | 2.576(2) | 2.857(2) |
| Ag–P | 2.354(2) | 2.374(2) | 2.415(3) |
| Ag–N | | | 2.76(1) |
| Ag··· Ag′ | 3.488(2) | 3.493(1) | 2.977(2) |
| X··· X′ | 3.718(3) | 3.981(2) | 4.548(3) |
| Ag–X–Ag′ | 86.33(6) | 82.52(4) | 63.24(4) |
| X–Ag–X′ | 93.67(7) | 97.48(5) | 106.43(5) |
| P–Ag–X | 118.85(6) | 119.55(6) | 128.56(8) |
| P–Ag–X′ | 147.48(6) | 142.96(6) | 122.43(8) |
| Ag–N–Ag′ | | | 65.5(3) |
| N–Ag–P | | | 107.9(2) |
| N–Ag–I | | | 88.1(1) |
| N–Ag–I′ | | | 87.4(1) |

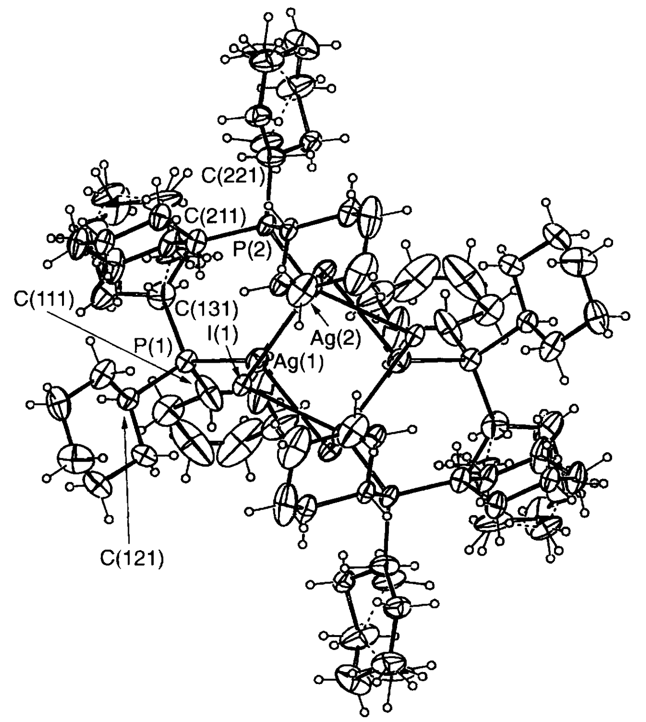
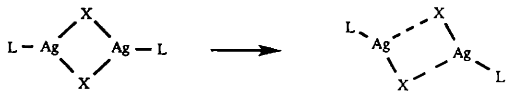


**Fig. 3** Structure of $[\{AgI[P(C_6H_{11})_3]\}_4]$ projected down the two-fold axis

**Table 2** Silver environments (distances in Å, angles in °) in tetrameric $[\{AgI[P(C_6H_{11})_3]\}_4]$

| | | | |
|---|---|---|---|
| Ag(1)–I(1) | 2.889(2) | Ag(2)–I(1) | 2.848(2) |
| Ag(1)–I(2) | 2.902(2) | Ag(2)–I(2) | 3.095(2) |
| Ag(1)–I(1′) | 2.975(2) | Ag(2)–I(2′) | 2.861(2) |
| Ag(1)–P(1) | 2.470(4) | Ag(2)–P(2) | 2.435(3) |
| Ag(1) ··· Ag(1′) | 3.555(2) | I(1) ··· I(1′) | 4.602(2) |
| Ag(1) ··· Ag(2′) | 3.749(2) | I(1) ··· I(2′) | 4.226(1) |
| Ag(1) ··· Ag(2) | 3.356(2) | I(1) ··· I(2) | 4.811(2) |
| Ag(2) ··· Ag(2′) | 3.818(2) | I(2) ··· I(2′) | 4.512(2) |
| I(1)–Ag(1)–I(2) | 112.38(5) | I(1)–Ag(2)–I(2) | 108.02(5) |
| I(1)–Ag(1)–I(1′) | 103.41(6) | I(1)–Ag(2)–I(2′) | 95.50(4) |
| I(2)–Ag(1)–I(1′) | 91.95(4) | I(2)–Ag(2)–I(2′) | 98.45(5) |
| P(1)–Ag(1)–I(1) | 110.4(1) | P(2)–Ag(2)–I(1) | 122.07(9) |
| P(1)–Ag(1)–I(2) | 124.4(1) | P(2)–Ag(2)–I(2) | 100.9(1) |
| P(1)–Ag(1)–I(1′) | 110.8(1) | P(2)–Ag(2)–I(2′) | 128.7(1) |
| Ag(1)–I(1)–Ag(2) | 71.60(5) | Ag(1)–I(2)–Ag(2) | 67.97(4) |
| Ag(1)–I(1)–Ag(1′) | 74.63(5) | Ag(1)–I(2)–Ag(2′) | 81.17(4) |
| Ag(2)–I(1)–Ag(1′) | 80.12(4) | Ag(2)–I(2)–Ag(2′) | 79.62(5) |

Primed atoms related to unprimed equivalents by $1 - x, y, \frac{3}{2} - z$.



**Scheme 1**

plex [AgCl(tmpp)] [2.379(1) Å]. For $[\{AgBr[P(C_6H_{11})_3]\}_2]$, the Ag–P bond length increases to 2.374(2) Å which is slightly shorter than ⟨Ag–P⟩ for the bromide 'cubane' tetramers [2.41(1) Å] and the same within experimental error as that recorded for [AgBr(tmpp)] [2.374(2) Å]. Overall, these results for the chloride and bromide complexes indicate that the Ag–P bond length in these complexes is relatively insensitive to changes in ligand, halide or co-ordination number. By contrast, ⟨Ag–X⟩ increases significantly through the transition from two- to three- to four-co-ordination; values for the two structures are also shorter than comparable values found in $[\{AgX(PPh_3)_2\}_2]$ arrays.[11]

The Ag–P bond lengths for the iodide 'cubane' tetramers are generally slightly longer than those for the chloride or bromide complexes with ⟨Ag–P⟩ 2.43(1) Å and the comparable values for the $[\{AgI[P(C_6H_{11})_3]\}_4]$ are consistent with this. Similarly, Ag–X lies within the same range of values found for other cubane tetramers. In the $[\{AgI(py)_{0.5}[P(C_6H_{11})_3]\}_2]$ 'crevice' complex the Ag–P bond length decreases to 2.415(3) Å which is shorter than values recorded for any of the above iodide complexes and also shorter than the value of 2.430(3) Å found for the three-co-ordinate silver in the $[\{AgI(PPh_3)]\}_4]$ step tetramer.[4] The Ag–I distances of 2.822(1) and 2.857(2) Å are shorter than comparable values for the cubane complexes (⟨$2.9_1$ Å⟩), but longer than the distance of 2.76(6) Å recorded for the Ag–I bond associated with the three-co-ordinate silver in 'step' $[\{AgI(PPh_3)\}_4]$. These results are consistent with weak pyridine–silver interactions in this complex and the essentially three-co-ordinate planar $AgI_2P$ environment.

A feature of the structures of the chloride and bromide dimers is that the planar $PAgX_2AgP$ units show substantial in-plane distortions about the silver atom with differences in the two Ag–X distances and P–Ag–X angles of $0.14_2$ Å and $23.4_1$° for the bromide complex, increasing to $0.18_3$ Å and $28.6_3$° for the chloride (Table 1). This distortion can be described as a partial separation of the $[\{AgX[P(C_6H_{11})_3]\}_2]$ dimer into two $[AgX\{P(C_6H_{11})_3\}]$ monomers (Scheme 1). In the cubane $[\{AgX(PPh_3)\}_4]$ complexes similar variations in the P–Ag–X angles are observed and ascribed to steric interactions between the ligands.[6] However, in the present series of complexes, the cyclohexyl rings each adopt 'comfortable' dispositions as described in the figures and tables; ring 3 lies with its 'plane' quasi-normal to the Ag–P line, while rings 1 and 2 lie quasi-parallel with normal hydrogen–halogen contacts X ··· H(36A) $2.8_9$, $2.9_9$, X′ ··· H(26A) $2.8_4$, $2.9_8$ Å (X = Cl, Br respectively in each case). Further, the differences in Cu–Cl and P–Cu–Cl in the analogous (and isomorphous) copper chloride complex [Δ(Cu–Cl) = 0.037 Å, Δ(P–Cu–Cl) = 8.65°] are much less whereas it might have been expected on steric consideration alone that the decreased M–P bond length for the copper compounds would result in more steric strain and greater distortion. Stabilization of complexes with low co-ordination numbers is also favoured by co-ordination of basic ligands to the silver atoms[7] and it seems that for the present structures a combination of the high basicity of $P(C_6H_{11})_3$ ($pK_a = 9.65$[12]) and the bulkiness of the ligand substituents is sufficient to result in the observed distortions. The distortion observed for the bromide complex is considerably less than that of the chloride and the effects appear to be further diminished for the iodide to the extent that four-co-ordination is favoured with complexes crystallizing as either a relatively undistorted cubane tetramer with $AgI_3P$ co-ordination on the one hand or as a bridging pyridine 'crevice' dimer with $AgI_2P$ ··· N co-ordination on the other.

**Table 3** Average molecular core geometries (distances in Å, angles in °) for $[\{AgX(L)\}_n]$ (X = Cl, Br or I)

| Molecule | Ag–P | Ag–X | Ag···Ag | X···X | P–Ag–X | X–Ag–X | Ag–X–Ag | Ref. |
|---|---|---|---|---|---|---|---|---|
| X = Cl | | | | | | | | |
| [AgCl(tmpp)] | 2.379(1) | 2.342(1) | — | — | 175.0(1) | — | — | 7 |
| $[\{AgCl[P(C_6H_{11})_3]\}_2]$ | 2.354(2) | 2.5(1) | 3.488(2) | 3.718(3) | 133(20) | 93.67(7) | 86.33(6) | This work |
| $[\{AgCl(PEt_3)\}_4]$ | 2.389(2) | 2.6(3) | 3.5(3) | 3.926(3) | 120(13) | 96(7) | 84(6) | 1 |
| $[\{AgCl(PPh_2Bu)\}_4]$ | 2.365(8) | 2.65(8) | 3.6(2) | 3.80(8) | 124(6) | 91(3) | 88(3) | 3 |
| $[\{AgCl(PPh_3)\}_4]$ | 2.381(8) | 2.65(9) | 3.65(2) | 3.81(2) | 122(12) | 93(5) | 86(5) | 6 |
| X = Br | | | | | | | | |
| [AgBr(tmpp)] | 2.374(2) | 2.448(1) | — | — | 174.40(6) | — | — | 7 |
| $[\{AgBr[P(C_6H_{11})_3]\}_2]$ | 2.374(2) | 2.6(1) | 3.493(1) | 3.981(2) | 131(16) | 97.48(5) | 82.52(4) | This work |
| $[\{AgBr(PEt_3)\}_4]$ | 2.402(5) | 2.74(3) | 3.5(3) | 4.201(3) | 116(11) | 100(6) | 79(5) | 1 |
| $[\{AgBr(PPh_2Bu)\}_4]$ | 2.408(6) | 2.76(8) | 3.7(1) | 4.06(5) | 122(7) | 94(3) | 85(2) | 3 |
| $[\{AgBr(PPh_3)\}_4]$ | 2.42(1) | 2.8(1) | 3.8(1) | 4.1(2) | 122(–) | 93(–) | 86(–) | 5 |
| X = I | | | | | | | | |
| $[\{AgI[P(C_6H_{11})_3]\}_4]$ | 2.45(2) | 2.93(9) | 3.6(2) | 4.5(2) | 116(1) | 102(7) | 76(5) | This work |
| $[\{AgI(PEt_3)\}_4]$ | 2.438(2) | 2.918(1) | 3.21(2) | 4.75(3) | 109.9(7) | 109.0(9) | 66.7(4) | 2 |
| $[\{AgI(PPh_2Bu)\}_4]$ | 2.43(1) | 2.90(3) | 3.47(3) | 4.56(2) | 114(3) | 104.0(1) | 73.8(1) | 3 |
| $[\{AgI(PPh_3)\}_4]$ cube | 2.458(3) | 2.91(8) | 3.5(2) | 4.6(2) | 114(6) | 104(6) | 73(5) | 4 |
| step | 2.454(3) | 2.89(9) | 3.438(2) | 4.712(2) | 111(6) | 107(2) | 86(19) | 4 |
| | 2.430(3) | 2.76(6) | 3.095(1) | 4.765(1) | 119(11) | 118.90(4) | 66(2) | |

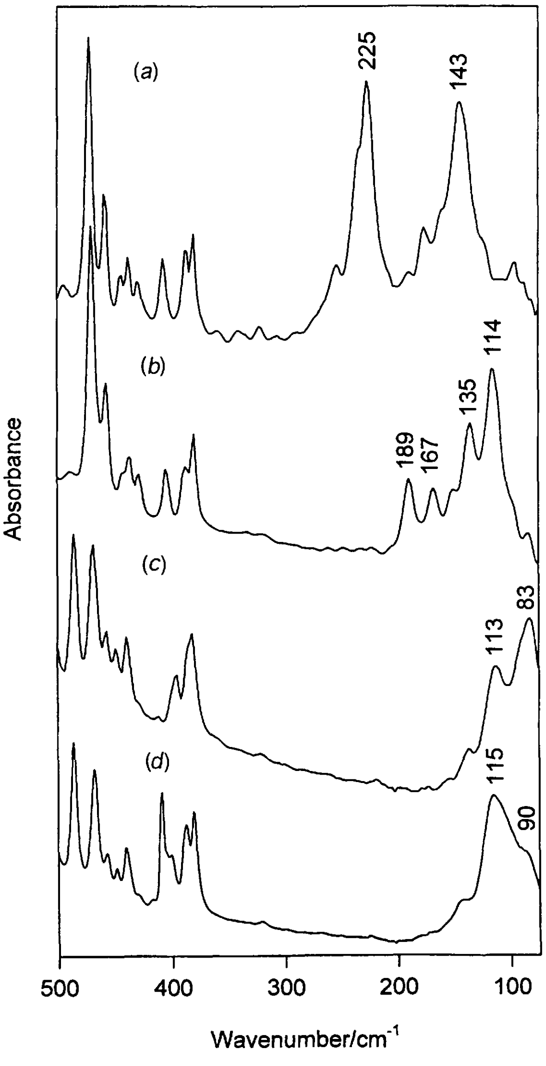


**Fig. 4** Far-IR spectra of $[LAgX_2AgL]$ [X = Cl (*a*) or Br (*b*), $[\{AgI(L)\}_4]$ (*c*) and of $[LAgI_2(py)AgL]$ (*d*) [L = $P(C_6H_{11})_3$]. The bands assigned to the ν(AgX) modes are labelled with their wavenumbers

The Ag ··· Ag distances for the chloride and bromide dimers are 3.488(2) and 3.493(1) Å respectively and lie in the middle of the range 3.4–3.6 Å found for cubane tetramers. In the iodide crevice dimer the Ag ··· Ag distance decreases to 2.977(2) Å which is comparable with the distances of 3.095(1) Å for 'step' $[\{AgI(PPh_3)\}_4]\cdot CH_2Cl_2$ [4] and 2.956(1) Å for $[\{AgI(py)(PPh_3)\}_2]$ in which a pyridine molecule is σ co-ordinated to each silver atom.[13] In these latter two complexes the shorter Ag ··· Ag distances are achieved by the silver atoms moving closer together in the $AgX_2Ag$ plane accompanied by an increase in the I–Ag–I angle from 102–107 to *ca.* 118°. For the crevice compound θ(I–Ag–I) remains unchanged and the Ag ··· Ag distance is reduced through folding of the silver atoms about the I ··· I axis. This complex can be compared to the previously reported $[(Ph_3P)CuI_3(PPh_3)]^-$ species in the sense that the two metal atoms are connected by three doubly bridging ligands, and in the copper complex this results in a short Cu ··· Cu distance.[14] The extent of this effect in the present compound is of interest, despite the weakness of the interaction of the pyridine with the silver atoms.

### Far-IR spectroscopy

The far-IR spectra of the complexes are shown in Fig. 4. Uncomplexed $P(C_6H_{11})_3$ shows no bands of significant intensity below 370 $cm^{-1}$. In the region below 250 $cm^{-1}$ there are strong, halogen-sensitive bands which are assigned to the ν(AgX) modes. The wavenumbers of these bands are compared in Table 4 with those of related complexes. For the chloride dimer two ν(AgCl) bands are observed. The situation is similar to that discussed previously for the $[\{AgX(PPh_3)_2\}_2]$ dimers.[11] For an isolated dimer of $D_{2h}$ symmetry two IR-active ν(AgX) modes of $B_{2u}$ and $B_{3u}$ symmetry are predicted. For a perfectly square $Ag(\mu\text{-}X)_2Ag$ unit (*x* parallel to the Ag ··· Ag diagonal, *y* parallel to the X ··· X diagonal) the two IR-active normal modes involve displacement of X and Ag along the positive and negative directions respectively ($B_{3u}$) or a similar vibration in the *y* direction ($B_{2u}$). For an isolated square $Ag(\mu\text{-}X)_2Ag$ unit these two modes would have the same frequency. This is the situation which was observed for the chloroform solvates $[\{AgX(PPh_3)_2\}_2]\cdot 2CHCl_3$ (X = Cl or Br).[11] 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, while the other mainly involves stretching of the two long Ag–X bonds, so that the two modes should give rise to bands at significantly different wavenumbers. This situation

**Table 4** Metal–halogen vibrational frequencies for complexes of $P(C_6H_{11})_3$, tmpp and $PPh_3$ with silver(I) halides

| | X | | | |
|---|---|---|---|---|
| Compound | Cl | Br | I | Ref. |
| [AgX(tmpp)] | 282 | 215 | — | 7 |
| $[\{AgX[P(C_6H_{11})_3]\}_2]$ | 225, 143 | 189, 167<br>135, 114 | — | This work |
| $[AgX\{P(C_6H_{11})_3\}_2]$ | 207 | 149 | 121 | 8 |
| $[\{AgX(PPh_3)_2\}_2]\cdot CHCl_3$ | 166 | 120 | — | 11 |
| $[\{AgX(PPh_3)_2\}_2]$ | 179, 127 | — | — | 11 |
| $[\{AgX[P(C_6H_{11})_3]\}_4]$ | — | — | 113, 83 | This work |
| $[\{AgX(PPh_3)\}_4]$ cube | 178, 140 | 131, 116 | 109, 82 | 15 |
| $[\{AgX(py)_{0.5}[P(C_6H_{11})_3]\}_2]$ | — | — | 115, 90 | This work |

is obtained for unsolvated $[\{AgCl(PPh_3)_2\}_2]$, the crystal structure[16] of which shows a distorted $Ag(\mu\text{-}Cl)_2Ag$ core with two sets of Ag–Cl bond lengths which give rise to two IR bands which differ in wavenumber by about 50 cm$^{-1}$.[11] The larger splitting of about 80 cm$^{-1}$ observed in the present study for $[\{AgCl[P(C_6H_{11})_3]\}_2]$ correlates well with the greater difference in the Ag–Cl bond lengths in this compound. This is evident in the data presented in Fig. 5, which shows the relationship between the ν(AgCl) wavenumbers and the corresponding bond lengths *d*(Ag–Cl) for the halide-bridged complexes discussed above, and for [AgCl(tmpp)][7] and $[AgCl\{P(C_6H_{11})_3\}_2]$.[8] The situation for $[\{AgBr[P(C_6H_{11})_3]\}_2]$ is slightly more complicated. This complex, like the chloro analogue, shows a centrosymmetric $Ag(\mu\text{-}Br)_2Ag$ core with two quite different Ag–Br bond lengths, so that two well separated ν(AgBr) bands are expected. However, the spectrum shows at least four bands in the expected region of 100–200 cm$^{-1}$, and comparison with the simpler spectrum of the 1 : 2 complex[8] shows that there are no strong ligand bands which can complicate the spectrum in this region. We assign the two bands at 189, 167 cm$^{-1}$ to the shorter of the AgBr bonds and those at 135, 114 cm$^{-1}$ to the longer. The average positions of these pairs fit well with the ν(AgBr) *vs.* *d*(Ag–Br) correlation shown in Fig. 5, which includes data for [AgBr(tmpp)][7] and $[AgBr\{P(C_6H_{11})_3\}_2]$.[8] The reason for the additional splitting observed in ν(AgBr) bands in the present case is not known. Other trends in the ν(AgX) wavenumbers of the Cl and Br complexes correlate well with the structures. There is a decrease in the wavenumber of the highest ν(AgX) band from the 1 : 1 $P(C_6H_{11})_3$ complexes to the 1 : 2 $PPh_3$ complexes, and this is as expected for a change from three- to four-co-ordination. However, the magnitude of this change is greater for the chloride complexes.

Spectra of the cubane iodide tetramer show two ν(AgI) bands at 113 and 83 cm$^{-1}$ which correspond closely with those for the corresponding cubane $PPh_3$ complex,[15] in agreement with the observation that the $Ag_4I_4$ cores in these compounds have similar structures. The spectrum of the 'crevice' dimer shows a strong band at 115 cm$^{-1}$ with a shoulder at 90 cm$^{-1}$ which are assigned to ν(AgI) vibrational modes. Comparison with the spectra of the chloride and bromide dimers shows that the band splitting is much smaller in this case which is consistent with the considerably smaller differences in the two Ag–I bond lengths (0.035 Å, compared with 0.186, 0.142 Å for the chloride and bromide complexes).

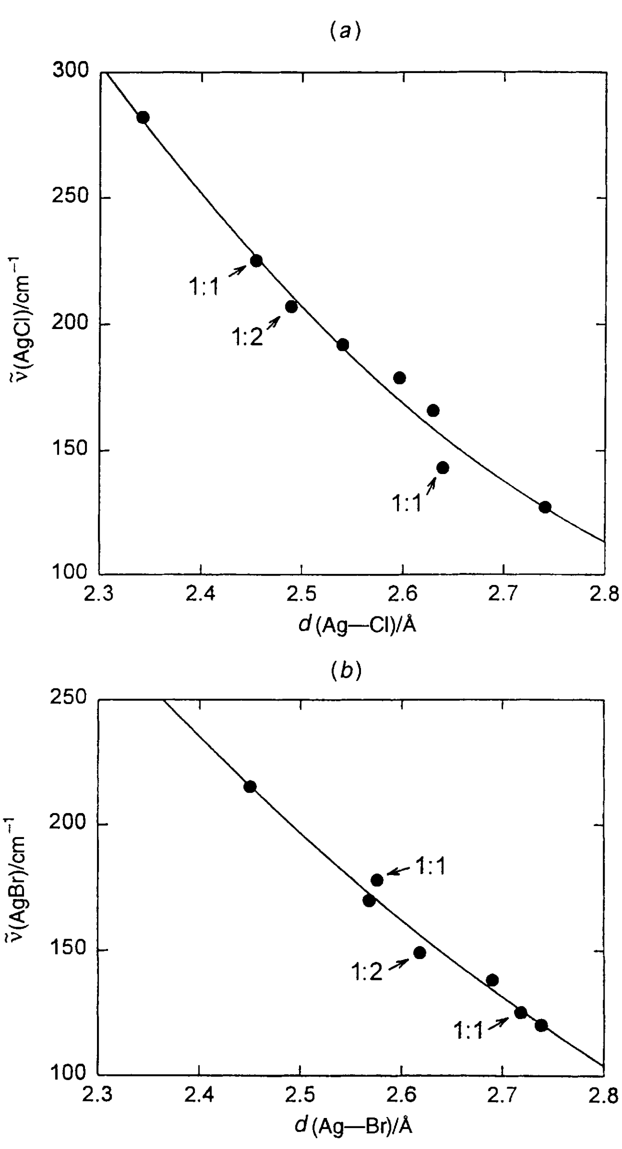


**Fig. 5** Dependence of ν(AgX) on the Ag–X bond length for X = Cl (*a*) or Br (*b*). The points corresponding to 1 : 1 and 1 : 2 AgX : $P(C_6H_{11})_3$ complexes are labelled. The sources of the other data are given in the text

## $^{31}P$ NMR spectroscopy

The chemical shift and coupling-constant data determined from the solid-state CP MAS and solution spectra for the present series of compounds are presented in Table 5. Equivalent data on other structurally characterized 1 : 1 $[\{AgX(PR_3)\}_n]$ complexes are sparse, being available only for the [AgX(tmpp)][7] and $[\{AgX(PPh_2Bu)\}_4]$[3] (solid-state data only) and as part of this work we re-recorded the solid-state data for these complexes utilizing our present instrumentation (obtaining a well resolved doublet for $[\{AgI(PPh_2Bu)\}_4]$ in contrast to the broad signal previously recorded), and low-temperature solution data for the $[\{AgX(PPh_2Bu)\}_4]$ complexes. These results are incorporated into Table 5 and permit comparison for the first time of data for the series of mono-, di- and tetra-meric complexes: [AgX(tmpp)],[7] $[\{AgX[P(C_6H_{11})_3]\}_2]$ and $[\{AgX(PPh_2Bu)\}_4]$,[3] with AgXP, $AgX_2P$ and $AgX_3P$ co-ordination respectively. The crystal lattice symmetry in each of these

**Table 5** Solid-state CP MAS $^{31}$P and solution ($CH_2Cl_2$–10% $CD_2Cl_2$) $^{31}$P NMR parameters for [$\{AgX[P(C_6H_{11})_3\}_n$] and related complexes of 1 : 1 stoichiometry. Estimated errors in the coupling constants are ± 10 (solid state) and ± 5 Hz (solution state)

| | Solid state | | Solution | | | |
|---|---|---|---|---|---|---|
| Compound | δ | $^1J$(P–Ag)/Hz | δ | $^1J$(P–$^{107,109}$Ag)/Hz | $^1J$(P–Ag) (av.)/Hz | $T$/°C |
| X = Cl | | | | | | |
| [AgCl(tmpp)] | −67 | 740 | −67 | 711, 821 | 765 | 25 |
| [$\{AgCl[P(C_6H_{11})_3]\}_2$] | 38 | 648 | 43 | 595, 690 | 642 | 25 |
| [$\{AgCl(PPh_2Bu)\}_4$] | 1 | 633 | 2 | — | 625 | −88 |
| X = Br | | | | | | |
| [AgBr(tmpp)] | −66 | 720 | −66 | 690, 796 | 742 | 25 |
| [$\{AgBr[P(C_6H_{11})_3]\}_2$] | 37 | 612 | 42 | 584, 670 | 627 | 25 |
| [$\{AgBr(PPh_2Bu)\}_4$] | −2 | 610 | −2 | 570, 658 | 614 | −88 |
| X = I | | | | | | |
| [AgI(tmpp)] | — | — | −65 | 646, 745 | 695 | 25 |
| [$\{AgI[P(C_6H_{11})_3]\}_4$] | 4–7 | *ca.* 500 | 12 | 505, 582 | 544 | −88 |
| [$\{AgI(PPh_2Bu)\}_4$] | −20 | 510 | −14 | 472, 545 | 508 | −88 |
| [$\{AgI(py)_{0.5}[P(C_6H_{11})_3]\}_2$] | 20 | 552 | 14 | 517, 600 | 558 | −88 |

Results for the tmpp complexes are taken from ref. 7.

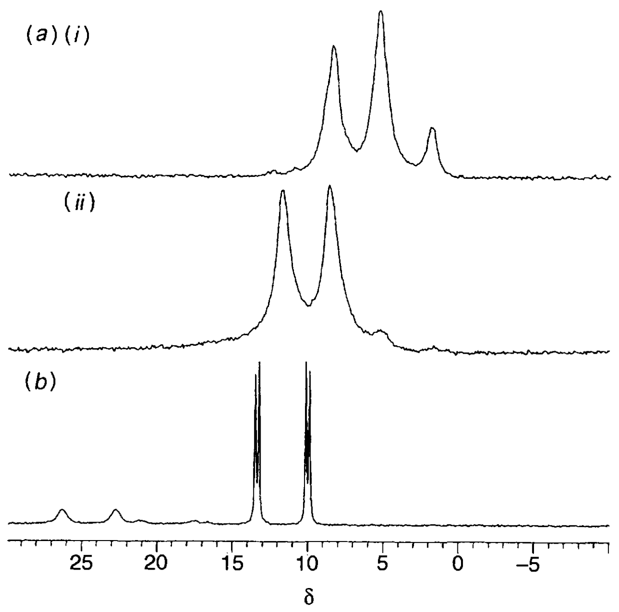


**Fig. 6** (*a*) Solid-state $^{31}$P NMR spectra of solid '[$\{AgI[P(C_6H_{11})_3]\}_4$]' obtained under two different recrystallization conditions from 2-methylpyridine and (*b*) the corresponding solution spectrum in $CH_2Cl_2$–10% $CD_2Cl_2$ at −88 °C (saturated solution)

complexes is such that each asymmetric unit consists of a single $AgX(PR_3)$ unit and the solid-state spectra are simple doublets arising from unresolved $^1J(^{31}P–^{107}Ag)$ and $^1J(^{31}P–^{109}Ag)$ coupling between the phosphorus and silver atoms. The corresponding solution spectra resolve into pairs of doublets arising from $^1J$(P–$^{107,109}$Ag) couplings at temperatures dependent on the complex (an exception to this was [$\{AgCl(PPh_2Bu)\}_4$] for which only a single unresolved doublet was observable in the accessible temperature range). The results for the chloride and bromide compounds show that in both the solution and solid states the magnitude of the coupling constants decrease in the order of decreasing basicity and steric bulk of the ligands [tmpp > $P(C_6H_{11})_3$ > $PPh_2Bu$]. The differences between the coupling constants for the tmpp and the other complexes are of the order of 15–20% while between $P(C_6H_{11})_3$ and $PPh_2Bu$ this decreases to 2–4%. These changes do not correspond closely with changes in the Ag–P bond lengths and it is difficult to ascertain whether these effects are a consequence of changes in co-ordination number or are related to the nature of the phosphine ligands. Further data are likely to be needed before these questions can be resolved. Comparative data on each ligand for the chloride and bromide complexes show that $^1J$(P–Ag) is consistently greater for chlorides in both solid and solution states. The magnitude of the differences is quite small, however, and consistent with the view that in these complexes the donor properties of chloride and bromide do not differ greatly.[8]

Solid-state spectra of the iodide species obtained from recrystallization from pyridine and substituted pyridine bases are found to be more complex than for either the bromide or chloride systems with the intensity and frequency of the bands dependent on the way the complexes are recrystallized. Generally, the spectra obtained can be interpreted as consisting of overlapping doublets with line spacings of the order of 500 Hz with the differences in intensities of these doublets consistent with precipitation of different 1 : 1 phases, *cf.* $^1J$(P–Ag) = 510 Hz for [$\{AgI(PPh_2Bu)\}_4$]. Examples of two typical spectra are shown in Fig. 6(*a*). These spectra do not correspond in any obvious way to the structure of the cubane complex recorded here which, on the basis of the presence of two crystallographically independent phosphorus atoms in the unit cell, would be expected to give two (possibly overlapping) doublets of equal intensity. The $^{31}$P NMR solution spectrum of the 1 : 1 iodide system shows several broad and unresolved peaks at room temperature indicative of an equilibrium mixture of 1 : 1 and 1 : 2 species. At −60 °C a sharp pair of doublets emerges at δ 10 with an average line spacing of 540 Hz [Fig. 6(*b*)]. This coupling constant is slightly greater than the solid-state value and is consistent with the notion that the complex may be dimeric rather than tetrameric in solution.

The solid-state spectrum obtained for the 'crevice' iodide complex [$\{AgI(py)_{0.5}[P(C_6H_{11})_3]\}_2$] differs significantly from those recorded for the unsolvated complexes, consisting of a doublet at δ 20 with a $^1J$(P–Ag) coupling constant of 552 Hz [Fig. 7(*a*)]. The magnitude of this coupling constant is slightly greater than that observed for the unsolvated complexes, consistent with the distorted trigonal $AgI_2P \cdots N$ co-ordination about the silver atom and the significant decrease observed in the Ag–P bond length. Solution spectra of either the pyridine-solvated crevice complex or a solution of [$\{AgI[P(C_6H_{11})_3]\}_4$] to which 1–2 equivalents of pyridine have been added do not to differ in any significant way from spectra of the unsolvated complex. However, addition of a ten-fold molar excess of pyridine results in formation of a new set of doublets at −88 °C which are shifted downfield to δ 14 with $^1J$(P–Ag) 558 Hz [Fig. 7(*b*)]. Analogous addition of an excess of pyridine

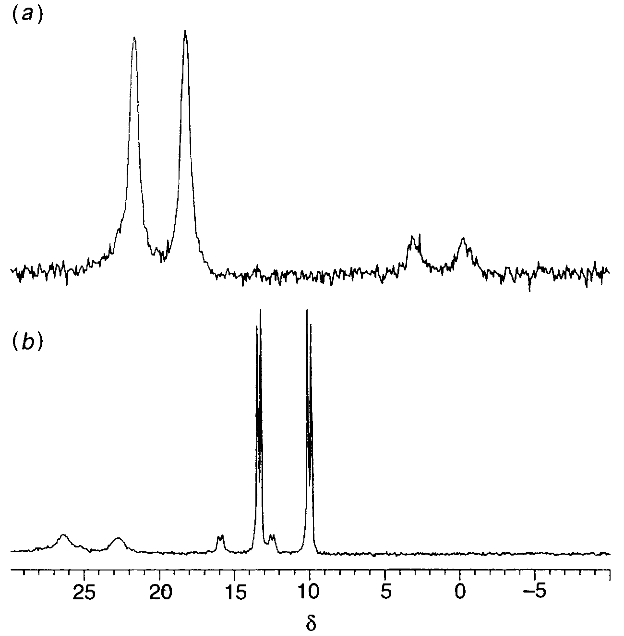


**Fig. 7** (*a*) Solid state and (*b*) solution $^{31}P$ NMR spectra of $[LAgI_2(py)AgL]$ $[L = P(C_6H_{11})_3]$ in $CH_2Cl_2$–10% $CD_2Cl_2$ and excess pyridine at −88 °C (saturated solution)

to solutions of the chloride and bromide complexes does not yield any changes in the spectra from those recorded for the unsolvated complexes. At this stage we tentatively assign this new signal in the iodide spectrum to the formation of a pyridine adduct with the 1 : 1 $AgI:P(C_6H_{11})_3$ solution species, the structure of which remains uncertain given the significant chemical shift differences between the solid-state and solution spectra.

## Acknowledgements

We acknowledge support of this work by grants from the Australian Research Scheme and the University of Auckland Research Committee. We thank Dr. Sue Berners-Price (Director, Griffith University Magnetic Resonance Centre) for many helpful discussions throughout this study and Ms. Catherine Hobbis for recording the far-IR spectra.

## References

1 M. R. Churchill, J. Donahue and F. J. Rotella, *Inorg. Chem.*, 1976, **15**, 2752.
2 M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, 1975, **14**, 2502.
3 R. J. Bowen, D. Camp, Effendy, P. C. Healy, B. W. Skelton and A. H. White, *Aust. J. Chem.*, 1994, **47**, 693.
4 B.-K. Teo and J. C. Calabrese, *Inorg. Chem.*, 1976, **15**, 2474.
5 B.-K. Teo and J. C. Calabrese, *J. Chem. Soc., Chem. Commun.*, 1976, 185.
6 B.-K. Teo and J. C. Calabrese, *Inorg. Chem.*, 1976, **15**, 2467.
7 L.-J. Baker, G. A. Bowmaker, D. Camp, Effendy, P. C. Healy, H. Schmidbaur, O. Steigelmann and A. H. White, *Inorg. Chem.*, 1992, **31**, 3656.
8 G. A. Bowmaker, Effendy, P. J. Harvey, P. C. Healy, B. W. Skelton and A. H. White, preceding paper.
9 M. R. Churchill and F. J. Rotella, *Inorg. Chem.*, 1979, **18**, 166.
10 M. G. B. Drew, P. C. H. Mitchell and A. R. Read, *J. Chem. Soc., Chem. Commun.*, 1982, 238.
11 G. A. Bowmaker, Effendy, J. H. Hanna, P. C. Healy, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1993, 1387.
12 T. Allman and R. G. Goel, *Can. J. Chem.*, 1982, **60**, 716.
13 S. Gotsis, L. M. Engelhardt, P. C. Healy, J. D. Kildea and A. H. White, *Aust. J. Chem.*, 1989, **42**, 923; Effendy, L. M. Engelhardt, P. C. Healy, B. W. Skelton and A. H. White, *Aust. J. Chem.*, 1991, **44**, 1585.
14 G. A. Bowmaker, A. Camus, P. C. Healy, B. W. Skelton and A. H. White, *Inorg. Chem.*, 1989, **28**, 3883.
15 B. K. Teo and D. M. Barnes, *Inorg. Nucl. Chem. Lett.*, 1976, **12**, 681.
16 A. Cassel, *Acta Crystallogr., Sect. B*, 1979, **35**, 174.

*Received* 15*th December* 1995; *Paper* 5/08159I