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Structural, vibrational and solid state CP MAS ^{31}P NMR spectroscopic studies of complexes of trimethylphosphine with copper(I) and silver(I) halides

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New copper(I) and silver(I) halide–trimethylphosphine adducts have been prepared by reaction of MX with PMe_3 in benzene suspension, and characterised by room-temperature single-crystal X-ray studies and/or solid state CP MAS ^{31}P NMR and vibrational spectroscopy. The complex $[Ag_4Cl_4(PMe_3)_3]$ is a one-dimensional polymer of quasi-cubanoid Ag_4Cl_4 units disposed with their body diagonals coincident with the crystallographic 3 axis, and linked by Ag–Cl units between the four-co-ordinate apical atoms of successive Ag_4Cl_4 units, isomorphous with its Cu counterpart. The first solid state NMR study of Cu/Ag PMe_3 complexes is reported. The CP MAS ^{31}P NMR and the far-IR and Raman spectra of the complexes $[\{CuI(PMe_3)\}_4]$, $[CuCl(PMe_3)_3]$ and $[\{AgX(PMe_3)_2\}_2]$ (X = Cl or Br) show the structures to be tetrameric cubane, monomeric pseudo-tetrahedral and dimeric halide-bridged respectively.

Introduction

Complexes $[(MXL_n)_m]$ of the Group 11 or coinage metals (M = Cu, Ag or Au) with neutral Group 15 donor ligands L display a wide diversity of structure types involving a range of metal co-ordination numbers from two to four, and varying degrees of association ($m = 1, 2, 3, 4, \infty$).[1–7] Most of these studies have involved ligands such as triphenylphosphine (PPh_3), tricyclohexylphosphine (PCy_3), or other closely related species. It is something of an anomaly that data remain rather scarce for compounds involving the structurally simpler ligand trimethylphosphine (PMe_3).

In early study by Schmidbaur *et al.*,[8] 1 : 1, 1 : 2, 1 : 3 and 1 : 4 MCl : PMe_3 (M = Cu or Ag) complexes were prepared and characterised by NMR and NQR spectroscopy. This work established the stoichiometries and likely structures of most of the compounds that are formed in this system, but subsequent studies have revealed some additional, somewhat unexpected stoichiometries and structures. Thus, the 1 : 2 CuCl : PMe_3 adduct was found to have an ionic structure, $[Cu(PMe_3)_4]^+$-$[CuCl_2]^-$,[9] rather than the expected dimeric structure $[\{CuCl(PMe_3)_2\}_2]$, and this explained why the observed copper NQR frequencies for this compound were very similar to those which had been determined for $[CuCl_2]^-$. Also, the allowed stoichiometries were found not to be limited to the expected range 1 : 1, 1 : 2, 1 : 3, 1 : 4 with the discovery of the complex $[Cu_4Cl_4(PMe_3)_3]$, of 4 : 3 stoichiometry.[1]

Vibrational spectroscopy has proved to be valuable in the study of structure and bonding in Group 11 metal PMe_3 complexes, the structural simplicity of the PMe_3 ligand allowing more detailed band assignments to be made.[10–12] The most detailed reports to date have been for the complexes $[\{AgI(PMe_3)\}_4]$, $[\{CuI(PMe_3)_2\}_2]$, $[Cu_4Cl_4(PMe_3)_3]$,[1] and $[AuX(PMe_3)]$ (X = Cl, Br or I).[13]

Solid-state CP MAS ^{31}P NMR spectroscopy has also proved to be of value in studying the structural chemistry of Group 11 metal phosphine complexes.[5–7] Both naturally occurring isotopes of copper (^{63}Cu, ^{65}Cu) have quadrupolar nuclei ($I = 3/2$), and solid-state NMR provides information on the co-ordination environment of the copper nuclei within these compounds, utilising the fact that the ^1J(CuP) coupling and the copper nuclear quadrupole coupling constant (e^2qQ) are sensitive to changes in co-ordination environment. Both naturally occurring isotopes of silver (^{107}Ag, ^{109}Ag) have spin $I = 1/2$, and the CP MAS ^{31}P NMR spectra generally show splitting due to ^1J(AgP) coupling. For both metals, the ^{31}P chemical shifts and the line splittings measured from the CP MAS spectra yield useful structural information. Most work to date has concentrated on copper(I) and silver(I) triphenylphosphine complexes, and in this paper we examine the application of this technique to some copper(I) and silver(I) trimethylphosphine adducts.

In this study four additions to this diverse coinage metal chemistry are structurally and spectroscopically characterised to yield further information on the co-ordination and bonding in these systems.

Experimental

Preparations

Trimethylphosphine was prepared by a literature method.[14] The preparations of the PMe_3 complexes were carried out under an atmosphere of oxygen-free nitrogen using standard Schlenk techniques.

Iodo(trimethylphosphine)copper(I), $[\{CuI(PMe_3)\}_4]$. Copper(I) iodide (0.6 g, 2.25 mmol) was dissolved in a saturated solution of KI (5 mL) in a 25 mL Schlenk tube and the resulting solution degassed and placed under an N_2 atmosphere. To this solution was added PMe_3 (0.25 mL, 2.25 mmol) dropwise with stirring, whereupon a quantity of white/cream powder precipitated. The product was collected by vacuum filtration, washed with water, dried, and stored under N_2. Yield 0.7 g (91%), mp 197–199 °C (Found: C, 12.95; H, 3.40. Calc. for C_3H_9CuIP: C, 13.52; H, 3.40%).

Chlorotris(trimethylphosphine)copper(I), $[CuCl(PMe_3)_3]$. This compound was prepared by the literature method.[8] It readily lost PMe_3, as is reflected in the elemental analysis, mp 110 °C (lit.,[8] 108 °C) (Found: C, 32.32; H, 8.31. Calc. for $C_9H_9ClCuP_3$: C, 33.03; H, 8.32%).

***catena*-μ₃-Chloro-tri-μ-chloro-tris(trimethylphosphine)tetrasilver(I), $[Ag_4Cl_4(PMe_3)_3]$.** Silver chloride (0.374 g, 2.58 mmol) and dry benzene (7 mL) were placed in a 25 mL Schlenk tube under an atmosphere of dry nitrogen. Trimethylphosphine (0.20 mL, 1.82 mmol) was added dropwise with stirring to the resulting suspension. After 24 h some solid AgCl remained at the bottom of the tube, and this was removed by vacuum filtration. The volume of the solution was reduced to ≈3.5 mL, *n*-hexane (4 mL) was added, and the volume reduced by ≈2.0 mL. White crystals formed, which were filtered off, washed, vacuum dried and stored under N_2. Yield 0.09 g (19% based on PMe_3), mp 145–147 °C (Found: C, 13.96; H, 3.51. Calc. for $C_9H_{27}Ag_4Cl_4P_3$: C, 13.49; H, 3.40%).

Di-μ-chloro-tetrakis(trimethylphosphine)disilver(I), $[\{AgCl(PMe_3)_2\}_2]$. Dry benzene (3 mL) and AgCl (0.3 g, 2.09 mmol) were placed in a 25 mL Schlenk tube under an atmosphere of dry nitrogen. Trimethylphosphine (0.46 mL, 4.19 mmol) was added to the resulting suspension dropwise with stirring. During the addition the AgCl dissolved and heat was evolved. The volume of the solution was reduced to ≈2 mL and *n*-hexane (1.5 mL) added. During the addition of the hexane a white powder was simultaneously precipitated. The powder was collected by vacuum filtration, washed, dried and stored under N_2. Yield 0.27 g (47%), mp 98–99 °C (lit.,[8] 98–100 °C) (Found: C, 24.10; H, 5.95. Calc. for $C_6H_{18}AgClP_2$: C, 24.39; H, 6.14%).

Di-μ-bromo-tetrakis(trimethylphosphine)disilver(I), $[\{AgBr(PMe_3)_2\}_2]$. The same procedure as for $[\{AgCl(PMe_3)_2\}_2]$ was followed. The resulting microcrystalline white powder was filtered off, washed, dried and stored under N_2. Yield 0.413 g (86%), mp 107–113 °C (Found: C, 21.12; H, 5.29. Calc. for $C_6H_{18}P_2AgBr$: C, 21.20; H, 5.34%).

X-Ray crystallography

A crystal of $[Ag_4Cl_4(PMe_3)_3]$ was selected from the reaction product. A sphere of data was measured at *ca.* 295 K within the limit $2\theta_{max} = 60°$ using an Enraf-Nonius CAD-4 diffractometer (monochromatic Mo-Kα radiation, $\lambda = 0.71073$ Å; 2θ–θ scan mode) yielding 5218 total reflections, merging, after analytical absorption correction, to 878 unique ($R_{int} = 0.064$), with 530 with $I > 3\sigma(I)$ being considered "observed" and used in the full-matrix least-squares refinement after analytical absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Conventional residuals R, R' on $|F|$ at convergence were 0.034, 0.021 (preferred chirality), statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being used. Neutral-atom complex scattering factors were employed, with computation using the XTAL 3.2 program system implemented by S. R. Hall.[15] Pertinent results are given in Fig. 1 and Table 1.

Crystal/refinement data. $[Ag_4Cl_4(PMe_3)_3]$, $C_9H_{27}Ag_4Cl_4P_3$, $M = 801.5$, rhombohedral, space group $R3c$, $a = 18.160(6)$, $c = 11.900(5)$ Å, $V = 3399(3)$ Å^3 (hexagonal setting), D_c ($Z = 6$) = 2.349 g cm^{-3}, $F(000) = 2292$, $\mu_{Mo} = 40.8$ cm^{-1}, specimen 0.08 × 0.04 × 0.21 mm, $A^*_{min,max} = 1.19, 1.39$.

CCDC reference number 186/1334.

See http://www.rsc.org.suppdata/dt/1999/901/ for crystallographic files in .cif format.

Spectroscopy

Far-infrared spectra were recorded at 4 cm^{-1} resolution at room temperature as pressed Polythene discs on a Digilab FTS-60 Fourier-transform spectrometer employing an FTS-60V vacuum optical bench with a 6.25 μm mylar film beam splitter, a mercury lamp source and a pyroelectric TGS (triglycine sulfate) detector. Raman spectra were recorded at 4.5 cm^{-1} resolution using a Jobin-Yvon U1000 spectrometer equipped with a Spectrolab Laserspec III Pre-monochromator and a cooled photomultiplier (RCA C31034A) detector. The 514.8 nm exciting line from a Spectra-Physics model 2016 argon-ion laser was used.

Solid state cross-polarisation magic-angle spinning (CP MAS) ^{31}P-{^{1}H} NMR spectra were recorded at ambient temperature on a Varian Unity-400 spectrometer at 161.93 MHz. Single contact times of 2 ms were used with a proton pulse width of 6.5 μs, a proton decoupling field of 60 kHz and a recycle delay time of 45 s. The samples were packed in Kel-F inserts within silicon nitride rotors and spun at a speed of 5 kHz at the magic angle. A total of 32 free induction decays were collected and transformed with an experimental line broadening of 10 Hz. All ^{31}P chemical shifts were externally referenced to solid triphenylphosphine which has a shift of δ −9.9 with respect to 85% H_3PO_4.

Results and discussion

Synthesis

The compounds $[\{CuI(PMe_3)\}_4]$, $[CuCl(PMe_3)_3]$, $[Ag_4Cl_4(PMe_3)_3]$, $[\{AgCl(PMe_3)_2\}_2]$ and $[\{AgBr(PMe_3)_2\}_2]$ were prepared by reaction of PMe_3 with the appropriate metal(I) halides suspended in benzene, or (in the case of the CuI complex) in an aqueous KI solution. An attempted preparation of the 1 : 1 AgCl : PMe_3 adduct yielded a solid of the correct elemental composition, but this was shown by vibrational spectroscopy to consist of a mixture of the 4 : 3 and 1 : 2 adducts, $[Ag_4Cl_4(PMe_3)_3]$ and $[\{AgCl(PMe_3)_2\}_2]$ (see below). It therefore appears unlikely that any 1 : 1 adduct is accessible by this method.

The complexes $[\{CuI(PMe_3)\}_4]$, $[CuCl(PMe_3)_3]$, $[\{AgCl(PMe_3)_2\}_2]$ and $[\{AgBr(PMe_3)_2\}_2]$ lie within the stoichiometry range 1 : 1–1 : 4 established in the original study of the CuCl and AgCl systems.[8] The complex $[Ag_4Cl_4(PMe_3)_3]$ has 4 : 3 stoichiometry, which lies outside this range, but corresponds to the compositions of $[Cu_4Cl_4(PMe_3)_3]$ and $[Cu_4I_4(NEt_3)_3]$.[1,16]

X-Ray crystallography

In most cases the products of the reactions described above were obtained as powders or microcrystalline solids that were unsuitable for structure determinations. However, in the case of $[Ag_4Cl_4(PMe_3)_3]$ suitable crystals were obtained, the results of the room-temperature single-crystal study being consistent with the formation of this complex with the given stoichiometry. The structure (Fig. 1) is isomorphous with the corresponding copper complex,[1] although most of the dimensions are significantly different (Table 1). The structures of both of these complexes differ from that of the stoichiometrically related $[Cu_4I_4(NEt_3)_3]$.[16] While all three consist of infinite chains of linked quasi-cubanoid M_4X_4 units, these units are much more distorted from the ideal cubanoid structure, and the metal atom co-ordination is considerably more distorted from ideal tetrahedral in the PMe_3 compounds. This distortion is such that three of the M–Cl bonds involving the off-axis metal and halogen atoms are "broken" relative to the cube structure, so that these chlorine atoms are two-co-ordinate while the metal atoms are three-co-ordinate $(\mu\text{-Cl})_2MP$, the angle sum about the metal being exactly 360°, *i.e.* rigorously planar. However, there is a considerable distortion away from ideal trigonal geometry about the metal, with P–Ag(1)–Cl(2) being 36° larger than the normal trigonal angle of 120°, while P–Ag(1)–Cl(1) is 11° smaller; these differences compare with 29° larger and 11° smaller respectively for their counterparts in $[Cu_4Cl_4(PMe_3)_3]$.[1] The geometry about Ag(1) is dominated by a linear two-co-

Table 1 Core geometries (distances in Å, angles in °) for $[M_4Cl_4(PMe_3)_3]$

	M = Ag	M = Cu (Ref. 1)
M(1)–P	2.362(4)	2.184(3)
M(1)–Cl(1)	2.726(2)	2.502(2)
M(1)–Cl(2)	2.428(4)	2.192(2)
M(2)–Cl(1)	2.568(5)	2.354(4)
M(2)–Cl(2′)	2.665(3)	2.403(2)
P–C(1)	1.78(1)	1.818(9)
P–C(2)	1.82(1)	1.814(8)
P–C(3)	1.79(2)	1.80(1)
Cl(1)–M(1)–Cl(2)	95.4(1)	102.0(1)
Cl(1)–M(1)–P	108.6(1)	109.27(7)
Cl(2)–M(1)–P	156.0(1)	148.7(1)
Cl(1)–M(2)–Cl(2′)	102.74(8)	106.11(7)
Cl(2′)–M(2)–Cl(2″)	115.3(2)	112.6(1)
M(1)–Cl(1)–M(2)	118.20(8)	122.16(7)
M(1)–Cl(1)–M(1‴)	99.5(1)	94.38(9)
M(1)–Cl(2)–M(2*)	77.30(9)	82.54(7)
M(1)–P–C(1)	118.9(5)	121.3(3)
M(1)–P–C(2)	112.2(6)	112.3(4)
M(1)–P–C(3)	115.5(5)	113.4(4)
C(1)–P–C(2)	102.3(6)	101.7(4)
C(1)–P–C(3)	103.3(7)	102.7(5)
C(2)–P–C(3)	102.6(6)	103.4(4)

Symmetry operations: ′ $1 - y, 1 - x, z - \frac{1}{2}$; ″ $x, 1 + x - y, z - \frac{1}{2}$; ‴ $1 - y, 1 + x - y, z$; * $1 - y, 1 - x, \frac{1}{2} + z$.

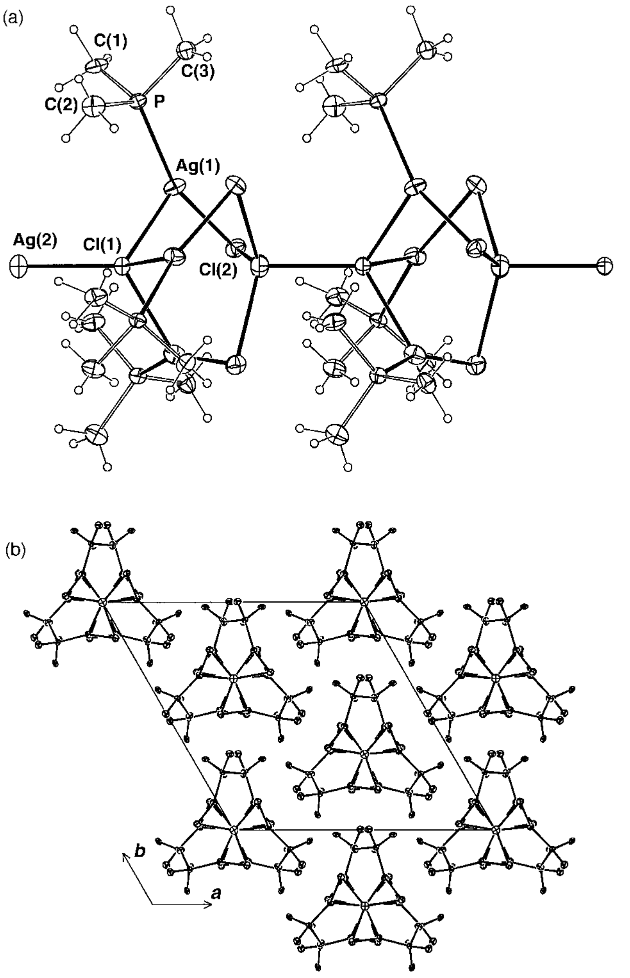

Fig. 1 The crystal structure of $[Ag_4Cl_4(PMe_3)_3]$. (a) A segment of the chain running parallel to *c*. (b) The unit cell viewed along *c*.

ordinate P–Ag(1)–Cl(2) arrangement distorted by a weaker Ag(1)–Cl(1) interaction. This is reflected in the considerably greater length of Ag(1)–Cl(1) compared to Ag(1)–Cl(2) (Table 1). The next strongest interaction after Ag(1)–Cl(2) is Ag(2)–Cl(1), the bridging bond that connects the Ag_4Cl_4 units into a chain. Of the two interactions found within the Ag_4Cl_4 units, Ag(2)–Cl(2′) and Ag(1)–Cl(1), the latter is the weaker. On the whole the AgCl bonds can largely be divided into 2 groups: the moderate strength Ag(1)–Cl(2) bond at 2.428(4) Å, and the weaker Ag(2)–Cl(1), Ag(2)–Cl(2), Ag(1)–Cl(1) bonds at 2.568(5), 2.665(3), 2.726(2) Å respectively.

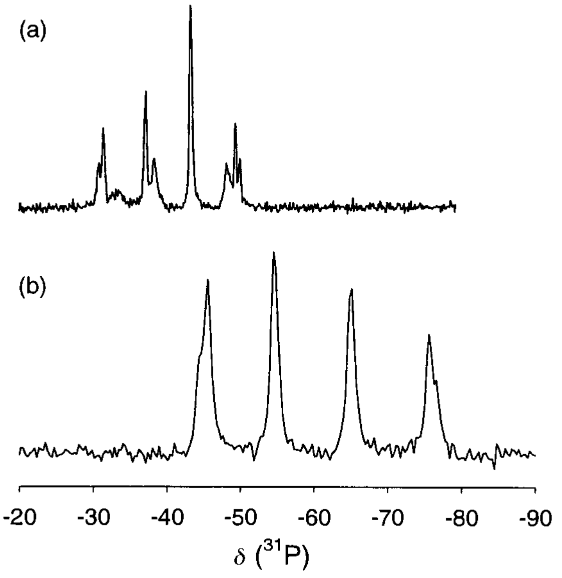

Fig. 2 Solid state CP MAS ^{31}P NMR spectra of (a) $[CuCl(PMe_3)_3]$, (b) $[\{CuI(PMe_3)\}_4]$.

Comparing Ag–P bond lengths in $[Ag_4Cl_4(PMe_3)_3]$ with those in $[\{AgCl(PPh_3)\}_4]$,[17] we find that this increases from 2.362 to 2.3822 Å (mean value) respectively, implying stronger M–P bonds in the former compound. The Ag–Cl bonds are also shorter in the quasi-cubanoid string than in the cubane complex. The strong distortion of the silver co-ordination environment away from an ideal tetrahedral $PAgCl_3$ arrangement to produce a single strong Ag–Cl bond in a position approximately *trans* to the Ag–P bond can be compared to the behaviour of complexes of mercury(II) halides with PMe_3, which have also shown unusual structures exhibiting approximately linear P–Hg–X units.[18]

CP MAS ^{31}P NMR Spectra

The ^{31}P CP MAS NMR spectra of $[CuCl(PMe_3)_3]$ and $[\{CuI(PMe_3)\}_4]$ at a field strength of 9.40 T are shown in Fig. 2 with corresponding NMR parameters for both complexes, together with structural and NMR data for a representative range of analogous four-co-ordinate copper(I) triphenylphosphine complexes,[19–21] given in Table 2. The spectra correspond to those reported for other copper(I) phosphine complexes in high magnetic fields (>7 T) and governed by slow $^{63,65}Cu$ relaxation conditions in that they consist of a superposition of two, similar ^{31}P–^{63}Cu and ^{31}P–^{65}Cu asymmetric quartets for each crystallographically independent phosphorus atom. The magnitude of this asymmetry is governed by the extent of the quadrupolar perturbation to the Zeeman states and how this perturbation impinges upon the overall MAS averaging when combined direct (dipolar) and indirect (scalar, *J*) couplings between the ^{31}P ($I = 1/2$) and the spin 3/2 ^{63}Cu and ^{65}Cu isotopes are taken into account.[22–26] Linewidths are generally too broad to permit complete resolution of two quartets and observed spectra are dominated by the ^{63}Cu spectrum, with the ^{65}Cu lines resolved, when the linewidth is sufficiently narrow, as a splitting of the outer peaks of the quartet. Analysis of the quadrupolar effects as a first order perturbation of the *J* spectrum predicts the outer two lines of the quartet (δ_1, δ_4) to shift to more negative ppm (upfield) and the inner two lines (δ_2, δ_3) to more positive

Table 2 Structural and solid state CP MAS ^{31}P NMR parameters for two-, three- and four-co-ordinate copper(I) phosphine complexes

	Cu–P/Å	B/T	Δ_{21}/kHz	Δ_{32}/kHz	Δ_{43}/kHz	J/kHz	$d\nu_{Cu}/10^9$ Hz^2
$[\{CuCl(PPh_3)\}_4]$	2.19	9.40	1.78	1.97	2.08	1.95	7.4
	2.19		1.80	1.99	2.08	1.96	7.2
$[\{CuBr(PPh_3)\}_4]$	2.21	9.40	1.69	1.90	1.97	1.86	7.2
	2.21		1.67	1.90	1.95	1.85	7.2
$[\{CuI(PPh_3)\}_4]$	2.25	9.40	1.43	1.58	1.63	1.55	5.3
	2.25		1.50	1.63	1.73	1.62	5.7
$[\{CuI(PMe_3)\}_4]$		9.40	1.50	1.70	1.72	1.65	5.6
$[Cu(PPh_3)_3(CH_3CN)]ClO_4$	2.32	7.05	0.94	1.06	1.06	1.03	1.0
	2.34		0.92	0.92	1.04	0.95	2.4
	3.33		0.96	1.00	1.03	1.00	1.4
$[CuCl(PPh_3)_3]\cdot(CH_3)_2CO$	2.33 (av.)	7.05	0.93	0.98	0.97	0.96	1.0
$[CuCl(PPh_3)_3]$	2.35 (av.)	7.05	0.94	0.94	0.90	0.93	0
	2.35		0.94	0.94	0.92	0.93	0
$[CuCl(PMe_3)_3]$		9.40	0.94	0.98	1.00	0.98	1.5

References to the structure and NMR data from the literature are indicated in the text.

ppm (downfield) by a parameter d such that $(\Delta_{32} - \Delta_{21}) = (\Delta_{43} - \Delta_{32}) = 2d$, from which $d = (\Delta_{43} - \Delta_{21})/4$.[25] Under the experimental conditions, d is inversely proportional to field strength and multiplication by the ^{63}Cu Zeeman frequency, ν_{Cu}, yields a field independent parameter $d\nu_{Cu}$ that enables direct comparison of the magnitude of these quadrupolar distortion effects from data recorded at different field strengths. In practice, higher order quadrupole effects result in the observed line spacings deviating from this first order model with $(\Delta_{32} - \Delta_{21}) > 2d > (\Delta_{43} - \Delta_{32})$.[22,26] Detailed consideration of these effects on the spectra is beyond the scope of this present study but a guide to the magnitude of these higher order interactions can be obtained as, under the experimental conditions, they cause an upfield shift of peaks 1 and 3 and a downfield shift of peaks 2 and 4 by a magnitude d_1 such that $\Delta_{21} = J - 2d - 2d_1$, $\Delta_{32} = J + 2d_1$ and $\Delta_{43} = J + 2d - 2d_1$, from which $J = (\Delta_{21} + 2\Delta_{32} + \Delta_{43})/4$, $d = (\Delta_{43} - \Delta_{21})/4$ and $d_1 = (\Delta_{32} - J)/2$.[27]

The spectrum of $[CuCl(PMe_3)_3]$ consists of a single quartet of peaks arising from the ^{63}Cu coupling with the linewidth sufficiently narrow that the splitting of the outer lines due to the ^{65}Cu coupling is readily apparent. This result is consistent with the presence of a single crystallographically independent $[CuCl(PMe_3)_3]$ molecule in the complex with a threefold symmetry axis (possibly crystallographically imposed) relating the three PMe_3 ligands. The value of 0.98 kHz for $^1J(^{31}P\text{–}^{63}Cu)$ is the same within experimental error as values observed for other 1 : 3 $[CuX(PPh_3)_3]$ complexes listed in Table 2, and confirms the stoichiometry of this complex. The asymmetry parameter $d\nu_{Cu}$ of 1.5×10^9 Hz^2 is greater than the value of zero found for unsolvated $[CuCl(PPh_3)_3]$ and comparable to the values observed for $[Cu(PPh_3)_3(CH_3CN)]ClO_4$ and the acetone solvate of $[CuCl(PPh_3)_3]$. In these latter complexes the P–Cu–P angle increases from the tetrahedral angle of 109.5° found for unsolvated $[CuCl(PPh_3)_3]$ to average values of 115°,[20,21] and it is reasonable to assume a similar P–Cu–P angle for the present complex and a corresponding P–Cu–Cl angle of *ca.* 103°.

First order perturbation theory allows $d\nu_{Cu}$ to be calculated according to expression (1) where $\chi_{Cu} = e^2qQ/h$ is the ^{63}Cu quadrupole coupling constant, $D_{eff} = (D - \Delta J/3)$ $[D = (\mu_0/4\pi)\gamma_P\gamma_{Cu}h/4\pi^2r^3$ is the Cu–P dipolar coupling constant and ΔJ the anisotropy in the J tensor], η is the asymmetry parameter of the electric field gradient (EFG) tensor, and a^D, β^D are the polar angles defining the direction of the Cu–P internuclear vector with respect to the principal axial system (PAS) of the EFG tensor.[25]

$$d\nu_{Cu} = (3\chi_{Cu}D_{eff}/20)(3\cos^2\beta^D - 1 + \eta\sin^2\beta^D\cos 2a^D) \quad (1)$$

For axially symmetric P_3CuX complexes the z axis of the electric field gradient lies along the Cu–X bond with the asymmetry parameter $\eta = 0$. Substitution of this in eqn. (1) and rearrangement yields eqn. (2).

$$\chi_{Cu} = [20/3D_{eff}(3\cos^2\beta^D - 1)]\ d\nu_{Cu} \quad (2)$$

Lack of structural information about the complex, the magnitude of ΔJ, or detailed knowledge of the effects of higher order perturbations precludes a precise determination of χ_{Cu} from eqn. (2). However, the reasonable assumption of values for d(Cu–P) of 2.26 Å, β^D (= Cl–Cu–P) of 103° and ΔJ ranging from 0 to 0.6 kHz[25] yields first order estimates of χ_{Cu} of the order of 10–12 MHz.

In the spectrum also there are three additional NMR signals at δ −33.3, −38.3 and −48.2. These are assigned to three of the expected four lines of the quartet due to $[Cu(PMe_3)_4]^+$ in $[Cu(PMe_3)_4]^+[CuCl_2]^-$ which is present as an impurity in this complex (see vibrational spectroscopy section below). The remaining line of the quartet should lie at δ −43.2 underneath the third line in the main quartet due to $[CuCl(PMe_3)_3]$. The NMR parameters for this quartet are δ −40.7, $^1J(^{31}P\text{–}^{63}Cu) = 0.80$ kHz and $d\nu_{Cu} = 0$, consistent with solution ^{31}P NMR data[13,28] and the tetrahedral symmetry found for the structure of the cation.[28,29] The presence of some $[Cu(PMe_3)_4]^+[CuCl_2]^-$ impurity in the sample would explain the previously reported observation of ^{63}Cu and ^{35}Cl NQR signals in $[CuCl(PMe_3)_3]$ at about 30 and 9 MHz respectively.[8] The ^{63}Cu frequency implies $\chi_{Cu} = 60$ MHz which is far higher than the estimated value of *ca.* 10 MHz determined in the present study and close to the value of 61.4 MHz reported for the $[CuCl_2]^-$ anion.[30]

The spectrum of the 1 : 1 CuI : PMe_3 complex consists also of a single asymmetric quartet with partial resolution of the ^{65}Cu signal in the outer two peaks. The values of $^1J(^{31}P\text{–}^{63}Cu) = 1.65$ kHz and $d\nu_{Cu} = 5.6 \times 10^9$ Hz^2 are very similar to corresponding values for the $[\{CuI(PPh_3)\}_4]$ heterocubane cluster. The single quartet for the present complex, compared to two for $[\{CuI(PPh_3)\}_4]$ implies the presence of only one crystallographically independent PMe_3 ligand in the complex and cubic symmetry for the cluster as found, for example, for the structure of the analogous $[\{CuX(PEt_3)\}_4]$ complexes for X = Cl, Br and I,[31,32] yielding threefold axial symmetry coincident with the Cu–P bond for each $PCuI_3$ unit. With values of both η and β^D both zero in this case, eqn. (2) simplifies to $\chi_{Cu} = (20/3D_{eff})\ d\nu_{Cu}$. The assumption of d(Cu–P) = 2.18 Å and values of ΔJ ranging from 0 to 0.6 kHz yields estimates of χ_{Cu} of the order of 30–35 MHz. This result is in reasonable agreement with the estimated values for χ_{Cu} of 26–28 MHz from the NQR resonance frequencies of 13.76 and 12.98 MHz recorded for the tetrameric cubane complex $[\{CuCl(PPh_3)\}_4]$.[33] The results for the two PMe_3 complexes in Table 2 provide an interesting comparison of the differences in the magnitude of the nuclear quadrupole coupling constants for axial symmetric four-co-ordinate P_3CuX and $PCuX_3$ complexes with the value for the latter complex nearly three times as large as the former.

The CP MAS ^{31}P NMR spectra of $[AgX(PMe_3)_2]$ (X = Cl or Br) are shown in Fig. 3, with the derived NMR parameters

Table 3 The CP MAS ^{31}P NMR parameters for $[Ag_2X_2(PMe_3)_4]$ (X = Cl or Br), $[Ag_4Cl_4(PMe_3)_3]$ and related compounds

Complex	δ	^1J(Ag–P)/Hz	^2J(P–P)/Hz	Ref.
$[\{AgCl(PMe_3)_2\}_2]$	−39.4, −43.3	447, 439	149	[a]
$[\{AgBr(PMe_3)_2\}_2]$	−40.4, −43.4	439, 427	134	[a]
$[\{AgI(DMPP)_2\}_2]$	−3.0, −9.5	276, 327	—	5
$[\{AgCl(PPh_3)_2\}_2]\cdot 2CHCl_3$	11.6, 7.7	423, 376	113	7
$[\{AgBr(PPh_3)_2\}_2]\cdot 2CHCl_3$	8.6, 5.4	410, 360	102	7
$[AgBr(PPh_3)_2]$	16.0	394	—	7
$[AgCl(PCy_3)_2]$[b]	22.1	400	—	35
$[AgCl(PCy_3)_2]$[c]	21.8, 25.9	400, 410	120	35
$[AgBr(PCy_3)_2]$	16.0	394	—	35
$[AgI(PCy_3)_2]$	22.1	386	—	35
$[Ag_4Cl_4(PMe_3)_3]$	−34.0	704	—	[a]
[AgCl(tmpp)]	−67	740	—	34
$[\{AgCl(PCy_3)\}_2]$	38	648	—	36
$[\{AgCl(PPh_2Bu)\}_4]$	1	633	—	36

[a] This work. [b] Monoclinic. [c] Triclinic.

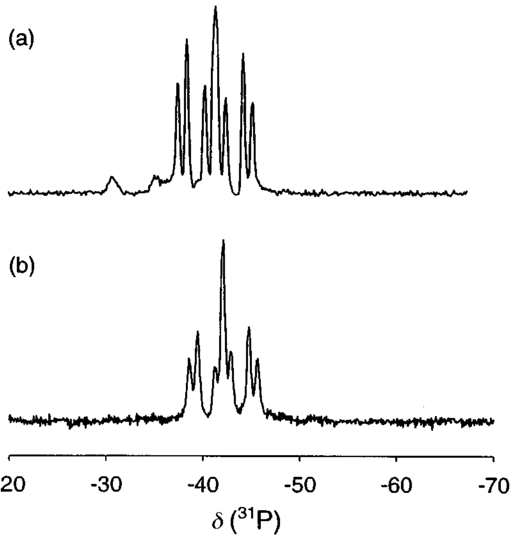

Fig. 3 Solid state CP MAS ^{31}P NMR spectra of $[\{AgX(PMe_3)_2\}_2]$: (a) X = Cl, (b) X = Br.

listed in Table 3. The naturally occurring isotopes of silver are ^{107,109}Ag, with natural abundances 51.82 and 48.18% respectively. Both isotopes have nuclear spin $I = 1/2$, and their magnetogyric ratios are similar in magnitude, $\gamma(^{109}Ag)/\gamma(^{107}Ag) = 1.15$. There has been a limited number of solid state ^{31}P NMR studies of silver(I) phosphine complexes.[5,7,34–37] The ^{31}P NMR spectra of these complexes of silver(I) with phosphorus donor ligands may show splitting due to ^1J(Ag–P) coupling. The resulting spectra can show a pair of doublets in which the separate couplings of ^{31}P to the ^{107}Ag and ^{109}Ag nuclei are resolved; whether these are seen depends on the resolution of the spectrometer, which relates to the frequency. The isotopic splitting is often not resolved due to the greater linewidths ($\Delta\nu_{1/2} \approx 40$ Hz).

The spectra of $[AgX(PMe_3)_2]$ (X = Cl or Br) are very similar, except that the chloride spectrum is better resolved (Fig. 3). The spectra of both complexes can be interpreted as the AM part of an AMX spin system where X represents the silver nucleus and A, M represent two inequivalent phosphorus nuclei. The spectra show a doublet of doublets, due to the two ^1J(Ag–P) couplings (*ca.* 440 Hz), with each of the resulting four lines split further into a doublet due to the ^2J(P–P) coupling (*ca.* = 140 Hz). The spectra overlap at the centre resulting in an approximate 1 : 1 : 1 : 2 : 1 : 1 : 1 ratio of relative intensities. The resulting NMR parameters are compared in Table 3 with those for some related compounds involving both mononuclear and binuclear (halide-bridged) structures. From this it is clear that it is not really possible to distinguish between the mononuclear and binuclear structures by NMR, since the coupling constants are quite similar. The binuclear structures studied to date always involve two inequivalent phosphine ligands bound to the silver atom, but the existence of the triclinic form of mononuclear $[AgCl(PCy_3)_2]$ shows that this situation can also occur for a mononuclear structure. However, it is clear from the vibrational spectra that the present complexes have the dimeric halide-bridged structures $[\{AgX(PMe_3)_2\}_2]$ (see below). The interpretation of the NMR spectra is that two L_2Ag units in the dimer are equivalent by symmetry and there is no observable coupling across the halide bridges. This situation has also been observed for $[\{AgCl(PPh_3)_2\}_2]$.[7] The mean ^1J(Ag–P) coupling constant of the different environments decreases from X = Cl to Br by 10 Hz. This parallels the observed behaviour for the complexes $[(AgXL_2)_2]$ [L = DMPP (3,4-dimethyl-1-phenylphosphole) or DBP (1-phenyldibenzophosphole)] and $[\{AgX(DMPP)\}_4]$.[5] This suggests that there is a progressive weakening of the Ag–P bond along this series. The most likely reason for this trend is that the donor strengths of the halide ligands are in the order $Cl^- < Br^-$, so that the phosphorus donor ligand is able to form the strongest dative bond (with least competition from the halide) in the chloride case. An equivalent way of stating this is to say that the Ag–P bond strength increases with increasing electronegativity of the X atom that is bonded to Ag.

An attempted preparation of the 1 : 1 AgCl : PMe_3 adduct yielded a solid of the correct elemental composition, but this was shown by IR spectroscopy to consist of a mixture of the 4 : 3 and 1 : 2 adducts, $[Ag_4Cl_4(PMe_3)_3]$ and $[\{AgCl(PMe_3)_2\}_2]$ (see below). The CP MAS ^{31}P NMR spectrum of this solid is dominated by a simple doublet, δ −34.0, ^1J(Ag–P) = 704 Hz that is assigned to $[Ag_4Cl_4(PMe_3)_3]$, together with very weak lines from the more complex spectrum of $[\{AgCl(PMe_3)_2\}_2]$ at $\delta \approx -40$). The value of ^1J(Ag–P) for $[Ag_4Cl_4(PMe_3)_3]$ lies between that observed in the mononuclear complex [AgCl(tmpp)] [tmpp = tris(2,4,6-trimethoxyphenyl)phosphine],[34] and those for the chloride bridged dimer $[\{AgCl(PCy_3)\}_2]$ and tetramer $[\{AgCl(PPh_2Bu)\}_4]$ (Table 3).[36] This correlates well with the structure of $[Ag_4Cl_4(PMe_3)_3]$, in which the Ag(1) environment shows a strong tendency towards linear P–Ag–Cl co-ordination, with additional weaker bonds arising from the chlorine bridging interactions (Table 1).

Vibrational spectra

The assignments of the low-frequency vibrational spectra are given in Table 4. The main bands below 500 cm^{-1} are those due to the metal–halogen stretching and bending modes, and the symmetric and asymmetric PMe_3 bending modes, $\delta_{sym}(PC_3)$ and $\delta_{asym}(PC_3)$ respectively.[1]

The assignments for $[\{CuI(PMe_3)\}_4]$ support the heterocubane structure deduced from the CP MAS ^{31}P NMR spectrum (see above), and are based on the principles established previously for other complexes with this structure.[4,38,39] Similarly, the assignments for $[CuCl(PMe_3)_3]$ support the non-ionic pseudo-tetrahedral structure found in the NMR study. The ν(CuCl) and ν(CuP) wavenumbers are respectively lower and higher than the values 225 and 107, 121 cm^{-1} of $[CuCl(PPh_3)_3]$,[40] and these differences are consistent with PMe_3 being a lighter ligand and a stronger base than PPh_3. Additional weak bands in the far-IR at 412 and 108 cm^{-1} are assigned to $[CuCl_2]^-$.[30,41] This indicates the presence of a small amount of the known ionic species $[Cu(PMe_3)_4]^+[CuCl_2]^-$.[9] This is consistent with the slightly low carbon analysis for this compound, and the detection of a weak ^{31}P NMR signal due to $[Cu(PMe_3)_4]^+$ in this compound (see CP MAS ^{31}P NMR section above).

The ν(AgCl) assignments for $[Ag_4Cl_4(PMe_3)_3]$ are analogous

Table 4 Wavenumbers (cm^{-1}) and assignments of the low-frequency bands in the IR and Raman spectra

[{$CuI(PMe_3)$}$_4$]			[$CuCl(PMe_3)_3$]		
IR	R	Assignment	IR	R	Assignment
330	331	$\delta_{sym}(PC_3)$	412		$\nu_{asym}(CuCl_2)^-$
259	259	$\delta_{asym}(PC_3)$	332	331	$\delta_{sym}(PC_3)$
150	143	T_2, A_1 $\nu(CuP)$	272	267	$\delta_{asym}(PC_3)$
133	128	T_2 $\nu(CuI)$	202		$\nu(CuCl)$
93		T_2 $\nu(CuI)$	166	162	$\nu(CuP)$
	51	A_1 def.	108		$\delta(CuCl_2)^-$

[$Ag_4Cl_4(PMe_3)_3$]			[{$AgCl(PMe_3)_2$}$_2$]			[{$AgBr(PMe_3)_2$}$_2$]		
IR	R	Assignment	IR	R	Assignment	IR	R	Assignment
342	340	$\delta_{sym}(PC_3)$	322	326	$\delta_{sym}(PC_3)$	323	325	$\delta_{sym}(PC_3)$
270	271	$\delta_{asym}(PC_3)$	263	268	$\delta_{asym}(PC_3)$	259	265	$\delta_{asym}(PC_3)$
247	250	$\nu(AgCl)$	181	179	$\nu(AgCl)$	149	142	$\nu(AgP)$
187	182	$\nu(AgCl)$	161		$\nu(AgCl)$	133		$\nu(AgBr)$
160	158	$\nu(AgCl)$		144	$\nu(AgCl)$		123	$\nu(AgBr)$
134		$\nu(AgCl)$	127	122	$\nu(AgCl)$	105		$\nu(AgBr)$
			100		$\nu(AgCl)$			
	67	def.		67	def.		56	def.

to the $\nu(CuCl)$ assignments for the corresponding copper complex, which showed four $\nu(CuCl)$ bands in the far-IR between 300 and 100 cm^{-1}.[1] The corresponding bands of the silver complex are found at lower frequencies, as expected, and correspond to the four symmetrically inequivalent Ag–Cl bonds in the structure. The positions of the bands are in very good agreement with those predicted from the bond lengths, according to a recently published correlation between $\nu(AgCl)$ and the Ag–Cl bond length.[42]

The far-IR and low-frequency Raman spectra of [{$AgX(PMe_3)_2$}$_2$] (X = Cl or Br) indicate that the complexes exist as halide-bridged dimers. The analysis of the spectra follows the principles previously established for the corresponding PPh_3 complexes.[7] The large $\nu(AgX)$ band splittings in the IR indicate that for both complexes the Ag_2X_2 core is rectangularly distorted as in [{$AgCl(PPh_3)_2$}$_2$].[7] The mean of the two highest and two lowest $\nu(AgCl)$ IR wavenumbers of [{$AgCl(PMe_3)_2$}$_2$] are 171, 114 cm^{-1}, and are similar to $\nu(AgCl) = 179$, 127 cm^{-1} of [{$AgCl(PPh_3)_2$}$_2$].[7] The additional splitting from the expected two to four bands may be due either to coupling with $\nu(AgP)$ or to factor group effects. The core of the silver chloride dimer is considerably more distorted than that of its bromide counterpart, as indicated by the relative splittings of the $\nu(AgX)$ IR bands (58 and 28 cm^{-1} respectively).

The synthesis of the complex [$AgCl(PMe_3)$] was attempted as described above; elemental analysis was consistent with 1 : 1 stoichiometry, but far-IR spectroscopy indicated that the product was a mixture of [$Ag_4Cl_4(PMe_3)_3$] and [{$AgCl(PMe_3)_2$}$_2$]. Bands at 342, 247, 187, 160 and 134 cm^{-1} were attributed to the 4 : 3 complex, while those at 322, 270 and 96 cm^{-1} were assigned to the 1 : 2 complex (the positions of the two lower wavenumber bands differ slightly from those given in Table 4 for the 1 : 2 complex, because measurement of these bands in the mixture is affected by overlap with bands due to the 3 : 4 complex). The dominance of bands due to the 4 : 3 complex in the $\nu(AgCl)$ region is not surprising, since, in a mixture of overall 1 : 1 stoichiometry, 80% of the AgCl would be present as the 4 : 3 complex and only 20% as the 1 : 2 complex.

Conclusion

The present study further extends our knowledge of the structural chemistry of adducts of the Group 11 metal halides with trimethylphosphine, and demonstrates the utility and complementary nature of vibrational and solid state NMR techniques in the study of these compounds. While several of the structures, such as those of [$Cu_4I_4(PMe_3)_4$] and [$CuCl(PMe_3)_3$], are similar to those of the more extensively studied PPh_3 analogues, others such as [$Ag_4Cl_4(PMe_3)_3$] and $[Cu(PMe_3)_4]^+[CuCl_2]^-$ have no such analogues, and demonstrate the significant structural changes that may accompany changes in the base strength and steric profile of the phosphine ligand.

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