Structural and Vibrational Spectroscopic Studies of Complexes of Trimethylphosphine with Copper(I) and Silver(I) Halides†

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New copper(I) halide–trimethylphosphine adducts were prepared by reaction of CuX with PMe_3 in benzene suspension, and characterized by room-temperature single-crystal X-ray studies and vibrational spectroscopy. $[(Me_3P)_2Cu(\mu\text{-}I)_2Cu(PMe_3)_2]$, monoclinic, space group $P2_1/c$, $a = 9.296(2)$, $b = 16.206(7)$, $c = 9.577(3)$ Å, $\beta = 113.76(2)°$, $Z = 2$ dimers, conventional R on $|F|$ 0.040 for 1369 'observed' $[I > 3\sigma(I)]$ reflections at convergence; $[\{Cu_4Cl_4(PMe_3)_3\}_\infty]$, rhombohedral, space group $R3c$, $a = 17.776(2)$, $c = 11.708(7)$ Å (hexagonal setting), $Z = 6$, $R = 0.045$ for 820 observed reflections. The latter is a novel one-dimensional polymer of quasi-cubanoid Cu_4Cl_4 units disposed with their body diagonals coincident with the crystallographic 3-axis and linked by Cu–Cl bonds between the four-co-ordinate apical atoms of successive Cu_4Cl_4 units. Unlike the related $[\{Cu_4I_4(NEt_3)_3\}_\infty]$ polymer, however, the off-axis copper atoms are planar three- rather than four-co-ordinate, having $(\mu\text{-}Cl)_2CuP$ environments. The far-IR and Raman spectra of the compounds, and of the 1:1 AgI–PMe_3 complex with the proposed tetrameric 'cubane' structure $[Ag_4I_4(PMe_3)_4]$, have been recorded and assigned. The frequencies and activities of the ν(MX) modes correlate well with the observed or proposed structures, and a comparison of the Raman spectra for the series of three compounds allows the first rational assignment of ν(MP) modes for multinuclear complexes of this type.

Complexes $[(MXL_n)_m]$ of the Group 11 or coinage metals (M = Cu, Ag or Au) with neutral ligands L display a wide diversity of structure types which involve a range of metal co-ordination numbers from two to four, and varying degrees of association (m = 1, 2, 3, 4, ∞).[1–3] Several of the spectroscopic methods which are applicable to transition-metal complexes are not available to these closed-shell d^{10} systems. However vibrational spectroscopy and solid-state NMR methods have proved to be very useful in providing information about their structure and bonding,[4–15] resulting in structure/spectra correlations for compounds the structures of which have been determined exactly by X-ray crystallography, and also in the discovery of several new structure types. However, most such investigations to date have been restricted to complexes in which the ligand L is triphenylphosphine, PPh_3, or other closely related ligands. Such ligands are quite bulky, a fact which partly dictates the type and stability and structure of the complexes which are formed. Relatively few studies of this type have been carried out on complexes of smaller phosphine ligands. The simplest trialkylphosphine is trimethylphosphine, PMe_3, and the previous rather limited array of studies has shown the advantages of using this ligand in structural studies of metal–phosphine complexes.[16–18] The principal benefit in relation to vibrational spectroscopic studies is that PMe_3 has a relatively small number of vibrational degrees of freedom, so that its vibrational spectrum is relatively simple, particularly in the low-wavenumber region where the metal–ligand vibrations, which give the most information about structure and bonding, occur. The disadvantages of PMe_3 as a ligand are its volatility and air-sensitivity, and these have apparently restricted the number of studies of its complexes with the Group 11 metals, the most extensive being one carried out by Schmidbaur *et al.*,[19] in which 1:1, 1:2, 1:3 and 1:4 complexes of PMe_3 with CuCl and AgCl were prepared and characterized by NMR and NQR spectroscopy. Structures for these complexes were proposed, but it was subsequently pointed out that, based on comparisons of the NQR frequencies with values which had subsequently been determined for similar complexes with known structures, some of the proposed structures were inconsistent with the observed frequencies.[4] In particular, the copper and chlorine NQR frequencies were very similar to those which had previously been determined for $[CuCl_2]^-$. The reason for this subsequently became clear in the case of the 1:2 CuCl–PMe_3 adduct which, instead of the proposed doubly chloro-bridged dimeric structure $[(Me_3P)_2CuCl_2Cu(PMe_3)_2]$, was shown to have the ionic structure $[Cu(PMe_3)_4]^+[CuCl_2]^-$.[20] Such structural differences are readily revealed by vibrational spectroscopy,[11] but very few studies of the vibrational spectra of PMe_3 complexes of the Group 11 metals have been reported. A detailed study of the IR and Raman spectra of the 1:1 AgI–PMe_3 adduct was published recently,[21] but some aspects of the assignments do not agree well with results obtained previously for closely related systems.[7,22] We have therefore undertaken a study of a selection of adducts of PMe_3 with copper(I) and silver(I) halides in order to establish more clearly the structural chemistry of these systems, and to provide a better basis for the assignment of their vibrational spectra.

Experimental

Preparation of Compounds.—Trimethylphosphine was prepared by a literature method.[23] A commercial sample (Aldrich) of the 1:1 AgI–PMe_3 adduct was used without further purification. In view of the recognized possibility that this

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp.xxv–xxx.

compound might be deficient in PMe_3,[24] a sample was subjected to elemental analysis (Found: C, 11.6; H, 2.8. Calc. for C_3H_9AgIP: C, 11.6; H, 2.9%). The preparations of the other PMe_3 complexes were carried out under an atmosphere of oxygen-free nitrogen using standard Schlenk techniques.

Di-μ-iodo-tetrakis(trimethylphosphine)dicopper(I), $[Cu_2I_2(PMe_3)_4]$. Into a Schlenk tube (25 cm^3) was placed dry benzene (5 cm^3) and copper(I) iodide (0.35 g, 1.8 mmol). The resulting suspension was cooled in an ice-bath and gently shaken as PMe_3 (0.20 cm^3, 1.9 mmol) was added dropwise. The reaction mixture became warm and the CuI dissolved during the addition of the PMe_3. The solution volume was reduced to *ca.* 3 cm^3, and the product was precipitated as small white crystals by addition of hexane (3 cm^3). The crystals were collected by vacuum filtration, dried in a vacuum desiccator, and stored under nitrogen. Yield 0.4 g (63% based on CuI), m.p. 152–154 °C (Found: C, 21.2; H, 5.2. Calc. for $C_{12}H_{36}Cu_2I_2P_4$: C, 21.05; H, 5.3%).

Catena-*μ*$_3$-*Chloro-tri-μ-chloro-tris(trimethylphosphine)tetracopper*(I), $[Cu_4Cl_4(PMe_3)_3]$. The preparation of this compound was similar to that described above for the CuI complex, but used benzene (10 cm^3), copper(I) chloride (0.396 g, 4.0 mmol), and PMe_3 (0.45 cm^3, 4.3 mmol). However, in contrast to the iodide preparation, total dissolution of the CuCl did not occur, leaving a very small amount of unreacted solid CuCl at the bottom of the tube after all of the PMe_3 had been added. The mixture was filtered, and the filtrate reduced in volume to *ca.* 5 cm^3, whereupon crystalline product began to separate. The mixture was warmed to 30 °C to redissolve the solid material and then allowed to cool slowly. The product formed as white crystals which were collected by vacuum filtration, dried in a vacuum desiccator, and stored under nitrogen. Yield 0.438 g (70% based on CuCl), m.p. 125–130 °C (Found: C, 17.4; H, 4.2. Calc. for $C_9H_{27}Cl_4Cu_4P_3$: C, 17.3; H, 4.35%).

Structure Determinations.—Unique data sets were measured at ≈295 K within the specified $2\theta_{max}$ limit using an Enraf-Nonius CAD-4 diffractometer (monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å; 2θ–θ scan mode) yielding N independent reflections, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix-least-squares refinements 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 on $|F|$ at convergence R, R' are quoted, 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, computation using the XTAL 3.2 program system implemented by S. R. Hall.[25] Pertinent results are quoted in Figs. 1 and 2 and in Tables 1–4.

Crystal/Refinement data. $[Cu_2I_2(PMe_3)_4]$, $C_{12}H_{36}Cu_2I_2P_4$, $M = 684.88$, monoclinic, space group $P2_1/c$ (C_{2h}^5, no. 14), $a = 9.296(2)$, $b = 16.206(7)$, $c = 9.577(3)$ Å, $\beta = 113.76(2)°$, $U = 1320(1)$ Å^3, D_c ($Z = 2$) = 1.72 g cm^{-3}, $F(000) = 664$, $\mu_{Mo} = 41.8$ cm^{-1}, specimen 0.20 × 0.20 × 0.18 mm, $A^*_{min,max} = 1.48, 2.15$, $2\theta_{max} = 50°$; $N = 2318$, $N_o = 1369$; $R = 0.040$, $R' = 0.039$.

$[Cu_4Cl_4(PMe_3)_3]$, $C_9H_{27}Cl_4Cu_4P_3$, $M = 624.23$; rhombohedral, space group $R3c$ (C_{3v}^6, no. 161); $a = 17.776(2)$, $c = 11.708(7)$ Å, $U = 3204(2)$ Å^3 (hexagonal setting); D_c ($Z = 6$) = 1.94 g cm^{-3}; $F(000) = 1860$, $\mu_{Mo} = 46.4$ cm^{-1}, specimen 0.11 × 0.10 × 0.55 mm, $A^*_{min,max} = 1.51, 1.59$; $2\theta_{max} = 55°$; $N = 826$, $N_o = 820$; $R = 0.045$, $R' = 0.036$ (preferred hand).

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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 triglycine sulfate detector. Raman spectra were recorded at 4.5 cm^{-1} resolution using a Jobin-Yvon U1000 spectrometer optically coupled to an Olympus BH-2 microscope employing a 20 objective, and equipped with a cooled photomultiplier (RCA C31034A) detector. The 488.0 nm exciting line from a Spectra-Physics model 2016 argon-ion laser was used.

Table 1 Non-hydrogen atom coordinates for $[Cu_2I_2(PMe_3)_4]$

Atom	*X/a*	*Y/b*	*Z/c*
I	0.400 83(8)	0.594 37(4)	0.595 33(7)
Cu	0.520 3(1)	0.567 07(7)	0.384 1(1)
P(1)	0.331 9(3)	0.592 1(2)	0.152 7(3)
P(2)	0.750 2(3)	0.633 9(1)	0.461 4(3)
C(11)	0.234(2)	0.504 1(7)	0.040(1)
C(12)	0.172(1)	0.655(1)	0.146(1)
C(13)	0.387(1)	0.647 5(8)	0.020(1)
C(21)	0.739(1)	0.744 4(6)	0.454(1)
C(22)	0.868(1)	0.611 7(8)	0.355(1)
C(23)	0.890(1)	0.616 2(8)	0.654(1)

Table 2 Non-hydrogen atom coordinates for $[Cu_4Cl_4(PMe_3)_3]$

Atom	*X/a*	*Y/b*	*Z/c*
Cu(1)	0.543 42(7)	0.325 01(7)	0.50*
Cu(2)	0.67	0.33	0.814 6(2)
Cl(1)	0.67	0.33	0.613 6(3)
Cl(2)	0.522 2(1)	0.226 5(1)	0.371 6(2)
P	0.507 0(1)	0.416 1(1)	0.570 4(2)
C(1)	0.411 7(5)	0.379 2(5)	0.660 7(7)
C(2)	0.591 6(5)	0.498 0(5)	0.659 9(8)
C(3)	0.490 6(6)	0.479 0(6)	0.463 1(7)

* Defines origin.

Results and Discussion

Syntheses.—The new compounds $[Cu_2I_2(PMe_3)_4]$ and $[Cu_4Cl_4(PMe_3)_3]$ were prepared by reaction of PMe_3 with CuI or CuCl suspended in benzene. In neither case did the composition of the compound obtained correspond to the stoichiometry of the reactants used (see Experimental section). This problem occurred in attempted syntheses of other members of the series of adducts of CuX or AgX with PMe_3, and it seems likely that this is at least partly due to the small scale on which the reactions were carried out, necessitated by the limited supply of PMe_3, and resulting in inaccuracies in the amount of PMe_3 delivered to the reaction.

The complex $[Cu_2I_2(PMe_3)_4]$ has 1:2 stoichiometry, which lies within the range 1:1–1:4 previously established for the CuCl compounds.[19] However, the structure is different from that determined for the 1:2 CuCl complex.[20] The complex $[Cu_4Cl_4(PMe_3)_3]$ has 4:3 stoichiometry, which lies outside the previously observed range of compositions,[19] but corresponds to that of the known $[Cu_4I_4(NEt_3)_3]$ compound.[26]

Structure Determinations.—CuI:PMe_3 (1:2) ≡ $[(Me_3P)_2Cu(\mu\text{-}I)_2Cu(PMe_3)_2]$. The results of the room-temperature single-crystal X-ray study are consistent with the formulation of the complex as a centrosymmetric dimer, one half of which comprises the asymmetric unit of the structure, with four-coordinate, $P_2Cu(\mu\text{-}I)_2$, copper. The core geometry parameters are given in Table 3, and selected parameters are compared in Table 5 with those for other copper(I) iodide complexes containing a $Cu(\mu\text{-}I)_2Cu$ core. No 1:2 complex of CuI involving the more commonly studied phosphine ligand PPh_3 is known. For this ligand only complexes of 1:1, 2:3 and 1:3 stoichiometry are formed. However, the dimeric complex $[Cu_2I_2(PPh_2Me)_4]$ has been prepared (as an SO_2 adduct),[27] so it appears that the changes in the properties of the ligand which are brought about by replacement of one of the phenyl groups in PPh_3 by a methyl group are sufficient to allow both of the copper atoms in the dimer to be co-ordinated to two phosphine ligands. One possible explanation of this observation is simply that the greater steric bulk of the PPh_3 ligand is sufficient to prevent co-ordination of two phosphine ligands at both of the copper atoms. This is supported by the observation that the bulkier ligand $P(C_6H_4Me\text{-}o)_3$, in which the phenyl groups of PPh_3 are replaced by *o*-tolyl groups, yields only the 1 : 1 adduct $[Cu_2I_2\{P(C_6H_4Me\text{-}o)_3\}_2]$ in which each of the copper atoms is co-ordinated to only one phosphine ligand.[14] The parameters in Table 5 thus reflect the changes which occur in complexes with a Cu_2I_2 core as the steric bulk and basicity of the phosphine ligand is systematically varied, and the results for the PMe_3 complex represent the extreme case of smallest ligand bulk and greatest ligand basicity. Therefore, it is not surprising that some of the core-geometry parameters for this compound are at the extreme of those listed in Table 5. Thus, for the sites involving P_2CuI_2 co-ordination, the P–Cu–P angle is the smallest and the I–Cu–I angle the largest. This is consistent with the smaller steric bulk of PMe_3, which permits the copper atom more closely to approach ideal tetrahedral co-ordination, with bond angles near 110°. Despite the above categorization of PPh_3 and PMe_3 as more or less bulky, the relative dispositions of the methyl substituents to one side of the CuI_2Cu plane are of interest, whereby those of the one phosphorus are 'geared' in relation to those of the other. With the exception of

Table 3 Core geometry (distances in Å, angles in °) for $[Cu_2I_2(PMe_3)_4]$

I · · · I′	4.336(1)	P(1)–C(11)	1.80(1)
Cu · · · Cu′	3.235(2)	P(1)–C(12)	1.78(1)
I–Cu	2.707(2)	P(1)–C(13)	1.79(1)
I–Cu′	2.703(2)	P(2)–C(21)	1.79(1)
Cu–P(1)	2.240(2)	P(2)–C(22)	1.81(1)
Cu–P(2)	2.239(3)	P(2)–C(23)	1.797(9)
Cu–I–Cu′	73.45(4)	C(11)–P(1)–C(12)	102.7(6)
I–Cu–P(1)	108.49(9)	C(11)–P(1)–C(13)	101.1(6)
I–Cu–P(2)	107.36(8)	C(12)–P(1)–C(13)	99.3(6)
I–Cu–I′	106.55(5)	Cu–P(2)–C(21)	116.1(4)
P(1)–Cu–P(2)	120.1(1)	Cu–P(2)–C(22)	115.6(4)
P(1)–Cu–I′	109.18(8)	Cu–P(2)–C(23)	117.5(4)
P(2)–Cu–I′	104.43(8)	C(21)–P(2)–C(22)	102.2(6)
Cu–P(1)–C(11)	116.9(4)	C(21)–P(2)–C(23)	101.8(5)
Cu–P(1)–C(12)	116.7(4)	C(22)–P(2)–C(23)	101.2(5)
Cu–P(1)–C(13)	117.3(3)		

Primes refer to inversion-related atoms.

Table 4 Core geometry (distances in Å, angles in °) for $[Cu_4Cl_4(PMe_3)_3]$

Cu(1)–Cl(1)	2.502(2)	Cu(2)–Cl(2′)	2.403(2)
Cu(1)–Cl(2)	2.192(2)	P–C(1)	1.818(9)
Cu(1)–P	2.184(3)	P–C(2)	1.814(8)
Cu(2)–Cl(1)	2.354(4)	P–C(3)	1.80(1)
Cl(1)–Cu(1)–Cl(2)	102.0(1)	Cu(1)–Cl(2)–Cu(2″″)	82.54(7)
Cl(1)–Cu(1)–P	109.27(7)	Cu(1)–P–C(1)	121.3(3)
Cl(2)–Cu(1)–P	148.7(1)	Cu(1)–P–C(2)	112.3(4)
Cl(1)–Cu(2)–Cl(2′)	106.11(7)	Cu(1)–P–C(3)	113.4(4)
Cl(2′)–Cu(2)–Cl(2″)	112.6(1)	C(1)–P–C(2)	101.7(4)
Cu(1)–Cl(1)–Cu(2)	122.16(7)	C(1)–P–C(3)	102.7(5)
Cu(1)–Cl(1)–Cu(1‴)	94.38(9)	C(2)–P–C(3)	103.4(4)

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

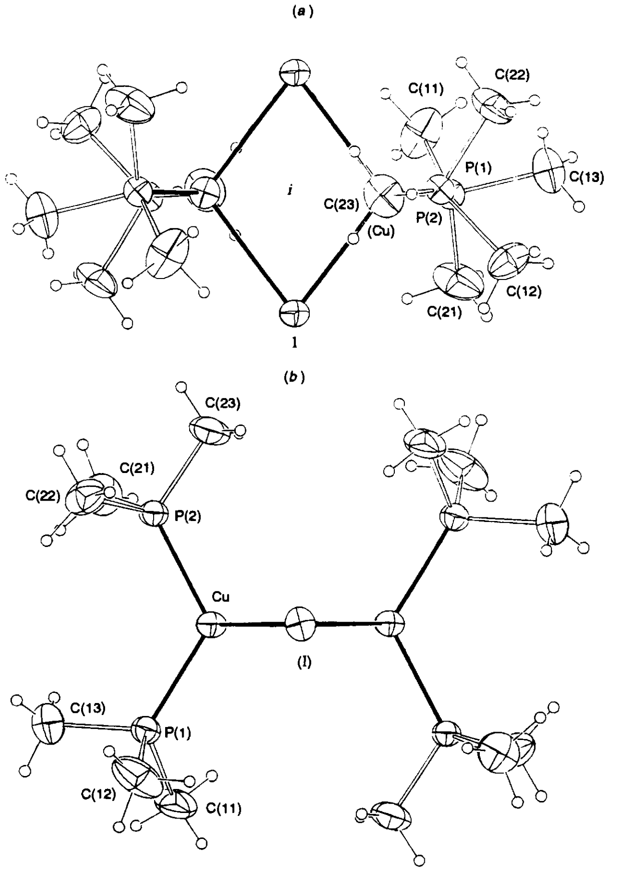

Fig. 1 The complex $[(Me_3P)_2Cu(\mu\text{-}I)_2Cu(PMe_3)_2]$ projected (*a*) normal to and (*b*) through the central $Cu(\mu\text{-}I)_2Cu$ plane; 20% thermal ellipsoids are shown for the non-hydrogen atoms. Hydrogen atoms have arbitrary radii of 0.1 Å

Table 5 Selected core-geometry parameters (distances in Å, angles in °) for copper(I) iodide complexes with a Cu_2I_2 core

Complex	Co-ordination number[a]	Cu–P	Cu–I	P–Cu–P	I–Cu–I	Cu–I–Cu	Cu · · · Cu	Ref.
$[Cu_2I_2(PMe_3)_4]$	4	2.240(2) 2.239(3)	2.707(2) 2.703(2)	120.1(1)	106.55(5)	73.45(4)	3.235(2)	*b*
$[Cu_2I_2(PPh_2Me)_4]\cdot SO_2$	4	2.250(2) 2.249(2)	2.724(1) 2.714(1)	127.89(9)	98.16(3)	83.40(5)	3.576(2)[c]	27
	4	2.274(2) 2.253(2)	2.650(1) 2.848(1)	122.85(9)	96.95(3)	79.99(5)		
$[Cu_2I_2(PPh_3)_3]$	4	2.259(3) 2.267(3)	2.707(1) 2.819(1)	125.24(11)	102.24(5)	70.43(4) 69.43(5)	3.041(3)	27
	3	2.219(3)	2.500(2) 2.563(1)		116.4(6)			
$[Cu_2I_2\{P(C_6H_4Me\text{-}o)_3\}_2]\cdot 2C_6H_5Me$	3	2.238(4)	2.525(2) 2.640(2)		105.66(6)	74.34(5)	3.122(3)	14

[a] Of copper. [b] This work. [c] Calculated on the assumption that *y*[Cu(2)] is in error and should be −0.052 76(10) [rather than −0.5276(10)].

$[Cu_2I_2(PPh_2Me)_4]\cdot SO_2$, the complexes listed in Table 5 have surprisingly similar Cu $\cdots$ Cu distances, despite the progressive change from three- to four-co-ordination for the copper atoms in these compounds. Indeed, the corresponding bond angles in the Cu_2I_2 cores in $[Cu_2I_2(PMe_3)_4]$ and $[Cu_2I_2\{P(C_6H_4Me\text{-}o)_3\}_2]$ are almost identical, and the main difference between the structure of these cores is the greater difference between the two inequivalent Cu–I distances, and the slightly smaller mean Cu–I distance in the latter complex. The observation of similar Cu $\cdots$ Cu distances in these two complexes is of some relevance in connection with a previously published investigation of possible Cu $\cdots$ Cu bonding in dimeric copper(I) compounds.[28] In this study it was predicted that the Cu $\cdots$ Cu distance should increase in going from a dimer in which the copper atom is three-co-ordinate to one in which it becomes four-co-ordinate by addition of a second terminal π-bonding ligand at each copper atom. The reason given for this is that the additional ligand removes from the copper atoms the π-electron density which is responsible for the proposed Cu $\cdots$ Cu bonding in the three-co-ordinate dimer.[28] A change of this kind has been seen upon co-ordination of MeCN to the copper atoms in $[Cu_2I_2\{P(C_6H_4Me\text{-}o)_3\}_2]$ where the Cu $\cdots$ Cu distance increases from 3.122(3) to 3.543(1) Å.[14] Prior to the present study, the increase in Cu $\cdots$ Cu from 3.12(2) Å in $[Cu_2I_2\{P(C_6H_4Me\text{-}o)_3\}_2]$ to 3.576(2) Å in $[Cu_2I_2(PPh_2Me)_4]\cdot SO_2$ might have been attributed to the same phenomenon. However, the present study shows that the Cu $\cdots$ Cu distance in $[Cu_2I_2(PMe_3)_4]$ is not much greater than that in $[Cu_2I_2\{P(C_6H_4Me\text{-}o)_3\}_2]$. The relatively large Cu $\cdots$ Cu distance in $[Cu_2I_2(PPh_2Me)_4]\cdot SO_2$ is associated with correspondingly large Cu–I–Cu angles, which are presumably a consequence of the interaction of one of the iodide ligands with the SO_2 molecule.

The structure of $[Cu_2I_2(PMe_3)_4]$ differs from that of the 1:2 CuCl–PMe_3 complex, which has been shown to have the ionic structure $[Cu(PMe_3)_4]^+[CuCl_2]^-$.[20] This situation parallels that observed previously for the 1:2 adducts of CuX with 3,4-dimethyl-1-phenylphosphole (dmpp), where vibrational and cross polarization magic angle spinning (CP MAS) ^{31}P NMR measurements suggested that a change from an ionic $[Cu(dmpp)_4]^+[CuCl_2]^-$ structure for the chloride to a dimeric doubly halide-bridged molecular structure occurs for the bromide and iodide.[11]

CuCl:PMe_3 (4:3) $\equiv [\{Cu_4Cl_4(PMe_3)_3\}_\infty]$. The results of the room-temperature single-crystal study are consistent with the formulation of the complex thus stoichiometrically. Stereochemically, it displays a novel connectivity without precedent among coinage metal(I) halide–Lewis base adducts. Derivative of the familiar $M_4X_4L_4$ 'cubane' array, the complex is comprised of tetrameric M_4X_4 cluster units disposed in space group *R*3*c* with the three-fold axis coincident with the 'cube' diagonal, and with the metal and halogen atoms at the cube apices at either pole of the diagonal linked to adjoining clusters to form an infinite one-dimensional polymer in which each cubane unit is now left with only three of the four metal atoms able to offer sites for the co-ordination of the phosphine ligands, as required by the above stoichiometry. Such is the array found in the related complex $[\{Cu_4I_4(NEt_3)_3\}_\infty]$, also a one-dimensional polymer of apically linked cubes.[26] In the latter, all copper atoms are four-co-ordinate, as is the apical halogen, while the other halogens at the cube corners are three-co-ordinate. Remarkably, the present complex differs in that the set of three 'off-axis' copper atoms with their halide counterparts have diminished connectivity *vis-à-vis* the above iodide, the chlorine atoms being two-co-ordinate, while the copper atoms are three-co-ordinate, $(\mu\text{-}Cl)_2CuP$, with the angle sum about the copper being exactly 360°, *i.e.* rigorously planar. However, there is a considerable distortion from ideal trigonal geometry, with P–Cu(1)–Cl(2) being nearly 30° greater than the ideal trigonal angle of 120°. In fact, the geometry about Cu(1) can equally be viewed as involving a linear two-co-ordinate P–Cu(1)–Cl(2) arrangement distorted by a weaker Cu(1)–Cl(1) interaction. This is reflected in the considerably greater length of Cu(1)–Cl(1) compared with that of Cu(1)–Cl(2) (Table 4). The next strongest Cu–Cl interaction after Cu(1)–Cl(2) is Cu(2)–Cl(1), the bond connecting the Cu_4Cl_4 units into a chain, and there is an additional weaker interaction Cu(2)–Cl(2) within the Cu_4Cl_4 units. Overall, the Cu–Cl bond lengths can thus be divided into two groups: the relatively strong Cu(1)–Cl(2) at 2.192(2) Å, and the weaker Cu(2)–Cl(1), Cu(2)–Cl(2′), Cu(1)–Cl(1) at 2.354(4), 2.403(2), 2.502(2) Å. This wide distribution of bond lengths is reflected in the far-IR spectrum (see below).

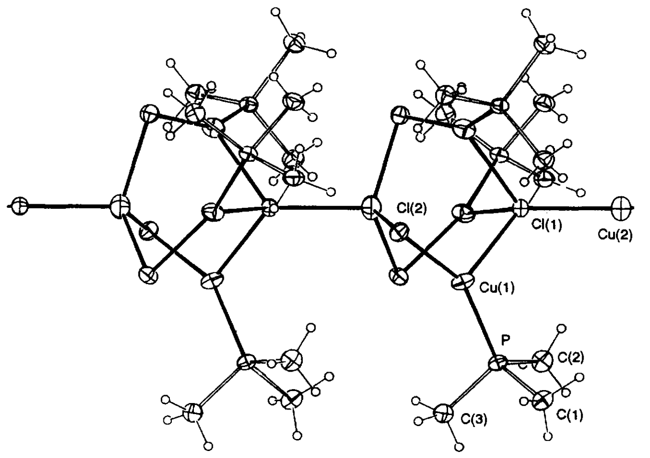

Fig. 2 The complex $[\{Cu_4Cl_4(PMe_3)_3\}]$ projected normal to the polymer/crystallographic 3 axis; thermal ellipsoids and hydrogen atoms as in Fig. 1

Although the structure of $[Cu_4Cl_4(PMe_3)_3]$ is closely related to that of $[Cu_4I_4(NEt_3)_3]$,[26] there are a number of significant differences. In the latter complex, the longest Cu–I bond is the one between the Cu_4I_4 clusters, at 2.917(9) Å. The Cu–I bond lengths within the tetrameric cluster are shorter, lying in the range 2.594(3)–2.820(6) Å. The I–Cu–I bond angles within the cluster lie within the relatively narrow range 106.0(2)–115.5(2)°, so the Cu_4I_4 cluster is not much distorted from ideal T_d symmetry, and the interactions between neighbouring clusters in the polymeric chain are weaker than those within the clusters. Neither of these situations obtains in the case of $[Cu_4Cl_4(PMe_3)_3]$, where the bonding within the tetramers is so distorted from that in the ideal 'cubane' structure that three bonds along the edges of the 'cube' are broken, and the Cu–Cl bonds between the tetramers are stronger than the majority of those within the tetramer. The differences between the structures of these complexes can presumably be attributed to differences in the ligand donor properties: PMe_3 is a stronger σ donor than NEt_3, and this results in a strong P–Cu bond. The Cu–P bond length is in fact significantly shorter than the average value of 2.192 Å observed for the Cu–P bonds in the 'cubane' $[Cu_4Cl_4(PPh_3)_4]$.[29] This might have been expected to cause the Cu–Cl bonds for the copper atoms which are bonded to the PMe_3 ligand to be longer than those in $[Cu_4Cl_4(PPh_3)_4]$, which have an average length of 2.44 Å.[29] However, an additional factor comes into play in the less-symmetrical PMe_3 complex. This is the strong distortion of the copper co-ordination environment away from the ideal tetrahedral $PCuCl_3$ arrangement to yield a single strong Cu–Cl bond in a position approximately *trans* to the Cu–P bond and only one other weak Cu–Cl bond approximately perpendicular to the strongly bound P–Cu–Cl unit. The ability of PMe_3 to yield complexes of unusual structure with metal halides as a result of the tendency to form approximately linear P–M–X units has been observed previously in the case of its complexes with mercury(II) halides.[30]

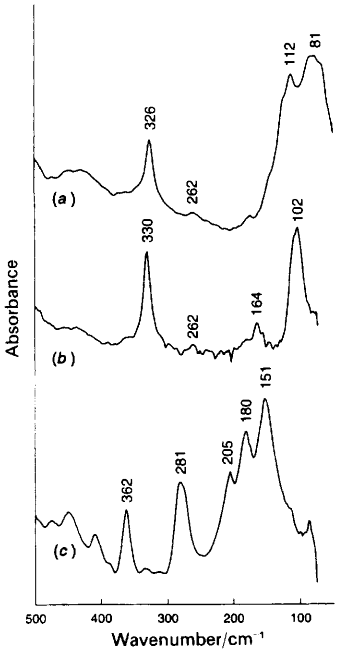

Fig. 3 Far-IR spectra of (*a*) $[Ag_4I_4(PMe_3)_4]$, (*b*) $[Cu_2I_2(PMe_3)_4]$ and (*c*) $[Cu_4Cl_4(PMe_3)_3]$

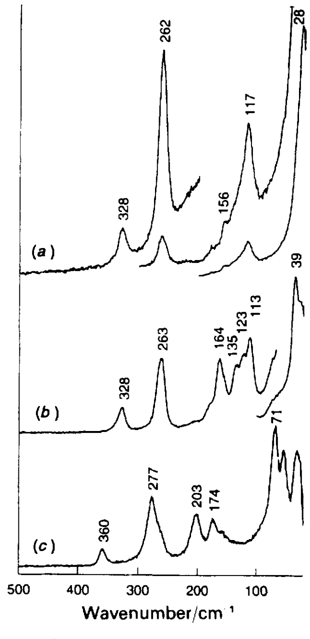

Fig. 4 Low-wavenumber Raman spectra of (*a*) $[Ag_4I_4(PMe_3)_4]$, (*b*) $[Cu_2I_2(PMe_3)_4]$ and (*c*) $[Cu_4Cl_4(PMe_3)_3]$

Vibrational Spectra.—The far-IR and low-frequency Raman spectra of $[Ag_4I_4(PMe_3)_4]$, $[Cu_2I_2(PMe_3)_4]$ and $[Cu_4Cl_4(PMe_3)_3]$ are shown in Figs. 3 and 4, and the wavenumbers and assignments of the low-frequency bands are given in Table 6.

The crystal structure of $[Ag_4I_4(PMe_3)_4]$ has not yet been determined, but a cubane structure which is analogous to that found for the corresponding PEt_3 complex[31] has previously been postulated to account for the vibrational spectra of this complex.[21] We recorded the spectra of this complex again, since some aspects of the previously published assignments did not agree well with results obtained previously for closely related systems,[7,22] and also to provide a direct comparison with the results for the new complexes reported here. The spectra in the wavenumber region above 500 cm^{-1} contain only bands due to the co-ordinated PMe_3 ligand, and these did not change much in position or relative intensity from one complex to another. A list of these bands and their assignments are given in the previous study of $[Ag_4I_4(PMe_3)_4]$,[21] so these are not given here. The only significant difference between our results and the literature results for the PMe_3 bands in $[Ag_4I_4(PMe_3)_4]$ is that the strongest band in the IR spectrum is a singlet at 959 cm^{-1}, whereas the previously reported spectrum shows this band as a broad partially resolved doublet.[21] It is observed as a very strong, sharp singlet in the IR spectra of all three compounds studied in the present work.

The far-IR and low-frequency Raman spectra of $[Ag_4I_4(PMe_3)_4]$ are in reasonable agreement with the previously published spectra,[21] but some of the assignments need to be reconsidered in the light of the results obtained in this and previous studies,[7,22] and in a study of the structurally simpler monomeric $[AuX(PMe_3)]$ species.[32] In particular, the question of the assignment of the ν(AgI) and ν(AgP) modes needs further consideration. The symmetry types and activities of the fundamentals due to vibrations of the $T_2M_4X_4$ core are $2A_1$(Raman) + 2E(Raman) + T_1 + $3T_2$(IR,Raman). These involve contributions from MX bond stretching ν(MX) (A_1 + E + T_1 + $2T_2$) and cage deformation (A_1 + E + T_2). In previous studies of $[M_4X_4L_4]$ systems with a cubane structure, the two T_2 ν(MX) modes are the strongest feature of the IR spectrum. The Raman spectrum is dominated by a very strong band below 100 cm^{-1} which is assigned to the A_1 cage deformation mode, and a higher-frequency band which coincides closely in wavenumber with that of the higher of the two T_2 ν(MX) modes which are observed in the IR, and which was therefore assigned to this mode. The assignment of the latter to the A_1 or E ν(MX) modes was precluded on the basis of a normal-coordinate analysis, which indicated that these modes should occur at significantly lower frequencies.[7] Application of these criteria to the results obtained in the present study for $[Ag_4I_4(PMe_3)_4]$ results in the assignments given in Table 6. These agree with the previously reported assignments for the IR spectrum of this compound,[21] but not for the Raman spectrum. The A_1 cage deformation mode is clearly seen as a very strong Raman band at 28 cm^{-1},

Table 6 Wavenumbers (cm^{-1}) and assignments of the low-frequency bands in the IR and Raman spectra

$[Ag_4I_4(PMe_3)_4]$			$[Cu_2I_2(PMe_3)_4]$			$[Cu_4Cl_4(PMe_3)_3]$		
IR	Raman	Assignment	IR	Raman	Assignment	IR	Raman	Assignment
326	328	$\delta_{sym}(PC_3)$	330	328	$\delta_{sym}(PC_3)$	362	360	$\delta_{sym}(PC_3)$
262	262	$\delta_{asym}(PC_3)$	262	263	$\delta_{asym}(PC_3)$			
	156	ν(AgP)	164	164	ν(CuP)	281	277	ν(CuCl)
112	117	T_2 ν(AgI)		135	ν(CuI)	205	203	ν(CuCl)
				123				
				113		180		ν(CuCl)
							174	ν(CuP)
81		T_2 ν(AgI)	102		ν(CuI)	151		ν(CuCl)
	28	A_1 def.		39	def.		71	def.

significantly lower than the value of about 50 cm^{-1} observed for compounds containing Cu_4I_4 clusters, but this shift is in the direction expected for replacement of Cu by the heavier Ag. This band was not reported in the previous study, which showed the Raman spectrum above 80 cm^{-1} only. Our spectrum shows only two bands in the region between 100 and 200 cm^{-1}, at 117 and 156 cm^{-1}. By the criterion mentioned above, the stronger of these at 117 cm^{-1} is assigned to the T_2 ν(AgI) mode. In assigning the bond at 156 cm^{-1} we first note that the normal-coordinate analysis on the M_4X_4 unit shows that the highest-frequency mode of this unit is always the T_2 ν(MX) mode.[22] Since this occurs below 120 cm^{-1}, the Raman band at 156 cm^{-1} must belong to a vibration which is external to this cluster unit, and the most likely possibility is the ν(AgP). The symmetry types and activities of the vibrations of the four Ag–P bonds in the cluster are A_1(Raman) + T_2(IR,Raman), so two ν(AgP) bands are expected in the Raman. However, the coupling between the vibrations of these bonds through the weaker AgI bonds is likely to be small, so the two modes would probably not be resolved. The problems associated with the assignment of ν(MP) modes in transition-metal complexes have been discussed previously.[4,33,34] Bands have been assigned over a wide wavenumber range, 90–460 cm^{-1}, but definitive assignments have been made only in a few cases. For the Group 11 metals, the most definitive assignments have been made for gold(I) complexes $[AuX(PPh_3)]$ and $[AuX(PPh_3)_2]$, yielding ν(AuP) values in the range 160–180 cm^{-1}.[13] The assignments are quite clear, since the only other bands which are expected in this region are ν(MX) and these simple mononuclear complexes can give rise to only one such band. The only ν(AgP) assignment available for a mononuclear silver(I) complex is a band in the Raman spectrum of $[AgBr(PPh_3)_2]$, at 132 cm^{-1}.[13] This is a little lower than the value 156 cm^{-1} assigned in the present study to ν(AgP) in $[Ag_4I_4(PMe_3)_4]$. However, the shift is in the expected direction for a change from the 'heavier' PPh_3 to the 'lighter' PMe_3 ligand. This type of dependence of ν(MP) on the nature of the phosphine ligand has been demonstrated previously. For example, ν(PdP) increases from 190 to 235 cm^{-1} in $[PdX_2L_2]$ from L = PPh_3 to PEt_3.[33,34]

Further support for our ν(AgP) assignment comes from the fact that assignments of ν(CuP) at similar wavenumbers can be made for the two copper(I) complexes studied in this work (see below) and for $[AuX(PMe_3)]$.[32] The authors of the previous study of $[Ag_4I_4(PMe_3)_4]$ made the reverse of the ν(AgI) and ν(AgP) assignment given here, and they also assigned bands at 110 and 175 cm^{-1} which are not evident in our Raman spectrum (nor indeed in their published spectrum in the case of the band at 175 cm^{-1}).[21] The rationalization of the assignments made in the present study shows that the spectra can be interpreted in a manner similar to those for other cubane $[M_4X_4L_4]$ clusters, and this lends strong support to the postulated tetrameric cubane structure for the present complex.

The $\delta(PC_3)$ deformation modes of the co-ordinated PMe_3 ligand occur at 326 at 262 cm^{-1}. These are assigned to the symmetric [A_1 in local C_{3v} symmetry, $\delta_{sym}(PC_3)$] and asymmetric [E, $\delta_{asym}(PC_3)$] modes respectively, the order of assignment being the same as in free PMe_3 [$\delta_{sym}(PC_3)$ 305, $\delta_{asym}(PC_3)$ 263 cm^{-1}].[35] The $\delta_{asym}(PC_3)$ frequency is essentially unchanged from that of the free phosphine, whereas that of the $\delta_{sym}(PC_3)$ mode increases by about 25 cm^{-1}. This is most likely due to mixing of the $\delta_{sym}(PC_3)$ mode with the lower-frequency ν(AgP) mode, both of which are A_1 modes in the C_{3v} symmetry of the local $AgPMe_3$ environment. Such mixing is not possible between $\delta_{asym}(PC_3)$ (E) and ν(AgP) (A_1) on symmetry grounds, so the $\delta_{sym}(PC_3)$ frequency in the complex is unshifted from the free phosphine value.

The ideal point-group symmetry of the isolated dimer $[Cu_2I_2(PMe_3)_4]$ is D_{2h}. The symmetry types and activities of the fundamentals due to vibrations of the D_{2h} M_2X_2 core (x parallel to the M···M diagonal, y parallel to the X···X diagonal) are $2A_g$(Raman) + B_{1g}(Raman) + B_{1u}(IR) + B_{2u}(IR) + B_{3u}(IR). These involve contributions from MX bond stretching ν(MX) (A_g + B_{1g} + B_{2u} + B_{3u}) and in-plane (A_g) and out-of-plane (B_{1u}) deformation. Thus two IR-active ν(CuI) modes of B_{2u} and B_{3u} symmetry are predicted for this structure. For a perfectly square Cu_2I_2 unit the two IR-active normal modes involve displacement of I and Cu along the positive and negative x directions respectively (B_{3u}) or a similar vibration in the y direction (B_{2u}). For an isolated square Cu_2I_2 unit these two modes would have the same frequency. A distortion in which two angles on opposite corners of the square are decreased and the other two are increased results in no change of symmetry, but leads in principle to a separation in frequency of the two ν(CuI) IR modes. Such a splitting has been observed in complexes of the type $[Cu_2X_2L_2]$ [L = $P(C_6H_4Me\text{-}o)_3$] in which the Cu–X–Cu angle is less than 90°, and the X–Cu–X angle is greater than 90°.[14] A similar situation obtains in $[Cu_2I_2(PMe_3)_4]$, but the far-IR spectrum (Fig. 3) shows only a single ν(CuI) band at 102 cm^{-1}, although the band is slightly asymmetric, with a shoulder at about 106 cm^{-1}. This suggests that the B_{2u} and B_{3u} ν(CuI) modes are nearly coincident in this complex, and that the larger splitting observed in the $P(C_6H_4Me\text{-}o)_3$ complex is due to the much greater difference between the two inequivalent Cu–I distances in this complex (Table 5), rather than to an angular distortion of the Cu_2I_2 core from a perfectly square structure. This type of splitting has been observed previously in the far-IR spectra of similarly distorted silver(I) complexes.[10,13] Two ν(CuI) modes (A_g + B_{1g}) are expected in the Raman spectra, and these should be similar in wavenumber to the corresponding IR modes which occur just above 100 cm^{-1}. The partially resolved multiplet in the range 113–135 cm^{-1} is therefore assigned to these modes. The only remaining Raman band in this region is one at 164 cm^{-1}, and this is assigned as ν(CuP). This fits well with the assignment of ν(AgP) at 156 cm^{-1} for $[Ag_4I_4(PMe_3)_4]$ (see above).

The compound $[Cu_4Cl_4(PMe_3)_3]$ has a more complex structure than the other two studied in this work. The structure contains ten Cu–Cl bonds (nine within the Cu_4Cl_4 cluster and one connecting the clusters). The symmetry types and activities of the resulting ν(CuCl) modes are $4A_1$(IR,Raman) + 3E(IR, Raman), so a total of seven bands are predicted in both the IR and Raman spectra. The spectra are rather simpler than this, the far-IR spectrum showing four bands between 100 and 300 cm^{-1}, and the Raman spectrum only three bands in this region (Figs. 3 and 4). The band at 281 cm^{-1} in the IR spectrum lies in the same region as the asymmetric $\delta(PC_3)$ frequency, but comparison of the intensity of this band with that of the $\delta(PC_3)$ band of the two other complexes in Fig. 3 indicates that it is too intense to be assigned to the $\delta(PC_3)$ mode. We therefore assign it to the highest-wavenumber ν(CuCl) mode. It seems most likely that this mode is associated with the strongest of the Cu–Cl bonds in the cluster, *i.e.* the bonds of length 2.19 Å which are almost directly *trans* to the Cu–P bonds. As discussed in the analysis of the crystal structure results above, the complex can be considered as an assembly of $CuCl(PMe_3)$ units in which the strongest bonds are those within these units. It appears that the vibrational coupling between these units is insufficient to produce distinguishable frequencies for the A_1 + E modes predicted for the three $CuCl(PMe_3)$ units within the cluster. If this is also the case for the other Cu–Cl bonds in the cluster, then a very simple interpretation of the four bands in the 100–300 cm^{-1} region in the far-IR is possible, *viz.* the four bands correspond to the four symmetrically inequivalent Cu–Cl bond types in the structure, which differ in length by 0.05 Å or more. We have previously shown that, for a wide range of copper(I) halide complexes with phosphine and amine ligands, the ν(CuX) frequencies can be empirically correlated with the Cu–X bond length r *via* a relationship of the type (1) where b =

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

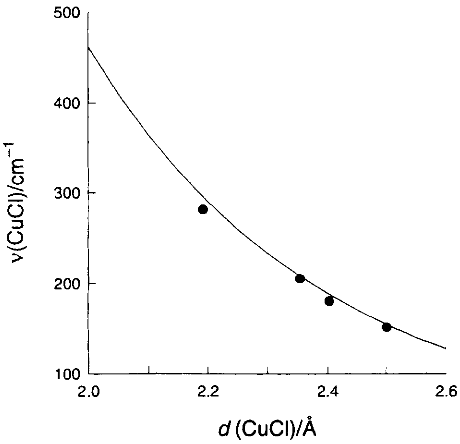

Fig. 5 Dependence of ν(CuCl) on r(CuCl). The continuous line is equation (1), and the points are data for $[Cu_4Cl_4(PMe_3)_3]$

13 800 and $m = 4.9$ for X = Cl.[8,9] This curve is plotted in Fig. 5. Assigning the four far-IR bands at 281, 205, 180, 151 cm^{-1} to the four sets of Cu–Cl bonds in order of increasing length (*i.e.* 2.192, 2.354, 2.403, 2.502 Å respectively), the points corresponding to each of these bands are also plotted in Fig. 5. It is clear that all of these points lie very close to the previously determined curve, thus lending strong support to the assignments. A further feature of the far-IR spectrum which is consistent with these assignments is the observation that the band at 205 cm^{-1} is significantly weaker than the other three. This band is assigned to the bond of length 2.354 Å, which is the bond connecting the Cu_4Cl_4 clusters. As there is only one of these bonds per cluster, compared to three for the other three Cu–Cl bond types, a weaker band would be expected in this case. It should be noted that the complexes for which the correlations of ν(CuX) with r(CuX) were established all involved terminal Cu–X bonds,[8] whereas the Cu–Cl bonds in the present complex are all bridging. The fact that the points derived from the assignments for this complex lie so close to the previously determined correlation line suggests that this correlation is not restricted to terminal Cu–X bonds, but can be extended to the case of bridging bonds as well. This observation has already been made by other workers in a similar study of the vibrational spectra of complexes of copper(I) halides with Se_6.[36]

There are three bands in the 100–300 cm^{-1} region of the Raman spectrum of $[Cu_4Cl_4(PMe_3)_3]$, compared with the four observed in the far-IR. The intensities of the Raman bands fall off rapidly with decreasing wavenumber. The two highest-wavenumber bands at 277 and 203 cm^{-1} are assigned as ν(CuCl) of the two strongest Cu–Cl bonds in the complex, as was done for the corresponding bands at 281 and 205 cm^{-1} in the far-IR (see above). The absence of Raman bands corresponding to the strong IR bands at 180 and 151 cm^{-1} is consistent with the assignment of these to the weaker Cu–Cl bonds (see above). These weaker bonds would give rise to smaller polarizability changes and therefore to less-intense Raman scattering. The Raman band at 174 cm^{-1} does not coincide closely with any of the ν(CuCl) IR bands, but is in the region expected for the ν(CuP) mode. For $[Cu_2I_2(PMe_3)_4]$ [d(Cu–P) = 2.24 Å] ν(CuP) occurs at 164 cm^{-1} (Table 6). The assignment of the slightly higher ν(CuP) at 174 cm^{-1} in $[Cu_4Cl_4(PMe_3)_3]$ [d(Cu–P) = 2.18 Å] is consistent with the slightly stronger Cu–P bond in the latter complex.

Conclusion

The present study significantly extends knowledge of the structural chemistry of complexes of the Group 11 metal(I) halides with PMe_3, and further highlights the unusual nature of the copper(I) chloride adducts. The structures reported in the present study for 4:3 CuCl–PMe_3 and 1:2 CuI–PMe_3 supplement those previously reported for 1:2 CuCl–PMe_3,[20] 1:3 CuBr–PMe_3[37] and 1:4 CuX–PMe_3 (X = Cl, Br or I).[38] Of the three CuCl complexes in this set, only the 1:4 compound corresponds in stoichiometry and structure to any of the four CuCl complexes described in the original work on these compounds.[19] The 1:2 CuCl–PMe_3 adduct has the ionic structure $[Cu(PMe_3)_4]^+[CuCl_2]^-$,[20] and a similar structure has been found for the corresponding dmpp complex,[11] suggesting that this behaviour may be typical for small highly basic phosphines and related ligands. The 4:3 CuCl–PMe_3 complex with the $[\{Cu_4Cl_4(PMe_3)_3\}_\infty]$ chain structure has no precedent in copper(I) halide/phosphine ligand chemistry, but is closely related to the corresponding CuI–NEt_3 complex, as discussed above. This suggests that this unusual structure is also associated with ligands which have small steric requirements.

The frequencies and activities of the ν(MX) modes of the three complexes studied here correlate well with the observed or proposed structures, and a comparison of the Raman spectra for the series of three compounds allows the first rational assignment of ν(MP) modes for multinuclear complexes of this type. This is a consequence of the advantage mentioned in the Introduction of studying complexes of the relatively simple PMe_3 ligand, and of the the fact that data for a series of three different but structurally related complexes were available for comparison.

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