

# Structural and spectroscopic studies on three-coordinate complexes of copper(I) halides with tricyclohexylphosphine

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Three-coordinate 1 : 1 and 1 : 2 compounds of copper(I) halides with tricyclohexylphosphine have been synthesised and characterized by single crystal X-ray structure determinations, <sup>63</sup>Cu NQR spectroscopy, solid state <sup>31</sup>P CPMAS NMR spectroscopy, and low frequency vibrational spectroscopy. The 1 : 1 compounds crystallize as isomorphous, centrosymmetric [(PCy<sub>3</sub>)Cu(μ-X)<sub>2</sub>Cu(PCy<sub>3</sub>)] dimers with three-coordinate (PCuX<sub>2</sub>) copper. Solid state <sup>31</sup>P CPMAS NMR spectra show asymmetric quartets with the spectra of the chloride and bromide compounds broadened by quadrupole relaxation effects. For X = I, <sup>1</sup>J(<sup>31</sup>P–<sup>63</sup>Cu) is 1.74 kHz with the quadrupole distortion parameter, *dv*<sub>Cu</sub>, 11.5 × 10<sup>9</sup> Hz<sup>2</sup>. Far infrared spectra of the compounds are unusually complex with groups of strong bands in the region expected for ν(CuX) vibrational modes (100–260 cm<sup>-1</sup>). The 1 : 2 compounds crystallize as [CuX(PCy<sub>3</sub>)<sub>2</sub>] monomers. The solid state <sup>31</sup>P NMR spectra of the bromide and iodide compounds show sharp asymmetric quartets with <sup>1</sup>J(P–Cu) 1.20 and 1.23 kHz and *dv*<sub>Cu</sub> 8.7 and 10.3 × 10<sup>9</sup> Hz<sup>2</sup> respectively. Relaxation effects collapse the spectrum of the chloride to a broad doublet. Room temperature <sup>63</sup>Cu NQR frequencies for [CuX(PCy<sub>3</sub>)<sub>2</sub>] are found to be 34.5, 33.43 and 32.06 MHz for X = Cl, Br and I respectively and are of the order of 4 MHz greater than values recorded for the 1 : 1 complexes. Far infrared spectra of the complexes exhibit strong bands due to ν(CuX) vibrational modes at 253, 189 and 156 cm<sup>-1</sup> for X = Cl, Br and I.

## Introduction

Reactions of copper(I) halides with unidentate tertiary organophosphine bases yield a diverse array of two-, three- and four-coordinate complexes with structural and spectroscopic properties that are determined by the specific choices of phosphine ligand and, to a lesser extent, by the choice of halide anion. Thus, for compounds of 1 : 1 stoichiometry, simple monomeric [CuX(PR<sub>3</sub>)] complexes with two-coordinate (PCuX) copper are obtained for trimesitylphosphine (Pmes<sub>3</sub>) (X = Br)<sup>1</sup> and tris(2,4,6-trimethoxyphenyl)phosphine (Ptmp<sub>3</sub>) (X = Cl, Br, I).<sup>2,3</sup> Dimeric [CuX(PR<sub>3</sub>)<sub>2</sub>] complexes with bridging halides and three-coordinate (PCuX<sub>2</sub>) copper are obtained for a number of phosphines, including tricyclohexylphosphine (PCy<sub>3</sub>) (X = Cl, I),<sup>4,5</sup> tris(*o*-tolylphosphine) (Po-tol<sub>3</sub>) (X = Cl, Br, I),<sup>6–8</sup> PPh<sub>2</sub>mes, PPhmes<sub>2</sub> (X = Cl, Br, I),<sup>9</sup> tris(*o*-anisylphosphine) (Po-anis<sub>3</sub>) (X = Br)<sup>10</sup> and tribenzylphosphine (PBn<sub>3</sub>) (X = I),<sup>11</sup> while the stellaquadrangula or “cubane” [CuX(PR<sub>3</sub>)<sub>4</sub>] complexes, with μ<sub>3</sub> bridging halides and four-coordinate (PCuX<sub>3</sub>) copper, are obtained for PEt<sub>3</sub> (X = Cl, Br, I),<sup>12,13</sup> PMePh<sub>2</sub> (X = I),<sup>14</sup> PPh<sub>3</sub> (X = Cl, Br, I)<sup>15–17</sup> and P<sup>t</sup>Bu<sub>3</sub> (X = Br).<sup>18</sup> A “step” tetrameric structure which incorporates both three- (PCuX<sub>2</sub>) and four- (PCuX<sub>3</sub>) coordinate copper has also been reported for PPh<sub>3</sub> (X = Br, I).<sup>19–21</sup> Compounds of 1 : 2 stoichiometry, CuX(PR<sub>3</sub>)<sub>2</sub>, crystallize either as [CuX(PR<sub>3</sub>)<sub>2</sub>]<sub>2</sub> dimers with four-coordinate (P<sub>2</sub>CuX<sub>2</sub>) copper for PPhH<sub>2</sub> (X = I),<sup>22</sup> PMePh<sub>2</sub> (X = I)<sup>23</sup> and PMe<sub>3</sub> (X = I),<sup>24</sup> or as [CuX(PR<sub>3</sub>)<sub>2</sub>] monomers with three-coordinate (P<sub>2</sub>CuX) copper for PPh<sub>3</sub> (X = Cl, Br, I),<sup>25–27</sup> PPh<sub>2</sub>*o*-tol (X = Cl, Br, I),<sup>28</sup> PCy<sub>3</sub> (X = Br, I)<sup>5,29</sup> and PBn<sub>3</sub> (X = Cl, Br, I).<sup>11</sup>

In our continuing investigations into the dependence of the structural and spectroscopic properties of these compounds on the choice of phosphine and halide, we have sought to extend the array of available data for three-coordinate complexes of copper(I) halides with tricyclohexylphosphine. Single crystal X-ray structures have been determined for the 1 : 1 adducts for X = Br and I, and for the 1 : 2 adducts for X = Cl (two polymorphs) and Br. The structure of the analogous 1 : 2 nitrate compound was also redetermined. Spectroscopic data has been obtained from low frequency infrared spectroscopy, solid state <sup>31</sup>P CPMAS NMR spectroscopy and <sup>63</sup>Cu NQR spectroscopy. The outcomes of this study, which are reported here, also complete a series of studies on the 1 : 1 and 1 : 2 two-, three- and four-coordinate complexes of copper, silver and gold(I) halides with tricyclohexylphosphine.<sup>30–33</sup>

## Experimental

### Preparation of the complexes

**[CuCl(PCy<sub>3</sub>)<sub>2</sub>].** CuCl (0.100 g, 1.0 mmol) and PCy<sub>3</sub> (0.280 g, 1.0 mmol) were dissolved in 20 ml of hot dimethylformamide (dmf). The resultant solution was filtered and allowed to stand overnight to give a white crystalline precipitate. (Found: C 56.9, H 8.9; C<sub>18</sub>H<sub>33</sub>ClCuP requires C 56.98, H 8.77%), mp 240–245 °C (darkens 215–225 °C). (Lit.<sup>34</sup> 218 °C).

**[CuBr(PCy<sub>3</sub>)<sub>2</sub>].** CuBr (0.150 g, 1.05 mmol) and PCy<sub>3</sub> (0.280 g, 1.0 mmol) and were dissolved in 20 ml of hot dmf. The resultant solution was filtered and left to stand overnight to give a

white crystalline precipitate. (Found: C 51.1, H 8.0;  $C_{18}H_{33}BrCuP$  requires C 51.00, H 7.85%), mp 245–250 °C (Lit.<sup>34</sup> 237–240 °C). The compound was also prepared according to published procedures<sup>34</sup> by the addition of ethanolic solutions of  $CuBr_2$  and  $PCy_3$  under an argon atmosphere in a 1 : 2 molar ratio. The mixture was refluxed for four hours and the resulting white precipitate removed by filtration. Crystals of the complex suitable for the X-ray diffraction study were obtained by slow evaporation of the filtrate. mp 240–245 °C.

**[CuI(PCy<sub>3</sub>)<sub>2</sub>].** CuI (0.190 g, 1.0 mmol) and  $PCy_3$  (0.288 g, 1.0 mmol) were dissolved in 20 ml of hot dmf. The resultant solution was filtered and left to stand overnight to give a crystalline precipitate of the complex suitable for X-ray diffraction studies. (Found: C 45.9, H 7.1;  $C_{18}H_{33}ICuP$  requires C 45.91, H 6.58%), mp 226–230 °C (Lit.<sup>34</sup> 232–235 °C).

**$\alpha$ -[CuCl(PCy<sub>3</sub>)<sub>2</sub>].** This compound was prepared according to published procedures,<sup>34</sup> by the addition of an ethanolic solutions of  $CuCl_2 \cdot 2H_2O$  and  $PCy_3$  in a 1 : 3 molar ratio under an argon atmosphere. The mixture was refluxed for four hours and the resulting white precipitate removed by filtration. Crystals of the complex suitable for X-ray diffraction studies were obtained by slow evaporation of the filtrate. (Found C 65.6; H 10.3;  $C_{36}H_{66}CuClP_2$  requires C 65.53; H 10.08%), mp 170–75 °C (lit.<sup>34</sup> 170 °C).

**$\beta$ -[CuCl(PCy<sub>3</sub>)<sub>2</sub>].** CuCl (0.05 g, 0.51 mmol) and  $PCy_3$  (0.30 g, 1.07 mmol) were dissolved in 10 ml of warm dmf. The resultant solution was filtered and allowed to stand overnight at room temperature to give a crystalline precipitate of the complex suitable for X-ray diffraction studies. (Found: C 66.4, H 10.4%), mp 167–174 °C.

**$\alpha$ -[CuBr(PCy<sub>3</sub>)<sub>2</sub>].** CuBr (0.066 g, 0.046 mmol) and  $PCy_3$  (0.30 g, 1.07 mmol) were dissolved in 10 ml of warm dmf. The resultant solution was filtered and allowed to stand overnight at room temperature to give crystals of the complex suitable for X-ray diffraction studies. (Found: C 61.4, H 9.7;  $C_{36}H_{66}BrCuP_2$  requires C 61.39, H 9.45%), mp 182–185 °C (lit. 172–174 °C,<sup>34</sup> 190–192 °C<sup>35</sup>).

**[CuI(PCy<sub>3</sub>)<sub>2</sub>].** CuI (0.198 g 1.04 mmol) and  $PCy_3$  (0.602 g, 2.15 mmol) were dissolved in 25 ml of warm dmf. The resultant clear solution was filtered and allowed to stand overnight at room temperature to give a microcrystalline precipitate of the complex. (Found: C 57.3, H 9.0;  $C_{36}H_{66}CuIP_2$  requires C 57.55, H 8.85%), mp. 180–82 °C (lit.<sup>35</sup> 176–77 °C).

**[CuNO<sub>3</sub>(PCy<sub>3</sub>)<sub>2</sub>].** This compound was prepared according to published procedures<sup>36</sup> by the addition of ethanolic solutions of  $CuNO_3 \cdot 3H_2O$  and  $PCy_3$  in a 1 : 3 molar ratio. The mixture was refluxed for 4 h and allowed to stand overnight to give well formed crystals of the complex suitable for X-ray diffraction studies. mp 220–225 °C (lit.<sup>36</sup> 225–227 °C).

## Crystallography

**Structure determinations.** Unique, room temperature, four circle diffractometer data sets ( $2\theta/\theta$  scan mode; monochromatic Mo- $K_\alpha$  radiation,  $\lambda = 0.7107$  Å,  $T = 295$  K) were measured for all structures.  $N$  independent reflections were obtained,  $N_o$  with  $I > 3\sigma(I)$  being considered 'observed' and used in the full matrix least squares refinements after absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; ( $x, y, z, U_{iso}$ )<sub>H</sub> were included constrained at estimated values. Conventional residuals at convergence,  $R, R'$  on  $|F|$  are quoted, statistical reflection weights being used. Neutral atom complex scattering factors were used; computation used XTAL 3.2,<sup>37</sup> TEXSAN<sup>38</sup> and ORTEP-3<sup>39</sup> software. Pertinent results are presented in Tables 1–3.

**Crystal data.**  $[CuBr(PCy_3)_2]_2 \equiv C_{36}H_{66}Br_2Cu_2P_2$ .  $M = 847.8$ , triclinic, space group  $P\bar{1}$  ( $C_i^1$ , No. 2),  $a = 8.619(3)$ ,  $b = 9.321(2)$ ,  $c = 13.351(4)$  Å,  $a = 101.23(2)$ ,  $\beta = 88.98(2)$ ,  $\gamma = 114.33(2)^\circ$ ,  $V = 956$  Å<sup>3</sup>,  $D_c = 1.46$  g cm<sup>-3</sup> ( $Z = 1$  dimer),  $\mu = 33.1$  cm<sup>-1</sup>. Crystal size:  $0.33 \times 0.12 \times 0.08$  mm;  $A^*_{min,max} = 1.27, 1.47$ ;  $2\theta_{max} = 45^\circ$ ,  $N = 2492$ ,  $N_o = 1892$ ;  $R = 0.043$ ,  $R_w = 0.047$ .

$[CuI(PCy_3)_2]_2 \equiv C_{36}H_{66}I_2Cu_2P_2$ .  $M = 941.2$ , triclinic, space group  $P\bar{1}$ ,  $a = 8.802(3)$ ,  $b = 9.832(4)$ ,  $c = 12.935(3)$  Å,  $a = 100.31(3)$ ,  $\beta = 86.07(3)$ ,  $\gamma = 116.94(2)^\circ$ ,  $V = 982$  Å<sup>3</sup>,  $D_c = 1.59$  g cm<sup>-3</sup> ( $Z = 1$  dimer),  $\mu = 27.6$  cm<sup>-1</sup>. Crystal size:  $0.45 \times 0.36 \times 0.44$  mm;  $A^*_{min,max} = 2.17, 2.77$ ;  $2\theta_{max} = 55^\circ$ ,  $N = 3837$ ,  $N_o = 2969$ ;  $R = 0.043$ ,  $R_w = 0.057$ .

$\alpha$ - $[CuCl(PCy_3)_2] \equiv C_{36}H_{66}ClCuP_2$ .  $M = 659.9$ , monoclinic, space group  $C2/c$  ( $C_{2h}^6$ , No. 15),  $a = 18.00(2)$ ,  $b = 9.113(2)$ ,  $c = 22.23(1)$  Å,  $\beta = 96.32(8)^\circ$ ,  $V = 3625$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.21$  g cm<sup>-3</sup>,  $\mu = 7.8$  cm<sup>-1</sup>. Crystal size:  $0.50 \times 0.35 \times 0.13$  mm;  $A^*_{min,max} = 1.10, 1.30$ ;  $2\theta_{max} = 50^\circ$ ,  $N = 3173$ ,  $N_o = 1983$ ;  $R = 0.059$ ,  $R_w = 0.061$ .

$\beta$ - $[CuCl(PCy_3)_2] \equiv C_{36}H_{66}ClCuP_2$ .  $M = 659.8$ , monoclinic, space group  $P2_1/n$  ( $C_{2h}^5$ , No. 14),  $a = 9.964(3)$ ,  $b = 15.593(4)$ ,  $c = 23.987(4)$  Å,  $\beta = 97.36(2)^\circ$ ,  $V = 3696$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.19$  g cm<sup>-3</sup>,  $\mu = 7.7$  cm<sup>-1</sup>. Crystal size:  $0.35 \times 0.25 \times 0.15$  mm;  $A^*_{min,max} = 1.12, 1.22$ ;  $2\theta_{max} = 50^\circ$ ,  $N = 6780$ ,  $N_o = 3154$ ;  $R = 0.042$ ,  $R_w = 0.043$ .

$\alpha$ - $[CuBr(PCy_3)_2] \equiv C_{36}H_{66}BrCuP_2$ .  $M = 704.3$ , monoclinic, space group  $C2/c$ ,  $a = 18.034(7)$ ,  $b = 9.104(11)$ ,  $c = 22.281(9)$  Å,  $\beta = 96.62(3)^\circ$ ,  $V = 3634$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.29$  g cm<sup>-3</sup>,  $\mu = 18.1$  cm<sup>-1</sup>. Crystal size:  $0.22 \times 0.16 \times 0.09$  mm;  $A^*_{min,max} = 1.19, 1.48$ ;  $2\theta_{max} = 46^\circ$ ,  $N = 2517$ ,  $N_o = 1703$ ;  $R = 0.057$ ,  $R_w = 0.070$ .

$[CuNO_3(PCy_3)_2] \equiv C_{36}H_{66}CuNO_3P_2$ .  $M = 686.4$ , monoclinic, space group  $C2/c$ ,  $a = 18.201(5)$ ,  $b = 9.306(3)$ ,  $c = 22.167(6)$  Å,  $\beta = 96.39(2)^\circ$ ,  $V = 3731$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.22$  g cm<sup>-3</sup>,  $\mu = 7.0$  cm<sup>-1</sup>. Crystal size:  $0.40 \times 0.40 \times 0.20$  mm;  $A^*_{min,max} = 1.14, 1.26$ ;  $2\theta_{max} = 50^\circ$ ,  $N = 3268$ ,  $N_o = 1997$ ;  $R = 0.045$ ,  $R_w = 0.047$ . In this complex, as modelled in the present space group, the nitrate peripheral NO atoms are resolved as disordered over pairs of sites related by the 2-axis,  $N \cdots N 0.65(3)$ ,  $O \cdots O 1.26(2)$  Å.

CCDC reference numbers 175631–175636.

See <http://www.rsc.org/suppdata/dt/b1/b111121n/> for crystallographic data in CIF or other electronic format.

## Spectroscopy

<sup>31</sup>P CPMAS solid state NMR spectra were acquired at room temperature operating at a field strength of  $B_0 = 9.40$  T and a <sup>31</sup>P Zeeman frequency of 162.92 MHz. Conventional cross polarisation and magic angle spinning techniques, coupled with spin temperature alternation to eliminate spectral artifacts were implemented using a Bruker 4 mm double air bearing probe in which MAS frequencies  $> 10$  kHz were achieved. A recycle delay of 20 s, a <sup>1</sup>H–<sup>31</sup>P contact period of 10 ms and a <sup>1</sup>H  $\pi/2$  pulse length of 3  $\mu$ s were common to all spectra. No spectral smoothing was invoked prior to Fourier transformation. Chemical shifts were referenced to 85%  $H_3PO_4$  via solid triphenylphosphine ( $\delta -9.9$ ).

Far-infrared spectra were recorded at 2 cm<sup>-1</sup> resolution as polythene discs on a Digilab FTS-60 Fourier transform infrared spectrometer employing an FTS-60V vacuum optical bench with a 5 lines/mm wire mesh beam splitter, a mercury lamp source and a pyroelectric triglycine sulfate detector. All measurements were carried out at room temperature.

<sup>63</sup>Cu and <sup>65</sup>Cu NQR frequencies were measured on ca. 50 mg of powdered sample of the complex at room temperature using a Bruker CXP console pulsing into a probe arrangement that was well removed from the magnet ( $> 5$  m) and shielded from extraneous magnetic and radio frequency interference by a mumetal container. Solid-echo experiments were employed in the measurements using hard pulses of 2  $\mu$ s duration and recycle delays of 0.5 s and with extended phase cycles to eliminate baseline distortions and echo tails. The location of both

**Table 1** PCuX<sub>2</sub>CuP core geometries for dimeric [PR<sub>3</sub>Cu(μ-X)<sub>2</sub>CuPR<sub>3</sub>] complexes

X	PR <sub>3</sub>	Cu–P	Cu–X	Cu–X'	X ⋯ X	Cu ⋯ Cu	CuXCu	XCuX	PCuX	PCuX'	Ref.
Cl	Po-tol <sub>3</sub>	2.191(1)	2.289(2)	2.316(2)	3.402(2)	3.103(1)	84.74(6)	95.26(5)	132.56(6)	131.98(6)	6
Cl	PPh <sub>2</sub> mes	2.196(2)	2.287(2)	2.329(3)	3.447(2)	3.076(2)	83.56(8)	96.44(8)	135.40(8)	128.15(7)	9
Cl	PPhmes <sub>2</sub>	2.202(2)	2.281(2)	2.326(1)	3.442(2)	3.086(1)	84.08(5)	95.9(1)	135.8(1)	128.0(1)	9
Cl	PCy <sub>3</sub>	2.183(2)	2.285(2)	2.332(2)	3.439(3)	3.066(1)	83.44(7)	96.56(7)	136.05(7)	124.40(7)	4
Cl	PBn <sub>3</sub>	2.185(1)	2.302(1)	2.305(1)	3.439(1)	3.065(1)	83.41(4)	96.59(4)	132.07(4)	131.14(4)	11
Br	Po-tol <sub>3</sub>	2.208(1)	2.414(1)	2.431(1)	3.716(1)	3.109(1)	79.83(4)	100.17(3)	130.00(6)	129.64(6)	6
Br	Po-anis <sub>3</sub>	2.194(1)	2.356(1)	2.541(1)	3.807(1)	3.085(1)	78.01(3)	101.99(3)	141.38(5)	116.53(5)	10
Br	PPh <sub>2</sub> mes	2.198(3)	2.397(2)	2.441(2)	3.748(2)	3.083(2)	79.18(6)	100.8(1)	132.2(1)	127.0(1)	9
Br	PPhmes <sub>2</sub>	2.197(3)	2.393(2)	2.415(2)	3.684(2)	3.052(3)	78.80(7)	100.1(1)	130.9(1)	128.7(1)	9
Br	PCy <sub>3</sub>	2.191(2)	2.409(1)	2.430(1)	3.717(1)	3.098(1)	79.62(4)	100.38(5)	132.88(6)	126.74(6)	<sup>a</sup>
I	Po-tol <sub>3</sub>	2.238(4)	2.525(2)	2.640(2)	4.116(1)	3.122(3)	74.34(5)	105.66(6)	136.60(8)	117.66(7)	6
I	PPh <sub>2</sub> mes	2.225(5)	2.553(2)	2.569(3)	4.316(2)	2.690(3)	63.94(7)	114.9(1)	121.9(1)	122.8(1)	9
		2.226(5)	2.544(3)	2.584(2)				114.6(1)	127.0(1)	118.3(1)	
I	PPhmes <sub>2</sub>	2.201(4)	2.554(3)	2.589(3)	4.361(3)	2.728(3)	63.49(7)	116.0(1)	128.3(1)	114.9(1)	9
		2.264(5)	2.552(4)	2.597(3)				115.8(1)	125.1(1)	118.3(2)	
I	PCy <sub>3</sub> RT	2.215(2)	2.539(1)	2.563(1)	4.133(1)	2.992(1)	71.80(3)	108.20(3)	125.43(5)	126.23(5)	<sup>a</sup>
I	PCy <sub>3</sub> LT	2.225(2)	2.562(1)	2.579(1)	4.498(9)	2.893(2)	68.48(3)	111.52(3)	123.34(5)	124.93(5)	5

<sup>a</sup> This work.**Table 2** P<sub>2</sub>CuX core geometries for monomeric [CuX(PCy<sub>3</sub>)<sub>2</sub>] and [CuX(PR<sub>3</sub>)<sub>2</sub>] complexes, X = Cl, Br, I

X	PR <sub>3</sub>	Cu–P	Cu–P'	Cu–X	P–Cu–P	P–Cu–X	P'–Cu–X	Ref.
Cl	PPh <sub>3</sub>	2.272(2)	2.260(2)	2.208(2)	125.48(7)	113.76(7)	120.74(6)	25 <sup>a</sup>
Cl	PPh <sub>2</sub> o-tol	2.257(2)	2.241(2)	2.205(2)	126.96(7)	113.61(7)	118.55(7)	28
Cl	PCy <sub>3</sub> (α)	2.261(2)	2.261(2)	2.243(3)	134.44(8)	112.78(8)	112.78(8)	<sup>b</sup>
Cl	PCy <sub>3</sub> (β)	2.261(2)	2.282(2)	2.247(2)	134.54(6)	115.82(7)	109.27(6)	<sup>b</sup>
Cl	PBn <sub>3</sub>	2.2399(5)	2.2275(5)	2.2521(6)	136.53(2)	105.34(2)	117.76(2)	11
Br	PPh <sub>3</sub>	2.263(2)	2.282(3)	2.346(2)	126.0(1)	112.8(1)	121.0(1)	26 <sup>a</sup>
Br	PPh <sub>2</sub> o-tol	2.255(2)	2.240(2)	2.336(1)	127.89(7)	112.52(6)	118.25(6)	28
Br	PCy <sub>3</sub> (α)	2.257(2)	2.257(2)	2.392(3)	135.6(1)	112.20(6)	112.20(6)	<sup>b</sup>
Br	PBn <sub>3</sub> (i)	2.2436(7)	2.2127(8)	2.4034(4)	138.92(3)	100.76(2)	119.83(2)	11
	(ii)	2.2509(7)	2.2396(7)	2.3995(4)	139.86(3)	106.92(2)	113.09(2)	
I	PPh <sub>3</sub>	2.273(2)	2.273(2)	2.524(2)	126.9(1)	116.61(5)	116.61(5)	25
I	PPh <sub>2</sub> o-tol	2.255(1)	2.255(1)	2.507(1)	126.36(7)	116.82(4)	116.82(4)	28
I	PCy <sub>3</sub> (γ) LT	2.275(1)	2.285(1)	2.5913(7)	134.06(4)	114.79(3)	110.99(3)	5
I	PBn <sub>3</sub>	2.239(1)	2.2324(1)	2.5865(8)	139.78(5)	105.11(4)	115.07(4)	11

<sup>a</sup> Hemibenzene solvate. <sup>b</sup> This work.**Table 3** P<sub>2</sub>MX core geometries for monomeric [MX(PCy<sub>3</sub>)<sub>2</sub>] complexes for M = Cu, Ag, Au and X = Cl, Br, I

MX	M–P	M–P'	M–X	P–M–P	P–M–X	P'–M–X	Ref.
CuCl (α)	2.261(2)	2.261(2)	2.243(3)	134.44(8)	112.78(5)	112.78(5)	<sup>a</sup>
CuCl (β)	2.261(2)	2.282(2)	2.247(2)	134.54(6)	115.82(7)	109.27(6)	<sup>a</sup>
CuBr (α)	2.257(2)	2.257(2)	2.392(4)	135.6(1)	112.20(6)	112.20(6)	<sup>a</sup>
CuI (γ)	2.275(1)	2.285(1)	2.591(1)	134.06(4)	114.79(3)	110.99(3)	5
AgCl (δ)	2.471(1)	2.471(1)	2.489(1)	128.29(3)	115.85(2)	115.85(2)	31
AgBr (δ)	2.474(1)	2.474(1)	2.618(1)	129.42(3)	115.29(2)	115.29(2)	31
AgI (δ)	2.478(1)	2.478(1)	2.778(1)	130.75(4)	114.63(3)	114.63(3)	31
AuCl	2.321(2)	2.321(2)	—	180.0(—)	—	—	33
AuBr (α)	2.323(2)	2.323(2)	2.777(2)	147.5(1)	106.27(6)	106.27(6)	33
AuBr (ζ <sub>1</sub> ) <sup>b</sup>	2.317(3)	2.311(3)	2.894(1)	162.06(9)	99.56(7)	97.69(7)	33
AuBr (ζ <sub>2</sub> )	2.302(3)	2.292(3)	2.842(1)	157.7(1)	101.65(8)	100.51(8)	
AuBr (ε) <sup>b</sup>	2.328(3)	2.305(3)	3.765(2)	178.4(1)	72.52(9)	109.0(1)	33
AuI (γ)	2.344(2)	2.328(2)	2.895(2)	143.1(1)	106.26(7)	110.45(7)	33
AuI·PCy <sub>3</sub>	2.315(3)	2.310(3)	3.008(1)	159.1(1)	98.69(7)	101.87(8)	33

<sup>a</sup> This work. <sup>b</sup> Designated α and β respectively in ref. 33.

<sup>63</sup>Cu and <sup>65</sup>Cu isotope resonances (related by a ratio  $\nu_Q(^{63}\text{Cu})/\nu_Q(^{65}\text{Cu}) = 1.081$ ) verified that the true copper NQR frequencies were being observed.

## Results and discussion

### Synthesis

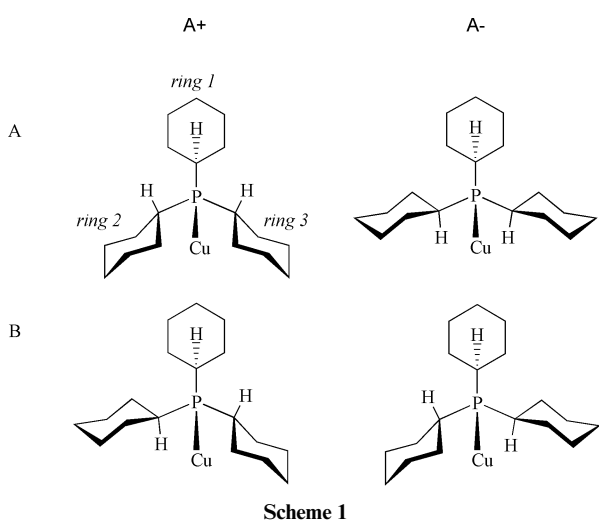
The 1 : 1 and 1 : 2 chloride and bromide complexes were initially prepared according to literature procedures,<sup>34</sup> by precipitation from ethanolic solutions of CuX<sub>2</sub> and PCy<sub>3</sub> in 1 : 2 and 1 : 3

molar ratios for X = Cl, Br and from CuI and PCy<sub>3</sub> in 1 : 1 and 1 : 2 molar ratios for X = I. Colourless crystals suitable for X-ray studies were obtained by slow evaporation of the filtrates obtained from these reaction mixtures. Spectroscopic data on these samples revealed on occasion, however, co-crystallization of both 1 : 1 and 1 : 2 complexes. We found that dissolution of a suspension of appropriate molar ratios of CuX and PCy<sub>3</sub> in an aprotic solvent such as dimethylformamide, followed by cooling to room temperature and slow evaporation of solvent, resulted in crystallization of pure crystalline products in all cases except

for the 1 : 2 iodide where both the 1 : 1 and 1 : 2 complexes crystallized. Precipitation of the 1 : 1 compound was prevented in this case by addition of a small excess of PCy<sub>3</sub> to the reaction mixture.

### Structures

The single crystal structure determinations of this series of 1 : 1 and 1 : 2 complexes are consistent with formulation of the complexes as centrosymmetric [(PCy<sub>3</sub>)Cu(μ-X)<sub>2</sub>Cu(PCy<sub>3</sub>)] dimers and [CuX(PCy<sub>3</sub>)<sub>2</sub>] monomers respectively; the latter compounds crystallizing as a number of polymorphs. The cyclohexyl rings adopt chair conformations in all ligands with P equatorial. One ring in each ligand (designated ring 1) lies orthogonal to the Cu–P–C(11) plane with the P–Cu and C(11)–H(11) bonds antiperiplanar. Rings 2 and 3 are disposed to either side of the Cu–P–C(11) plane with the C(*n*1)–H(*n*1) bonds (*n* = 2 or 3) variously (+, –) synclinal, (+, –) anticlinal or orthogonal to the P–Cu bond. The conformational dispositions for each ligand fall into one of two groups, designated here A and B (Scheme 1). In the A (“meso”) group, C(*n*1)–H(*n*1)



Scheme 1

(*n* = 2, 3) point in the same direction (either towards (A+) or away (A-) from ring 1). In the B group, the two C–H bonds point in opposite directions, forming a pair of possible enantiomers.

**[CuX(PCy<sub>3</sub>)<sub>2</sub>].** The room temperature structures of the bromide and iodide complexes are isomorphous with the chloride,<sup>4</sup> crystallizing in the triclinic space group *P* $\bar{1}$  with *a* ≈ 8.5, *b* ≈ 9.5, *c* ≈ 13.0 Å, *α* ≈ 100, *β* ≈ 90, *γ* ≈ 115°. This lattice, which has also been observed in the analogous silver complexes [AgX(PCy<sub>3</sub>)<sub>2</sub>] (*X* = Cl, Br)<sup>30</sup> and [AgCl(AsCy<sub>3</sub>)<sub>2</sub>],<sup>40</sup> contains one centrosymmetric dimer of the form [(ECy<sub>3</sub>)M(μ-X)<sub>2</sub>M(ECy<sub>3</sub>)]. A representative view of the dimer is shown in Fig. 1. The PCu(μ-X)<sub>2</sub>CuP unit is planar within experimental error. The two phosphine ligands are staggered and adopt B dispositions of opposite chirality. Ring 1 is orthogonal to the Cu(μ-X)<sub>2</sub>Cu plane. The detailed structural features of this dimer are found to be influenced by the halide. For the chloride and bromide complexes, the P–C(11) bond rotates out of the Cu(μ-X)<sub>2</sub>Cu plane with torsion angles X'–Cu–P–C(11) of 13 and 14° respectively. This rotation results in unsymmetrical interactions between the halide anion and neighbouring cyclohexyl group hydrogen atoms such that Cu–X is smaller than Cu–X' and P–Cu–X is greater than P–Cu–X' (Table 1). This distortion is accommodated by dislocation of the two Cy<sub>3</sub>PCuX fragments within the PCu(μ-X)<sub>2</sub>CuP plane. In the case of the iodide complex, weaker C–H ⋯ I interactions and the greater covalency of the Cu–I bonds result in a decrease of X'–Cu–P–C(11) to

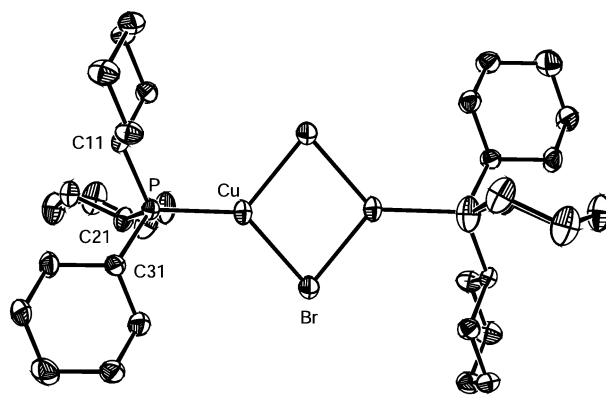


Fig. 1 ORTEP diagram of [CuBrPCy<sub>3</sub>]<sub>2</sub> projected normal to the central Cu<sub>2</sub>Br<sub>2</sub> plane. Displacement ellipsoids are drawn at the 30% probability level.

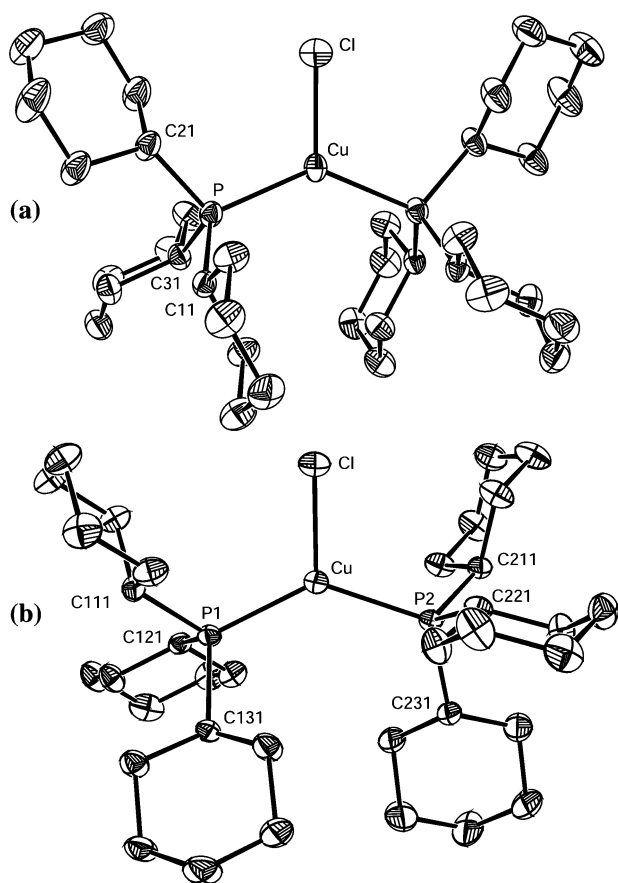
5°, with a corresponding reduction in the asymmetry of the PCu(μ-X)<sub>2</sub>CuP molecular fragment.

(a) The geometric data listed in Table 1 for these and related [CuX(PR<sub>3</sub>)<sub>2</sub>] complexes show that the Cu–P bond lengths and the Cu ⋯ Cu distances are essentially the same for both the chloride and bromide complexes with average values and standard uncertainties for Cu–P of 2.190(8) and 2.198(6) Å and for Cu ⋯ Cu of 3.09(2) Å and 3.09(2) Å respectively. Significant differences are observed, however, for the iodide complexes, with the average Cu–P bond length for these compounds increasing to 2.23(2) Å and the average Cu ⋯ Cu distance decreasing to 2.9(2) Å. The spread of values for these distances is also considerably greater than that found for either the chloride or bromide complexes, reflecting the increased size and polarizability of iodine by comparison with chlorine or bromine.

(b) The iodide has also been the subject of an independent low temperature study<sup>5</sup> wherein it crystallized in a reduced cell very similar to that reported here for the room temperature structure, with the conformational dispositions of the PCy<sub>3</sub> ligands the same in both cases. Small but significant differences are observed, however, in the Cu(μ-I)<sub>2</sub>Cu geometries. The most noticeable differences are decreases in the Cu–I, Cu–I' bond lengths and increases in the Cu–I–Cu' angle and Cu ⋯ Cu distance with increasing temperature. In the discussion of the results of the low temperature study,<sup>5</sup> it was suggested that the unusually short Cu ⋯ Cu distance is due to a Cu ⋯ Cu bonding interaction, and that the Cu(μ-I)<sub>2</sub>Cu rhomb has a broad potential energy well that is easily distorted by external influences. This latter hypothesis is supported by the large variability observed in the values of the Cu–I and Cu ⋯ Cu distances recorded for the complexes listed in Table 1, and also the quite large increases in the Cu–I and Cu ⋯ Cu distances which occur upon the addition of a fourth ligand to each copper atom in [(PR<sub>3</sub>)Cu(μ-X)<sub>2</sub>Cu(PR<sub>3</sub>)].<sup>6,41</sup> Perhaps a more fundamental indicator of the “softness” of the potential energy surface of the Cu(μ-I)<sub>2</sub>Cu rhomb, however, is the temperature dependence of the Cu(μ-I)<sub>2</sub>Cu geometry observed in the present study, as it involves no significant variation in the specific chemical environment of the unit. The reason for the direction of the observed change – an increase in the Cu ⋯ Cu distance with increasing temperature – is not so obvious, however. One possible explanation is that the interactions which involve a small degree of orbital overlap result in a shallow, anharmonic potential surface which is more sensitive to thermal excitation. This would be the case for any Cu ⋯ Cu interaction which might be present, suggesting that the Cu ⋯ Cu distance should be sensitive to temperature in a manner consistent with thermal occupancy of the higher vibrational levels. This suggests that further structural studies of [(PR<sub>3</sub>)Cu(μ-X)<sub>2</sub>Cu(PR<sub>3</sub>)] complexes over a range of

temperatures may assist development of a better understanding of the origins and nature of Cu...Cu bonding interactions in these polynuclear copper(I) complexes.

**[CuX(PCy<sub>3</sub>)<sub>2</sub>].** The structural studies conducted on these complexes both here and previously,<sup>5,29</sup> show a tendency for the complexes to crystallize in a number of polymorphic forms, with three identified to date. The first (designated *α*), obtained from ethanol for X = Cl, Br, dimethylformamide for X = Br, and from hexane for X = Br, I,<sup>29</sup> crystallizes in space group *C2/c* with *a* ≈ 18.1, *b* ≈ 9.2, *c* ≈ 22.2 Å, β ≈ 96°. This polymorph is found also for the nitrate complex<sup>36</sup> (redetermined herein), the perchlorate complex,<sup>42,43</sup> and the analogous gold complex [AuBr(PCy<sub>3</sub>)<sub>2</sub>].<sup>33</sup> The molecules in this lattice are disposed about a crystallographic two-fold axis coincident with the Cu–X bonds so that one-half of the molecule represents the asymmetric unit (Fig. 2(a)). The two ligands are eclipsed, and adopt



**Fig. 2** Representative views of the molecular structures of (a) *α*-[CuCl(PCy<sub>3</sub>)<sub>2</sub>] and (b) *β*-[CuCl(PCy<sub>3</sub>)<sub>2</sub>].

*A+* dispositions. The Cu–X bond is anticlinal to P–C(11). Ring 2 on each ligand lies almost coplanar with the P<sub>2</sub>CuX plane, forming a pocket around the anion. The second copper polymorph (designated *β*), obtained from dmf for X = Cl, and from benzene for X = Br,<sup>29</sup> crystallizes in space group *P2<sub>1</sub>/n* with *a* ≈ 10.0, *b* ≈ 15.5, *c* ≈ 24.0 Å, β ≈ 95°. Here, the entire molecule constitutes the asymmetric unit (Fig. 2(b)). The conformational dispositions of the two ligands lie between eclipsed and staggered with respect to each other, with the Cu–X bond *cis* to P(1)–C(111) and *synclinal* to P(2)–C(211). Both ligands adopt *B* conformations of the same chirality. The third copper polymorph (designated *γ*) has been obtained in a low temperature study<sup>5</sup> of the iodide complex obtained from THF–pentane and is isomorphous with the azide complex,<sup>35</sup> crystallizing in the triclinic space group *P1̄* with *a* ≈ 9.5, *b* ≈ 23, *c* ≈ 9 Å, α ≈ 95, β ≈

115, γ ≈ 95°. Here, the PCy<sub>3</sub> ligands adopt *A+* and *B* conformations respectively. Cu–P bond lengths and P–Cu–P angles for these complexes (Table 2) are not significantly influenced by either the choice of halide or differences in the conformational dispositions of the phosphine ligands, with values lying between 2.257(2) and 2.285(1) Å for Cu–P and 134.06(4) and 135.7(1)° for P–Cu–P. Comparison with data for complexes with more weakly coordinating anions: NO<sub>3</sub><sup>−</sup>, 2.245(1), 2.245(1) Å, 140.00(6)° (this work); ClO<sub>4</sub><sup>−</sup>, 2.247(2), 2.247(2) Å, 144.49(9)°;<sup>43</sup> and BF<sub>4</sub><sup>−</sup>, 2.235(2), 2.237(2) Å, 159.98(8)°;<sup>44</sup> however, reveal a significant increase in the P–Cu–P bond angles with corresponding small but observable decreases in the Cu–P bond lengths.

P<sub>2</sub>CuX geometric data available for a number of three-coordinate [CuX(PR<sub>3</sub>)<sub>2</sub>] complexes are listed in Table 2. These results show a greater dispersion of the Cu–P bond lengths than found for the PCy<sub>3</sub> complexes alone, with values ranging from 2.213(1) Å for [CuBr(PBn<sub>3</sub>)<sub>2</sub>] to 2.285(1) Å for *γ*-[CuI(PCy<sub>3</sub>)<sub>2</sub>]. The P–Cu–P angles divide into two distinct groups with values ranging between 125.48(7) and 127.89(7)° for the PPh<sub>3</sub> and PPh<sub>2</sub>*o*-tol ligands and 134.06(4)–139.78(5)° for the bulkier PBn<sub>3</sub> and PCy<sub>3</sub> ligands, with the Cu–X bond lengths for this second group of complexes some 0.04–0.08 Å longer than those of the first group.

Comparison of these results with those obtained for the analogous silver(I) and gold(I) halide complexes,<sup>31,33</sup> show the silver complexes also crystallize as [AgX(PCy<sub>3</sub>)<sub>2</sub>] monomers with three-coordinate silver atoms, but in a different polymorph (designated *δ*). Interestingly, these complexes crystallize in a *C2/c* lattice with half the molecule forming the asymmetric unit as found for the *α* complexes. However, the phosphine ligands adopt *B* rather than *A* conformations. The gold(I) complexes show a greater diversity in their structural chemistry. The chloride complex crystallizes as a two-coordinate ionic complex, the bromide as three distinct forms (*α*, *ζ*, and *ε*) with both coordinated and semi-coordinated bromide, while the iodide crystallizes as the *γ* polymorph with coordinated iodide. The results of these studies yield comprehensive structural data for [MX(PCy<sub>3</sub>)<sub>2</sub>] complexes for M = Cu, Ag and Au and X = Cl, Br and I. Table 3 details the P<sub>2</sub>MX core geometries for these complexes and shows the M–P bond lengths to increase in the order Cu < Au < Ag, in accord with previously established trends,<sup>25,45</sup> with average values and standard uncertainties of 2.27(2), 2.33(2) and 2.47(1) Å respectively. Comparison of these results with the corresponding M–P bond lengths of 2.242(2), 2.353(1) and 2.441(1) Å for the two-coordinate complexes [M(Pmes<sub>3</sub>)<sub>2</sub>]-BF<sub>4</sub>,<sup>45</sup> reveal a small increase of the order of 0.03 Å on coordination of halide to the copper and silver complexes, but a decrease of *ca.* 0.02 Å for the gold complexes, reflecting the strong preference for the formation of only very weak bonds with a third ligand in the case of gold(I) complexes.

### Copper NQR spectroscopy

<sup>63</sup>Cu nuclear quadrupolar resonance frequencies were measured at room temperature for the 1 : 2 complexes [CuX(PCy<sub>3</sub>)<sub>2</sub>] for X = Cl, Br, I as well as for the analogous copper iodide triphenylphosphine complex [CuI(PPh<sub>3</sub>)<sub>2</sub>] in order to complete the availability of data for both series of complexes. Literature data are available for the resonant frequencies of the 1 : 1 [CuX(PCy<sub>3</sub>)<sub>2</sub>] complexes for X = Cl and I.<sup>8</sup> These results, together with room temperature (298 K) data taken or derived from literature results for CuX<sub>2</sub><sup>−</sup>, PCuX<sub>2</sub><sup>−</sup>, PCuX<sub>2</sub><sup>−</sup> and P<sub>2</sub>CuX complexes are listed in Table 4. For <sup>63</sup>Cu (nuclear spin *I* = 3/2) there is a single NQR frequency *ν*(1/2 ↔ 3/2) whose value is determined by the nuclear quadrupole coupling constant *e*<sup>2</sup>*qQ*/*h* (= *χ*<sub>Cu</sub>) and the electric field gradient (EFG) asymmetry parameter *η* (0 ≤ *η* ≤ 1 by definition) according to eqn. (1):

$$\nu(1/2 \leftrightarrow 3/2) = (e^2qQ/2h)(1 + \eta^2/3)^{1/2} \quad (1)$$

**Table 4**  $^{63}\text{Cu}$  NQR frequencies (MHz, 298 K) for  $\text{CuX}_2^-$ ,  $\text{PCuX}_2$ ,  $\text{PCuX}_2^-$  and  $\text{P}_2\text{CuX}$  complexes

Type	Compound	Cl	Br	I	Ref.
$\text{CuX}_2^-$	$[\text{NBu}_4][\text{CuX}_2]$	30.05	28.25	—	49
$\text{PCuX}_2$	$[(\text{CuX})_2(\text{PPh}_3)_3]$	29.95	28.36	27.35	47
	$[\text{CuX}(\text{PPh}_3)_4]$	—	28.09	26.09	50 <sup>a</sup>
	$[\text{CuX}(\text{PCy}_3)_2]$	30.14	—	28.17	8
	$[\text{CuX}(\text{P}o\text{-tol}_3)_2]$	30.79	29.34	—	8
	$[\text{CuX}(\text{P}o\text{-anis}_3)_2]$	29.18	27.75	—	10
$\text{PCuX}_2^-$	$[\text{NEt}_4][\text{PPh}_3\text{CuX}_2]$	33.89	31.88	—	51
	$[\text{NPr}_4][\text{PPh}_3\text{CuX}_2]$	—	31.15	28.54	51
	$[\text{PEt}_4][\text{PPh}_3\text{CuX}_2]$	34.57	31.81	—	51
$\text{P}_2\text{CuX}$	$[\text{CuX}(\text{PPh}_3)_2]^b$	33.17 <sup>b</sup>	32.16	31.17	50 <sup>c</sup>
	$[\text{CuX}(\text{PCy}_3)_2]$	34.5	33.43	32.06	<sup>c</sup>

<sup>a</sup> Chloroform solvates. <sup>b</sup> Hemibenzene solvates for X = Cl, Br. <sup>c</sup> This work.

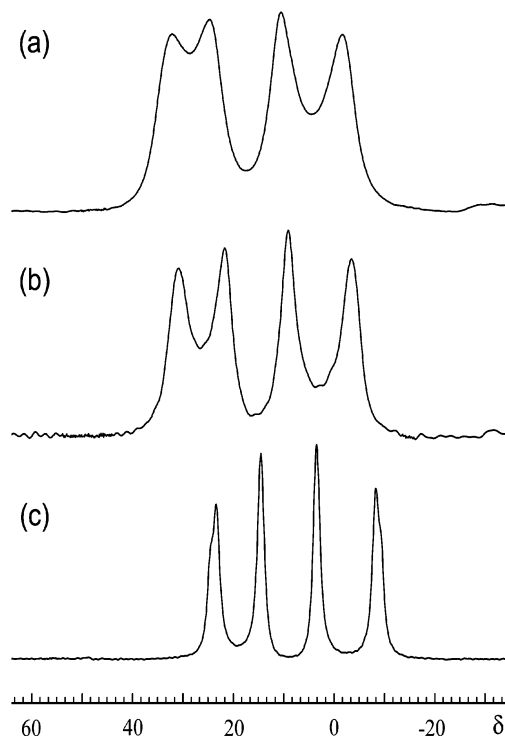
From the single observed pure quadrupole resonance frequency it is not possible to determine both  $\chi_{\text{Cu}}$  and  $\eta$ ; single crystal Zeeman studies are required to determine these parameters separately. Such studies have been reported for the  $\text{P}_2\text{CuX}$  site in  $[\text{CuBr}(\text{PPh}_3)_2]$  and for the trigonal  $\text{PCuX}_2$  sites in  $[(\text{PPh}_3)\text{CuX}_2\text{Cu}(\text{PPh}_3)_2]$  (X = Cl, Br, I),<sup>46,47</sup> which show the asymmetry parameters to be about 0.1 and 0.3 respectively for these two types of site. It is clear from eqn. (1) that  $\eta$  values of this magnitude do not affect the value of the resonance frequency to a large extent, and that changes in the resonance frequency are therefore largely a reflection of changes in the coupling constant. We assume that this is also true for the  $\text{P}_2\text{CuX}$  sites and the other compounds listed in Table 4.

For all of the complexes listed in Table 4, the frequencies of the observed signals follow a well-established trend, decreasing monotonically from the chlorides to the iodides. The likely cause of this effect is the influence of the halogen atoms on the electric field gradient at the copper nucleus. Electronic structure calculations have shown that the increase in the  $^{63}\text{Cu}$  resonance frequency from  $\text{CuBr}_2^-$  to  $\text{CuCl}_2^-$  is due to a contraction of the Cu 4p orbital involved in the bonding, and that the magnitude of this effect varies with the Cu–X bond length.<sup>48</sup> It is reasonable to assume that the same explanation applies to the other compounds in Table 4. This effect is greater if there are two halide ligands present ( $\text{PCuX}_2$ ,  $\text{CuX}_2^-$ ,  $\text{PCuX}_2^-$ ) than if there is only one ( $\text{P}_2\text{CuX}$ ), which is consistent with the calculated effect of halide on the copper p orbital field gradient in  $\text{CuX}$  and  $\text{CuX}_2^-$ .

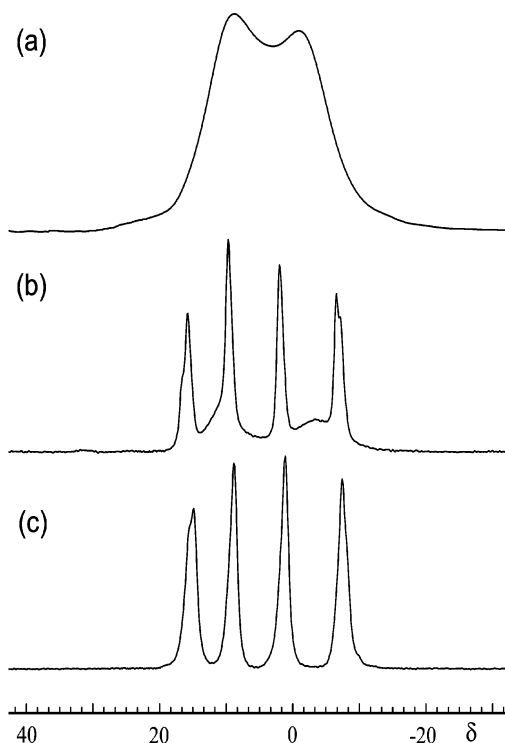
Comparison of the results in Table 4 for the monomeric  $\text{PCuX}_2^-$  and  $\text{P}_2\text{CuX}$  complexes shows that the copper resonance frequencies increase on going from the  $\text{PCuX}_2^-$  to the  $\text{P}_2\text{CuX}$  environments for the bromide and iodide compounds. This can be ascribed to be a consequence of replacing a weak  $\sigma$ -donor (the halide) with a stronger one (the phosphine). The increase in the amount of charge transferred to the Cu 4p orbitals causes an increase in the copper quadrupole coupling constant and hence the resonance frequency. For the chloride compounds, this effect appears to be counteracted by the effect of decreasing the number of chloride ligands from two to one (see discussion above), so that the frequencies for these two environments are almost the same in this case. Also evident in the results in Table 5 is a decrease in the resonance frequency for the  $\text{PCuX}_2$  environment (involving bridging halide ligands X) relative to the  $\text{PCuX}_2^-$  environment (involving terminal halide). This is attributed to the fact that a bridging halide does not donate as much charge to the Cu atom as a terminal halide does, since the bridging halide is shared by two Cu atoms. Within the  $\text{P}_2\text{CuX}$  complexes, the observed increase in the resonance frequencies of the  $\text{PCy}_3$  complexes compared to those for the  $\text{PPh}_3$  complexes can be ascribed to the increased  $\sigma$  donor capacity of the more basic  $\text{PCy}_3$  ligand and to the increase in the P–Cu–P angle.

### Solid state $^{31}\text{P}$ CPMAS NMR spectroscopy

Solid state  $^{31}\text{P}$  CPMAS NMR spectra recorded on the 1 : 1 and 1 : 2 complexes are presented in Figs. 3 and 4 respectively. Chemical shift and coupling constant data are listed in Table 5. The spectra of copper(i) phosphine complexes recorded under high field ( $B_0 \approx 5$  T) and slow  $^{63,65}\text{Cu}$  quadrupolar relaxation conditions yield signals for each crystallographically independent phosphine ligand which are split into pairs of closely spaced asymmetric quartets as a result of the quadrupole perturbed



**Fig. 3** Solid state  $^{31}\text{P}$  CPMAS NMR spectra of the 1 : 1 complexes (a)  $[\text{CuCl}(\text{PCy}_3)_2]$ , (b)  $[\text{CuBr}(\text{PCy}_3)_2]$  and (c)  $[\text{CuI}(\text{PCy}_3)_2]$ .



**Fig. 4** Solid state  $^{31}\text{P}$  CPMAS NMR spectra of the 1 : 2 complexes: (a)  $[\text{CuCl}(\text{PCy}_3)_2]$ , (b)  $[\text{CuBr}(\text{PCy}_3)_2]$  and (c)  $[\text{CuI}(\text{PCy}_3)_2]$ .

**Table 5**  $^{31}\text{P}$  CP-MAS NMR data for dimeric  $[\text{CuX}(\text{PR}_3)_2]$  and monomeric  $[\text{CuX}(\text{PR}_3)_2]$  complexes

Type	X	PR <sub>3</sub>	B <sub>0</sub>	$\delta_{\text{iso}}^a/\text{ppm}$	$\Delta_{21}/\text{kHz}$	$\Delta_{32}/\text{kHz}$	$\Delta_{43}/\text{kHz}$	J/kHz	$d\nu_{\text{Cu}}^b/10^9 \text{ Hz}^2$	Ref.
[CuX(PR <sub>3</sub> ) <sub>2</sub> ]	Cl	P <i>o</i> -tol <sub>3</sub>	9.40	-19.6	1.63	1.97	2.12	1.93	12.9	41
	Cl	PPhmes <sub>2</sub>	9.40	-20.6	1.64	1.99	2.15	1.94	13.5	41
	Br	P <i>o</i> -tol <sub>3</sub>	9.40	-17.5	1.58	1.90	2.05	1.86	12.5	41
	Br	PPhmes <sub>2</sub>	9.40	-21.2	1.62	1.93	2.05	1.88	11.4	41
	I	PCy <sub>3</sub>	9.40	8.4	1.45	1.81	1.91	1.74	11.5	<sup>c</sup>
	I	P <i>o</i> -tol <sub>3</sub>	9.40	-15.2	1.45	1.73	1.88	1.70	11.7	41
	I	PPhmes <sub>2</sub>	9.40	-15.4	1.43	1.71	1.84	1.67	10.6	41
[CuX(PR <sub>3</sub> ) <sub>2</sub> ]	Cl	PPh <sub>2</sub> <i>o</i> -tol	7.02	6	0.90	1.25	1.40	1.20	9.9	28
				1	0.95	1.30	1.60	1.29	12.9	
	Cl	PBn <sub>3</sub>	9.40	-3.1	1.15	1.43	1.64	1.41	13.0	11
				-13.4	1.00	1.27	1.37	1.23	9.8	
	Br	PCy <sub>3</sub>	9.40	5.2	1.07	1.16	1.40	1.20	8.7	<sup>c</sup>
	Br	PPh <sub>2</sub> <i>o</i> -tol	7.02	7	1.00	1.15	1.40	1.17	8.0	28
				1	1.05	1.30	1.55	1.30	9.9	
	Br	PBn <sub>3</sub>	9.40	-3.6	1.30	1.46	1.60	1.46	8.0	11
				-8.1	1.03	1.26	1.50	1.26	12.4	
				-5.7	1.09	1.39	1.58	1.36	13.0	
	I	PCy <sub>3</sub>	9.40	4.7	1.00	1.26	1.39	1.23	10.3	<sup>c</sup>
	I	PPh <sub>3</sub>	7.02	-5	0.88	1.20	1.43	1.17	10.9	25
	I	PBn <sub>3</sub>	9.40	-3.9	1.09	1.37	1.56	1.34	12.4	11

<sup>a</sup>  $\delta_{\text{iso}}$  is the average chemical shift with respect to 85% H<sub>3</sub>PO<sub>4</sub> of the centre points of the four lines of the quartet. <sup>b</sup> The estimated error in determination of  $d\nu_{\text{Cu}}$  is  $\pm 1.0 \times 10^9 \text{ Hz}^2$ . <sup>c</sup> This work.

scalar ( $J$ ) and dipolar coupling between the spin 3/2  $^{63}\text{Cu}$  ( $\gamma = 7.0965 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}$ , natural abundance 69.09%) and  $^{65}\text{Cu}$  ( $\gamma = 7.6018 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}$ , natural abundance 30.91%) and the spin 1/2  $^{31}\text{P}$  nuclei.<sup>52-55</sup> The line widths of the peaks are such that the two quartets are not generally resolved and the observed spectra are dominated by the  $^{63}\text{Cu}$  spectrum, with the  $^{65}\text{Cu}$  spectrum identified where the linewidth is sufficiently narrow as a splitting of the outer peaks of the quartet. Under fast  $^{63,65}\text{Cu}$  quadrupole relaxation conditions, the lines broaden with the inner two moving outward and the outer two moving inwards to afford a broad doublet. Under very fast relaxation conditions, a single peak is observed.<sup>56</sup> In this present study, a well defined quartet for the 1 : 1 complexes was observed for the 1 : 1 [Cu(PCy<sub>3</sub>)<sub>2</sub>] complex, while in the spectra of [CuCl(PCy<sub>3</sub>)<sub>2</sub>] and [CuBr(PCy<sub>3</sub>)<sub>2</sub>], relaxation effects cause both a broadening and shifting of the lines of the quartet (Fig. 3). Single quartets were observed for the 1 : 2 iodide and bromide complexes. These are assigned to the  $\alpha$  form of the complex on the basis that this is the only polymorph that contains just one crystallographically independent ligand in the unit cell. The presence of a broad weak doublet can also be identified in the spectrum of the bromide complex, indicating the likely presence of more than one polymorph in the sample used. Strong relaxation effects are apparent in the spectrum of chloride, which consists of a broad doublet (Fig. 4). It is interesting to note that these quadrupole relaxation effects are even stronger in the case of the analogous nitrate complex, [CuNO<sub>3</sub>(PCy<sub>3</sub>)<sub>2</sub>], the spectrum of which is found to consist of a single broad peak centred at  $\delta$  0.5 ppm with  $\nu_{1/2}$  of 1000 Hz. The increasing influence of relaxation effects on the spectra of these complexes along the sequence I < Br < Cl < NO<sub>3</sub> suggests a possible correlation with increasing ionic character of the copper-anion bond. We are exploring this phenomenon further through a study of the structural, NQR, and solid state  $^{31}\text{P}$  NMR properties of this system with a range of semi- and non-coordinating anions.

The asymmetric spacing between the lines of each quartet arises from perturbation of the simple  $J$  spectrum by dipolar interactions between the phosphorus and the quadrupolar copper nuclei. First order analysis<sup>57</sup> predicts the outer two lines to shift upfield and the inner two lines ( $\delta_2, \delta_3$ ) downfield by a magnitude  $d$  such that  $(\Delta_{32} - \Delta_{21}) = (\Delta_{43} - \Delta_{32}) = 2d$ , from which  $d = (\Delta_{43} - \Delta_{21})/4$ . Higher order quadrupole effects result in the line spacings deviating from this first order model with  $(\Delta_{32} - \Delta_{21}) > 2d > (\Delta_{43} - \Delta_{32})$ . These effects are generally small and manifest as upfield shifts of peaks 1 and 3 and a downfield

shift of peaks 2 and 4 by a correction term of magnitude  $d_j$  such that  $\Delta_{21} = J - 2d - 2d_j$ ,  $\Delta_{32} = J + 2d_j$  and  $\Delta_{43} = J + 2d - 2d_j$ ; from which  $d = (\Delta_{43} - \Delta_{21})/4$  as before,  $d_j = (\Delta_{32} - J)/2$  while  $J = (\Delta_{21} + 2\Delta_{32} + \Delta_{43})/4$ . Multiplication of  $d$  by the  $^{63}\text{Cu}$  Zeeman frequency yields a field independent parameter  $d\nu_{\text{Cu}}$  that is suitable for comparison of results obtained from spectra recorded at different field strengths. The first order theory generates eqn. (2) for  $d\nu_{\text{Cu}}$ :

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

where  $\chi_{\text{Cu}} = e^2qQ/h$  is the  $^{63}\text{Cu}$  quadrupolar coupling constant,  $D_{\text{eff}} = (D - \Delta J/3)$  ( $D = (\mu_0/4\pi)\gamma_{\text{P}}\gamma_{\text{Cu}}\hbar/4\pi^2r^3$  is the Cu-P dipolar coupling constant and  $\Delta J$  is the anisotropy in the  $J$  tensor),  $\eta$  is the asymmetry parameter of the electric field gradient (EFG) tensor, and  $\alpha^{\text{D}}, \beta^{\text{D}}$  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.

The value of 1.74 kHz for  $^1J(^{31}\text{P}-^{63}\text{Cu})$  ( $J$ ) in [CuI(PCy<sub>3</sub>)<sub>2</sub>] is in accord with the values obtained for the other PCuX<sub>2</sub> complexes listed in Table 5 and supports the general trends reported previously where the magnitude of  $J$  decreases along the series Cl > Br > I. The values of 1.20 and 1.23 kHz respectively for 1 : 2 bromide and iodide complexes are also in accord with the values listed in Table 5 for P<sub>2</sub>CuX complexes; the decrease in magnitude of ca. 30% by comparison with the PCuX<sub>2</sub> complexes reflecting the increase in the number of coordinated phosphorus atoms from one to two.

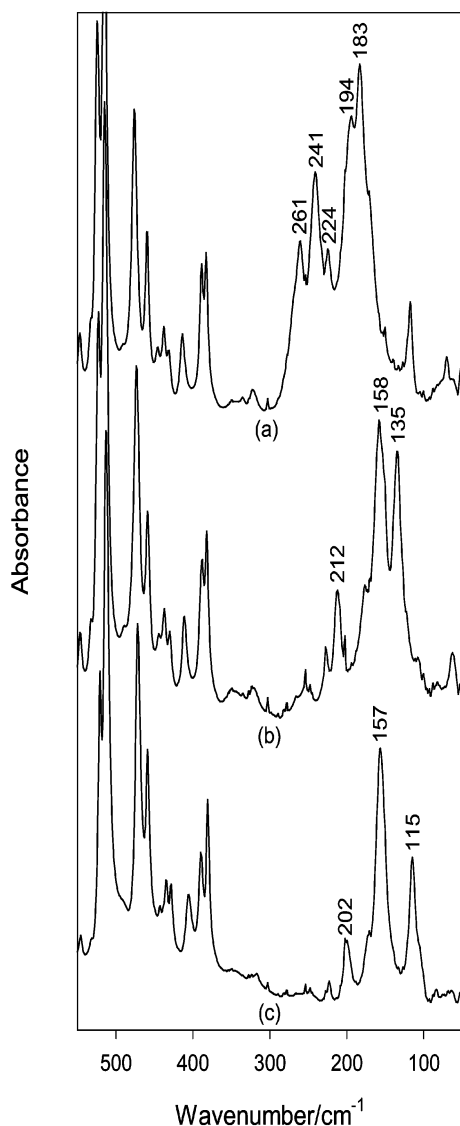
For [CuI(PCy<sub>3</sub>)<sub>2</sub>],  $d\nu_{\text{Cu}}$  is  $11.5 \times 10^9 \text{ Hz}^2$  which is of the same order of magnitude as values reported for the other [CuI(PR<sub>3</sub>)<sub>2</sub>] complexes listed in Table 5. These data also show a discernable trend towards increasing  $d\nu_{\text{Cu}}$  along the sequence I < Br < Cl, paralleling the trend observed for the copper NQR frequencies. From eqn. (2) it can be seen that  $d\nu_{\text{Cu}}$  is dependent on a number of geometric and molecular parameters, in addition to the quadrupole coupling constant. However, the similar trends observed for both the NQR and NMR results here suggest that these factors are not significantly influenced by changes in the halide.

For the P<sub>2</sub>CuX complexes,  $d\nu_{\text{Cu}}$  varies over a much wider range of values ( $8-13 \times 10^9 \text{ Hz}^2$ ) compared to the PCuX<sub>2</sub> complexes, reflecting the increased complexity of the spectra arising from contributions to the spectra from two crystallographically independent phosphine ligands rather than one. There are no obvious halide dependent trends in these results. This is

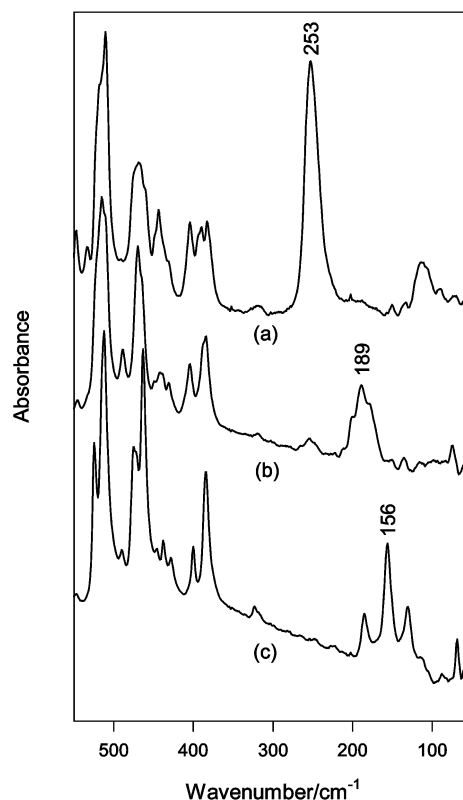
reflected also in the values of  $8.7$  and  $10.3 \times 10^9 \text{ Hz}^2$  recorded for the present bromide and iodide complexes. Consideration of the results obtained for  $[\text{CuI}(\text{PCy}_3)_2]$  and  $[\text{CuI}(\text{PCy}_3)_2]$ , the spectra of which each consisting of single well defined quartet, shows that  $d\nu_{\text{Cu}}$  for  $[\text{CuI}(\text{PCy}_3)_2]$  is less than that observed for the  $[\text{CuI}(\text{PCy}_3)_2]$ , despite the larger quadrupole resonance frequency (Table 4). It seems likely in this case, that the expected increase in  $d\nu_{\text{Cu}}$ , arising from an increase in the quadrupole coupling constant, is counteracted by decreases in the magnitude of some of the other structural and molecular parameters contained in eqn. (2); in particular, changes in the orientation of the principal axial system of the EFG with respect to the Cu–P vectors,<sup>57</sup> and a decrease in the asymmetry parameter,  $\eta$ .<sup>46,47</sup>

### Infrared spectroscopy

The far-IR spectra of the halide complexes are shown in Figs. 5 and 6. Uncomplexed  $\text{PCy}_3$  shows no bands of significant intensity below  $370 \text{ cm}^{-1}$ . The spectra of the complexes show bands above  $370 \text{ cm}^{-1}$  that are almost identical in wavenumber to those in  $\text{PCy}_3$ , and these are assigned to the coordinated phosphine. The spectra of the 1 : 1 complexes (Fig. 5) show halogen-sensitive bands in the region below  $300 \text{ cm}^{-1}$ . The spectrum of the chloride compound is unexpectedly complex in this region.



**Fig. 5** Far infrared spectra of the 1 : 1 complexes: (a)  $[\text{CuCl}(\text{PCy}_3)_2]$ , (b)  $[\text{CuBr}(\text{PCy}_3)_2]$  and (c)  $[\text{CuI}(\text{PCy}_3)_2]$ . The  $\nu(\text{CuX})$  bands are labelled with their wavenumbers.



**Fig. 6** Far infrared spectra of the 1 : 2 complexes: (a)  $[\text{CuCl}(\text{PCy}_3)_2]$ , (b)  $[\text{CuBr}(\text{PCy}_3)_2]$  and (c)  $[\text{CuI}(\text{PCy}_3)_2]$ . The  $\nu(\text{CuX})$  bands are labelled with their wavenumbers.

The far-IR spectrum of the corresponding silver(i) complex shows only two strong bands in this region, at  $225$  and  $143 \text{ cm}^{-1}$ , and these are readily assigned to the two  $\nu(\text{MX})$  modes that are expected for the  $C_{2h}$   $\text{M}_2\text{X}_2$  core that is present in the structure.<sup>30</sup> The  $\text{CuCl}$  complex shows two groups of bands centred at  $240$  and  $190 \text{ cm}^{-1}$ , and the increase in frequency of these relative to the two bands in the  $\text{AgCl}$  complex supports the assignment of these as  $\nu(\text{CuCl})$  modes. The splitting of these bands should not be due to factor group effects, as there is only one dimer in the crystallographic unit cell. Similar unexplained splittings of the  $\nu(\text{AgBr})$  modes in the corresponding  $\text{AgBr}$  complex have been noted previously.<sup>30</sup> The far-IR spectra of the  $\text{CuBr}$  and  $\text{CuI}$  complexes, while simpler than that of the  $\text{CuCl}$  complex, nevertheless show more than the expected two  $\nu(\text{CuX})$  bands (Fig. 5). Three bands are observed in the  $100$ – $220 \text{ cm}^{-1}$  region, which probably consist mainly of  $\nu(\text{CuX})$  vibrations. Comparison of the present far-IR spectra for  $[\text{CuX}(\text{PCy}_3)_2]$  with those for  $[\text{CuXP}o\text{-tol}_3]_2$ <sup>6</sup> reveals a remarkable similarity in the  $\nu(\text{CuX})$  region, and suggests that not all of the bands with  $\nu(\text{CuX})$  character were identified in the latter case. In particular, three bands at very similar positions in the range  $100$ – $220 \text{ cm}^{-1}$  are observed for the bromide and the iodide complexes, suggesting that the IR band patterns arising from vibrations of the  $\text{Cu}_2\text{X}_2$  core are fairly characteristic for this structure.

By analogy with the corresponding silver complexes,<sup>30</sup> strong bands in the spectra of the 1 : 2 complexes due to  $\nu(\text{CuX})$ , the stretching mode of the terminal Cu–X bonds, are expected in the far-IR region. We have shown previously that a relationship exists between the  $\nu(\text{CuX})$  wavenumber and the bond length  $r(\text{CuX})$  for a wide range of copper(i) halide complexes containing a terminal Cu–X bond and from one to three phosphine or amine ligands. This relationship has the form given in eqn. (3) below:

$$\nu/\text{cm}^{-1} = b(r/\text{\AA})^{-m} \quad (3)$$



with  $b = 13800, 18000, 32300$ ;  $m = 4.9, 5.2, 5.6$ .<sup>58</sup> Using the values of the Cu–X bond lengths for [CuX(PCy<sub>3</sub>)<sub>2</sub>] in Table 2, this equation yields  $\nu(\text{CuX}) = 265, 192, 156 \text{ cm}^{-1}$  for X = Cl, Br, I respectively. This permits the assignments  $\nu(\text{CuX}) = 253, 189, 156 \text{ cm}^{-1}$  for X = Cl, Br, I from the experimental spectra (Fig. 6). The spectrum of the chloride has been reported previously and a band at  $255 \text{ cm}^{-1}$  was assigned to  $\nu(\text{CuCl})$ , but no assignment was reported for the bromide.<sup>34</sup> The spectrum of the iodide is more complex than those of the other two halides; bands at  $185$  and  $131 \text{ cm}^{-1}$ , whose intensities are comparable to that of the  $\nu(\text{CuI})$  band, are also present.

## Conclusions

This present study shows that the reaction of copper(I) halides with tricyclohexylphosphine in aprotic solvents yields well defined air stable crystalline samples of 1 : 1 dimeric and 1 : 2 monomeric complexes with three-coordinate PCuX<sub>2</sub> and P<sub>2</sub>CuX copper environments respectively. The structural and spectroscopic data recorded for these complexes, together with those for the analogous silver and gold complexes, reflect the significant differences in the steric and electronic properties of the metal cation and the the halide anion.

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