Solid-state $^3$P n.m.r., far-i.r. spectroscopy and single-crystal X-ray diffraction techniques have been used to characterize a new type of ionic copper(I) compound: [PPh$_3$Me][Cu(PPh$_3$)Br$_2$]. X-ray analysis shows the PPh$_3$ ligand to be co-ordinated to the copper atom of the CuBr$_2$ unit in a trigonal planar arrangement, with Cu--P 2.210(3), Cu--Br 2.367(2), 2.386(2) Å and Br--Cu--Br 114.9(1)$^\circ$. (monoclinic, space group $Pn$, $a = 11.779(5)$, $b = 9.914(5)$, $c = 14.705(10)$ Å, $\beta = 94.92(5)^\circ$, $Z = 2$, $R = 0.037$ for 1570 observed, $|F| > 3\sigma(|F|)$ reflections.) The far-i.r. spectrum shows a strong band at 195 cm$^{-1}$ assigned to the antisymmetric Cu--Br stretching mode of the CuBr$_2$ unit, and a weaker band at 150 cm$^{-1}$ assigned to the symmetric Cu--Br stretching mode. This assignment is supported by an approximate normal-co-ordinate analysis, and the resulting Cu--Br force constant is compared with values obtained in similar analyses of related bromocopper(I) complexes. The cross-polarization magic angle spinning $^3$P n.m.r. spectrum shows a strong signal at 21 p.p.m. (relative to 85% H$_3$PO$_4$) due to the cation, and a weaker quartet centred at $-14$ p.p.m. due to the co-ordinated PPh$_3$ in the anion, with line spacings due to Cu--P coupling of 1.37, 1.69, and 1.92 kHz.

Copper(I) generally shows a preference for a co-ordination number of four in its complexes, although an increasing number of complexes have been reported in which it has co-ordination numbers of two or three.$^1$ The factors which determine the preferred co-ordination number are not entirely clear; however, and further data relevant to this question should be obtainable by studying related series of complexes to determine the range of possible co-ordination numbers in the series, and by measuring physical properties of the complexes which yield information about the changes in bond strength and valence-electron distribution which occur with change in co-ordination number. Thus, for the series CuX$_n$$^{11-3}$ with X = Br or I, complexes up to $n = 3$ are known, whereas for X = Cl only up to $n = 2$. The metal--halogen force constants obtained from the v(Cu--X) vibrational frequencies for the X = Br or I complexes decrease rapidly with $n$, and these results suggest that the number of 4 complexes should not exist for this series.$^2$ In the case of the series Cu(PPh$_3$)$_n$X, mononuclear complexes with $n = 2$ or 3 are known for X = Cl, Br, or I.$^{3,4}$ Thus, the replacement of a halide ligand X$^-$ by PPh$_3$ appears to favour higher co-ordination numbers in copper(I) complexes.

In a development of these studies, we are examining the ability of neutral ligands to co-ordinate to the two-co-ordinate series CuX$_n$(capillary), i.e., and solid-state cross-polarization magic angle spinning (c.p.m.s.) n.m.r. spectroscopy of the novel anion [Cu(PPh$_3$)Br$_2$] in the compound [PPh$_3$Me][Cu(PPh$_3$)Br$_2$]. Copper(I) bromide (0.36 g, 2.5 mmol), triphenylphosphine (0.66 g, 2.5 mmol), and methyltriphenylphosphonium bromide (0.89 g, 2.5 mmol) were added to dichloromethane (15 cm$^3$) and the mixture was stirred until all the solid material had dissolved. The solution was heated on a water-bath until it boiled, and then diethyl ether was slowly added until the first permanent precipitate formed. On cooling to room temperature the solution deposited white crystals which were collected by filtration and dried in a vacuum, m.p. 167--168.5 $^\circ$C (Found: C, 58.1; H, 4.9. Calc. for Cu$_3$H$_2$Br$_2$CuP$_3$: C, 58.3; H, 4.4%).

The unsolvated adducts of [(Ph$_3$P)CuBr,Cu(PPh$_3$)$_2$] and the 'step' isomer of [Cu(PPh$_3$)Br$_2$] were prepared as previously described.$^5$

### Structure Determination.

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Crystal data. Cu$_3$H$_2$Br$_2$CuP$_3$, M = 763.0, monoclinic, space group $Pn$ [$C_{2v}^2$, no. 7 (variant)], $a = 11.779(5)$, $b = 9.914(5)$, $c = 14.705(10)$ Å, $\beta = 94.92(5)^\circ$, $U = 1711(2)$ Å$^3$, $D_c(Z = 2) = 1.48$ g cm$^{-3}$, $\mu$(MoK$_x$) = 30.3 cm$^{-1}$, specimen 0.51 x 0.40 x 0.04 mm (capillary), $A_{\text{max}}^2$, $A_{\text{max}}^2 = 1.13, 2.50$ (Gaussian correction).

A unique data set was measured to 20$_{\text{max}}$ = 50$^\circ$ on a Syntex P2$_2$ four-circle diffractometer (monochromatic Mo-K$_x$ radiation source, $\lambda = 0.71069$ Å) in conventional 20--20 scan mode at 295 K, 243 Independent reflections were measured, 1570 with $|F| > 3\sigma(|F|)$ being considered 'observed' and used in the fullmatrix least-squares refinement after solution of the structure by vector methods. $(x, y, z)$ were included at estimated values. Residuals on $|F|$ were measured as $R = 0.037$, $R' = 0.024$ (preferred hand); statistical reflection weights were used, derived from $\sigma^2(/) = \sigma^2(/)|/ + 0.0001\sigma^2(/)|/$. The structure refined smoothly in the chosen space group with no anomalies with respect to features such as thermal envelopes or disorder. The residuals were lowest for the chosen enantiomer. Neutral atom complex scattering factors were used.$^6$ No significant extinction effects were observed. Computation used the XTAL83 program system$^7$ implemented by S. R. Hall on a Perkin-Elmer 3240
Table 1. Non-hydrogen atom co-ordinates for \([\text{Cu}(\text{PPh}_3)_2\text{Br}_2]^-\)

\[
\begin{array}{cccc}
\text{Atom} & x & y & z \\
\hline
\text{Cu}(1)* & 0 & 0.264(3) & 0 \\
\text{Br}(1) & 0.173(7) & 0.144(7) & 0.036(5) \\
\text{Br}(2) & -0.158(8) & 0.180(11) & 0.070(5) \\
\text{P}(1) & 0.022(1) & 0.449(13) & -0.083(3) \\
\text{C}(11) & 0.096(6) & 0.500(10) & -0.148(6) \\
\text{C}(12) & 0.205(8) & 0.450(9) & -0.119(7) \\
\text{C}(13) & 0.296(5) & 0.487(6) & -0.164(6) \\
\text{C}(14) & 0.286(6) & 0.574(11) & -0.235(8) \\
\text{C}(15) & 0.180(6) & 0.625(12) & -0.266(6) \\
\text{C}(16) & 0.086(8) & 0.587(11) & -0.220(6) \\
\text{C}(21) & -0.048(4) & 0.594(4) & -0.012(6) \\
\text{C}(22) & -0.120(7) & 0.578(9) & 0.055(7) \\
\text{C}(23) & -0.142(7) & 0.684(6) & 0.112(2) \\
\text{C}(24) & -0.092(8) & 0.806(10) & 0.102(5) \\
\text{C}(25) & -0.021(9) & 0.827(2) & 0.037(8) \\
\text{C}(26) & 0.002(4) & 0.723(10) & -0.021(7) \\
\text{C}(31) & -0.148(7) & 0.448(10) & -0.167(8) \\
\text{C}(32) & -0.187(10) & 0.328(6) & 0.020(3) \\
\text{C}(33) & -0.279(4) & 0.321(9) & 0.263(7) \\
\text{C}(34) & -0.335(5) & 0.439(13) & 0.293(6) \\
\text{C}(35) & -0.297(8) & 0.561(3) & 0.260(9) \\
\text{C}(36) & -0.203(3) & 0.567(3) & 0.197(9) \\
\text{Br}(1) & & & \\
\text{Br}(2) & & & \\
\end{array}
\]

### Results and Discussion

Copper(II) bromide, bromide ion, and triphenylphosphine combine in a 1:1:1 ratio to form the \([\text{Cu}(\text{PPh}_3)_2\text{Br}_2]^-\) ion which was crystallized from dichloromethane-diethyl ether as its \([\text{PPh}_3\text{Me}]^+\) salt. Attempts to prepare the 2:1 complex of \(\text{PPh}_3\) with \(\text{CuBr}_2\) by using an excess of \(\text{PPh}_3\) resulted only in the formation of the 1:1 complex.

**X-Ray Structure Determination.**—The structure of the \([\text{Cu}(\text{PPh}_3)_2\text{Br}_2]^-\) anion is shown in Figure 1. The \(\text{PPh}_3\) ligand is co-ordinated to the copper atom of the \(\text{CuBr}_2\) unit in a three-co-ordinate trigonal-planar arrangement, with \(\text{Cu} - \text{P} = 2.210(3),\) \(\text{Cu} - \text{Br} = 2.367(2),\) and \(\text{Br} - \text{Cu} - \text{Br} = 114.9(1),\) \(\text{P} - \text{Cu} - \text{Br} = 118.5(1), 126.5(1)\)°. The \(\text{Cu} - \text{P}\) distance is somewhat surprisingly similar to the distances of 2.191(2) Å found for \([\text{Ph}_3\text{P}]\text{CuBr}_2\) and 2.206(5) Å found in the ‘step’ isomer of \([\text{Cu}(\text{PPh}_3)_2\text{Br}_4]^-\) both of which contain the \(\text{PPh}_3\text{CuBr}_2\) unit (Table 2). The \(\text{Cu} - \text{Br}\) distances increase on co-ordination of the \(\text{PPh}_3\) molecule to \(\text{CuBr}_2\) from an average value of 2.22 Å found in compounds containing uncomplexed linear \(\text{CuBr}_2^-\) ions to a mean value of 2.377 Å in \([\text{Cu}(\text{PPh}_3)_2\text{Br}_2]^-\), with the \(\text{Br} - \text{Cu} - \text{Br}\) angle decreasing from linearity to a value less than 120°. In the complex \(\text{[ts]}^+\cdot \text{[CuBr}_2]^-\) (\(\text{tst} = \text{tetraselenotetracene},\) naph-
Table 2. Core geometries for molecules containing the \((\text{PPh}_3)\text{CuBr}_2\) fragment

<table>
<thead>
<tr>
<th>Parameter</th>
<th>([\text{Cu}(\text{PPh}_3)\text{Br}_2]^−)</th>
<th>([\langle\text{PPh}_3\rangle\text{CuBr}_2\text{Cu}(\text{PPh}_3)_2]^{-})</th>
<th>([\text{Cu}(\text{PPh}_3)\text{Br}_4\text{ step}]^{-})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-Br(1)</td>
<td>2.386(2)</td>
<td>2.409(2)</td>
<td>2.427(2)</td>
</tr>
<tr>
<td>Cu-Br(2)</td>
<td>2.367(2)</td>
<td>2.364(2)</td>
<td>2.371(3)</td>
</tr>
<tr>
<td>Cu-P</td>
<td>2.210(3)</td>
<td>2.191(2)</td>
<td>2.206(5)</td>
</tr>
<tr>
<td>P-Cu-Br(1)</td>
<td>126.5(1)</td>
<td>129.7(1)</td>
<td>119.2(1)</td>
</tr>
<tr>
<td>P-Cu-Br(2)</td>
<td>118.5(1)</td>
<td>117.8(1)</td>
<td>127.7(1)</td>
</tr>
<tr>
<td>Br(1)-Cu-Br(2)</td>
<td>114.9(1)</td>
<td>115.5(1)</td>
<td>112.9(1)</td>
</tr>
</tbody>
</table>

* Distances (Å), angles (°).  

Figure 2. Plot of Br–Cu–Br angle vs. Cu–Br distance in compounds containing a CuBr₂ unit.

Scheme.

Consistent with a greater σ-donor capacity for the \(\text{PPh}_3\) ligand relative to the Br⁻ anion, leading to strong Cu–P bonds in which the Cu–P distance is determined primarily by the packing requirements of one, two, or three \(\text{PPh}_3\) ligands around the relatively small Cu⁺ ion. It is possible to argue from these results that the Cu–Br bond is relatively ionic, and in this context the similarity in the PCuBr₃ core geometries of \([\text{Cu}(\text{PPh}_3)\text{Br}_2]^−\), \([\langle\text{PPh}_3\rangle\text{CuBr}_2\text{Cu}(\text{PPh}_3)_2]^{-}\), and the ‘step’ isomer of \([\text{Cu}(\text{PPh}_3)\text{Br}_4\text{ step}]^{-}\) is an important result.

Far-i.r. Spectrum.—The far i.r. spectrum of \([\text{PPh}_3\text{Me}]\text{Cu}(\text{PPh}_3)\text{Br}_2\) is shown in Figure 3. By comparison with the spectrum of \([\text{PPh}_3\text{Me}]\text{Br}\), the band at 376 cm⁻¹ can be assigned to the cation and the bands at 195 and 150 cm⁻¹ to the \([\text{Cu}(\text{PPh}_3)\text{Br}_2]^−\) complex. By analogy with the results for other triphenylphosphine bromocupper(i) complexes, the strongest bands in the far-i.r. are expected to be the Cu–Br stretching modes, \(ν(\text{CuBr})\). Thus the two bands at 195 and 150 cm⁻¹ are assigned to the two expected \(ν(\text{CuBr})\) modes of the CuBr₂ unit. We have found previously that the metal–halogen vibrational frequencies of the metal–halogen core in phosphate metal halide complexes can be calculated by carrying out a normal-coordinate analysis on the metal–halogen core only. We have used this approach here to calculate the frequencies of a CuBr₂ unit with two equivalent bonds and a Br–Cu–Br bond angle of 115°. A simple diagonal force field was used. This involves a Cu–Br bond stretching force constant \(f_{\text{Cu-Br}}\) and a Br–Cu–Br angle-bending force constant \(f_{\text{Br-Cu-Br}}\). With the assumption \(f_{\text{Br-Cu-Br}} = 0.1f_{\text{Cu-Br}}\), which we have used in this type of calculation previously, \(f_{\text{Cu-Br}}\) was varied and the vibrational frequencies calculated to give the best fit between the observed and experimental frequencies. The results are shown in Table 3. The agreement between the observed and...
calculated frequencies is sufficiently good to support the above assignment, and shows that the higher-frequency band is due to the antisymmetric stretch ($B_1$ symmetry) and the lower-frequency band to the symmetric stretch ($A_1$ symmetry).

As expected from the comparison of bond lengths discussed above, the CuBr force constant in $[\text{Cu(PPh}_3\text{)}\text{Br}]^-$ is significantly lower than the value found for CuBr$_2$. This result parallels that found previously for $[\text{M(PPh}_3\text{)}_n\text{X}]$ ($\text{M} = \text{Cu, Ag, or Au; X = Cl, Br, or I}$) where the $v(\text{MX})$ frequency and the MX force constant are found to be strongly dependent on co-ordination number and MX bond length.

Table 3 contains other data for comparison with the above results. Thus, the force constant $f_s$ for the terminal CuBr bond in $[\text{Cu(PPh}_3\text{)}_2\text{Br}]$ is significantly greater than that for the corresponding bonds in $[\text{Cu(PPh}_3\text{)}_2\text{Br}_2]^-$. This is in agreement with the trends in the CuBr bond lengths in these complexes, as discussed above. A similar normal-co-ordinate calculation was carried out on the Cu$_2$Br$_2$ core of $[(\text{Ph}_3\text{P})\text{CuBr}_2\text{Cu(Ph}_3\text{P)}_3]^-$. This analysis shows that the $v(\text{Cl})$ bands at 180 and 153 cm$^{-1}$ can be satisfactorily accounted for only if the force constant for the terminal Cu-Br bonds involving the trigonally co-ordinated copper atom is significantly greater than that involving the tetrahedrally co-ordinated copper atoms. From the results in Table 3 it can be seen that the force constant for the terminal Cu-Br bonds in this complex is only slightly smaller than that for the corresponding bonds in $[\text{Cu(Ph}_3\text{P)}_2\text{Br}_2]^-$. Again, this is in good agreement with observations made above concerning the relative bond lengths in these species. Likewise, the force constant for the Cu-Br bonds involving the tetrahedral copper atom in $[(\text{Ph}_3\text{P})\text{CuBr}_2\text{Cu(Ph}_3\text{P)}_3]$ is almost identical to that for the CuBr bonds in $[\text{Cu(PPh}_3\text{)}_2\text{Br}]$, which also involves tetrahedrally co-ordinated copper(i). Analysis of the potential-energy distribution for the four calculated $v(\text{CuBr})$ modes of $[(\text{Ph}_3\text{P})\text{CuBr}_2\text{Cu(Ph}_3\text{P)}_3]$ shows that the two higher-frequency modes are associated mainly with stretching of the CuBr bonds on the trigonal copper atom, while the two lower-frequency modes are associated with the tetrahedral copper atom. This result suggests an alternative explanation for the presence of only doubly bridging bromine atoms in the structure.

Solid-state $^{\text{31}}\text{P}$ N.M.R. Spectrum.—The solid-state c.p.m.a.s. $^{\text{31}}\text{P}$ n.m.r. spectrum of $[\text{PPh}_3\text{Me}]_2[\text{Cu(Ph}_3\text{P)}_2\text{Br}]$ is shown in Figure 4. It consists of a strong singlet at 21 p.p.m. (relative to 85% H$_3$PO$_4$ due to the phosphonium cation, and a weaker quartet centred at $-14$ p.p.m. due to the co-ordinated PPh$_3$ in the anion. As described previously, the quartet structure is due to spin–spin coupling of the phosphorus nucleus to the copper nucleus ($^4\text{Cu}, ^{13}\text{C}, \text{I} = \frac{1}{2}$). The line spacings in the quartet are unequal, due to the presence of a nuclear quadrupole coupling interaction between the copper nucleus and its surroundings. For a spherically symmetric charge distribution about the copper nucleus, the nuclear quadrupole coupling constant would be zero, and the components of the quartet would be equally spaced. The marked asymmetry observed in the present case is thus a reflection of the electrical asymmetry about the copper nucleus which results from the relatively low-symmetry trigonal-planar co-ordination environment.

In order to investigate possible relationships between the $^{\text{31}}\text{P}$ n.m.r. parameters and the co-ordination environment about the copper atom, the solid-state $^{\text{31}}\text{P}$ n.m.r. data obtained in the present study are compared with those for some related species in Table 4. The average chemical shift for $[\text{Cu(Ph}_3\text{P)}_2\text{Br}]^-$ is more negative than those for the other bromocopper(i) complexes listed in Table 4. Since the last two compounds in this table also contain trigonal (PPh$_3$)CuBr$_2$ units, it appears that the chemical shift is not a good indicator of the co-ordination environment. The average line spacing ($\Delta
u_r$) in the quartets increases with decreasing number of co-ordinated PPh$_3$ ligands and is usually found in the range 0.9–1.0 kHz for Cu(PPh$_3$)$_2$ compounds, 1.2–1.3 kHz for Cu(PPh$_3$)$_3$ compounds, and 1.6–1.8 kHz for Cu(PPh$_4$) compounds. This trend presumably reflects the decrease in Cu–P bond lengths with decreasing number of co-ordinated ligands and a correspondingly greater degree of copper 4s-orbital participation in the Cu–P bonding. It is also notable that the asymmetry, $\Delta
u_p$, in the quartet splittings is approximately the same for the two trigonal mononuclear complexes $[\text{Cu(Ph}_3\text{P)}_2\text{Br}]$ and $[\text{Cu(Ph}_3\text{P)}_2\text{Br}]^-$, but is much smaller for the tetrahedral mononuclear complex. This is in agreement with the expectation that the copper quadrupole coupling constant will be smaller for the tetrahedral than for the trigonal environment, as has been observed in related complexes by direct measurement of the nuclear
Table 4. C.p.m.a.s. solid-state $^{31}$P n.m.r. parameters for some bromocopper(i) complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta$</th>
<th>$\Delta_{\nu}$</th>
<th>$\Delta_{\nu_j}$</th>
<th>$\Delta_{\nu_i}$</th>
<th>$\Delta_{\nu}$</th>
<th>$\Delta_{\nu_i}$</th>
<th>$\Delta_{\nu_j}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu(PPh$_3$)$_2$Br]$_2$</td>
<td>4.9</td>
<td>-6.4</td>
<td>-20.3</td>
<td>-36.1</td>
<td>-14</td>
<td>1.37</td>
<td>1.69</td>
<td>1.92</td>
</tr>
<tr>
<td>[CuPPh$_3$)$_2$Br]$_2$</td>
<td>8.0</td>
<td>0.8</td>
<td>-9.7</td>
<td>-21.6</td>
<td>-6</td>
<td>0.88</td>
<td>1.28</td>
<td>1.44</td>
</tr>
<tr>
<td>[CuPPh$_3$Br]</td>
<td>6.5</td>
<td>-1.0</td>
<td>-9.0</td>
<td>-16.8</td>
<td>-5</td>
<td>0.90</td>
<td>0.96</td>
<td>0.95</td>
</tr>
<tr>
<td>[(P$_2$P)CuBr$_2$(PPh$_3$)$_2$]$_2$</td>
<td>18.1</td>
<td>5.9</td>
<td>-8.1</td>
<td>-24.7</td>
<td>-2</td>
<td>1.48</td>
<td>1.70</td>
<td>2.02</td>
</tr>
<tr>
<td>[(P$_2$P)CuBr$_2$(PPh$_3$)$_2$]$_2$ 'step'</td>
<td>10.5</td>
<td>-0.2</td>
<td>-11.2</td>
<td>-24.7</td>
<td>-6</td>
<td>1.25</td>
<td>1.40</td>
<td>1.65</td>
</tr>
<tr>
<td>[(P$_2$P)CuBr$_2$(PPh$_3$)$_2$]$_2$ 'step'</td>
<td>12.6</td>
<td>-4.0</td>
<td>-8.1</td>
<td>-19.2</td>
<td>-3</td>
<td>1.05</td>
<td>1.45</td>
<td>1.35</td>
</tr>
<tr>
<td>[(P$_2$P)CuBr$_2$(PPh$_3$)$_2$]$_2$ 'step'</td>
<td>15.9</td>
<td>-4.1</td>
<td>-11.4</td>
<td>-28.4</td>
<td>-5</td>
<td>1.43</td>
<td>1.88</td>
<td>2.06</td>
</tr>
</tbody>
</table>

$^a$ $\delta$ are the chemical shifts (± 0.5 p.p.m.) with respect to 85% H$_3$PO$_4$ ($\delta$ for solid PPh$_3$ = -9.9 p.p.m.); $\langle \delta \rangle$ is the average chemical shift for each quartet; $\Delta_{\nu}$ is the splitting in kHz (±0.03) between each of the four peaks of the quartet; $\langle \Delta_{\nu} \rangle$ is the average of the $\Delta_{\nu}$ for each quartet; $\Delta_{\nu_j} = \Delta_{\nu(max)} - \Delta_{\nu(min)}$ is the asymmetry parameter of the quartet. This work.

Acknowledgements

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References


Conclusions

The present study establishes the existence of the first anionic mixed-ligand complexes of copper(i) with halide and triphenylphosphine. The isolation of [Cu(PPh$_3$)$_2$Br]$_2$ in the presence of excess of PPh$_3$ suggests that CuBr$_2$ is only able to accommodate one PPh$_3$ molecule in its co-ordination sphere. Trends in metal–ligand bond lengths, $^{31}$P n.m.r. line spacings, and bond-stretching force constants between this and related species can be understood on the basis of a greater σ-donor capacity for PPh$_3$ relative to Br$^-$, and establish a close similarity between the (PPh$_3$)$_2$CuBr$_2$ unit in various structures, irrespective of whether the Br atoms are terminal or bridging.

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