

## Diaryltelluride Complexes of Copper(I) Halides

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*Copper(I) halide complexes of stoichiometry  $CuL_nX$  have been prepared where  $L$  is a diaryltelluride ( $n = 3$ ,  $L = Ph_2Te$ ,  $X = Cl$ ;  $n = 2$ ,  $L = Ph_2Te$ ,  $X = Br$ ;  $n = 2$ ,  $L = (p\text{-tolyl})_2Te$ ,  $X = Cl, Br, I$ ;  $n = 2$ ,  $L = (p\text{-EtOC}_6\text{H}_4)_2Te$ ,  $X = Cl, Br$ ;  $n = 1$ ,  $L = Ph_2Te$  or  $(p\text{-EtOC}_6\text{H}_4)_2Te$ ,  $X = I$ ). The new compounds have been examined by X-ray powder methods, conductivity studies and vibrational spectroscopy. It is concluded that the coordination number of copper(I) within the series may be 4 or 3 and that the geometry about the metal is either tetrahedral (CN 4) or trigonal planar (CN 3). Assignments of copper-halogen stretching vibrations are offered.*

### Introduction

The co-ordination compounds of copper(II) must be among the most widely studied complex compounds. By contrast copper(I) has received somewhat scant attention although there is evidence that interest in this area is growing. For example stable alkyl compounds of copper(I) were recently reported<sup>1</sup> and an increasing body of X-ray crystallographic data is beginning to establish the co-ordination geometries available to the ion and in particular to show a trigonal planar structure to be fairly common.<sup>2</sup>

Our current interest in organotellurium chemistry,<sup>3</sup> together with the fact that diaryltellurides have been relatively little studied as ligands<sup>4</sup> led us to investigate properties of telluride-metal salt systems. Experience has led us to regard a diaryltelluride as a base of mild class *b* character,<sup>5</sup> hence we selected the softish copper(I) cation for initial co-ordination studies.

### Experimental

Diphenyltelluride,<sup>6</sup> di-(*p*-tolyl)telluride<sup>6</sup> and di-(*p*-ethoxyphenyl)telluride<sup>6</sup> were prepared by a literature method. Diphenyltelluride was purified by vacuum distillation and the other compounds by recrystallisation. Copper(I) halides were commercial specimens. Copper(I) chloride and bromide were treated with

sulphurous acid before use but copper(I) iodide was used as received.

#### *Chlorotris(diphenyltelluride)copper(I)*

Diphenyltelluride (0.85 g, 3 mM) in ethanol (20 ml) was added to a hot solution of copper(I) chloride (0.1 g, 1 mM) in dilute hydrochloric acid (1M, 20 ml). The resulting solution was stirred for 5 min. after which a white solid which had deposited was filtered, washed with ethanol and dried *in vacuo* over  $P_4O_{10}$ . Found: C, 45.6; H, 3.30; Cu, 6.18.  $C_{36}H_{30}ClCuTe_3$  requires: C, 45.7; H, 3.18; Cu, 6.73%.

#### *Di-μ-bromotetrakis(diphenyltelluride)dicropper(I)*

Diphenyltelluride (0.6 g, 2 mM) in ethanol (20 ml) was mixed with a hot solution of copper(I) bromide (0.14 g, 1 mM) in dilute hydrobromic acid (1M, 20 ml). The solution was heated and stirred for five minutes after which a yellow-white compound was deposited. The product was filtered, washed with ethanol to afford a pure white solid which was dried *in vacuo*. Found: C, 40.1; H, 2.85; Cu, 8.16.  $C_{48}H_{40}Br_2Cu_2Te_4$  requires: C, 40.7; H, 2.83; Cu, 8.99%.

#### *Di-μ-iodobis(diphenyltelluride)dicropper(I)*

Diphenyltelluride (0.6 g, 2 mM) in ethanol (20 ml) was added to a solution of copper(I) iodide saturated with potassium iodide. The reaction mixture was stirred and heated for five minutes when a white product deposited. The precipitate was filtered, washed with ethanol and dried *in vacuo*. Found: C, 30.9; H, 2.22; Cu, 13.7.  $C_{24}H_{20}Cu_2I_2Te_4$  requires: C, 30.5; H, 2.12; Cu, 13.5%.

The complexes of di-(*p*-ethoxyphenyl)telluride and di-(*p*-tolyl)telluride were prepared following exactly similar methods. It was found that variation of the metal:ligand ratio afforded only the compounds indicated in the case of all three ligands considered. For the remaining compounds we indicate the metal:ligand ratio giving the optimum yield.

#### *Di-μ-chlorotetrakis(di-p-tolyltelluride)dicropper(I)*

Metal:ligand ratio used = 1:2. Found: C, 46.8; H, 4.02; Cu, 8.17.  $C_{56}H_{56}Cl_2Cu_2Te_4$  requires: C, 46.8; H, 3.90; Cu, 8.84%.

*Di-μ-bromotetrakis(di-p-tolytelluride)dycopper(I)*

Metal:ligand ratio used = 1:2. Found: C, 44.2; H, 3.75; Cu 8.25.  $C_{56}H_{56}Br_2Cu_2Te_4$  requires: C, 44.1; H, 3.67; Cu, 8.33%.

*Iodobis(di-p-tolytelluride)copper(I)*

Metal:ligand ratio used = 1:2. Found: C, 41.8; H, 3.52; Cu, 7.44.  $C_{28}H_{28}CuI_2Te_2$  requires: C, 41.5; H, 3.46; Cu, 7.84%.

*Di-μ-chlorotetrakis(di-p-ethoxyphenyltelluride)dycopper(I)*

Metal:ligand ratio used = 1:2. Found: C, 46.0; H, 4.29; Cu, 7.50.  $C_{64}H_{72}Cl_2Cu_2O_8Te_4$  requires: C, 45.8; H, 4.33; Cu, 7.56%.

*Di-μ-bromotetrakis(di-p-ethoxyphenyltelluride)dycopper(I)*

Metal:ligand ratio used = 1:2. Found: C, 44.1; H, 4.39; Cu, 7.20.  $C_{64}H_{72}Br_2Cu_2O_8Te_4$  requires: C, 43.5; H, 4.11; Cu, 7.19%.

*Di-μ-iodobis(di-p-ethoxyphenyltelluride)dycopper(I)*

Metal:ligand ratio used = 1:2. Found: C, 34.1; H, 3.32; Cu, 10.7.  $C_{32}H_{36}Cu_2I_2O_4Te_2$  requires: C, 34.3; H, 3.21; Cu, 11.3%.

**Physical Measurements**

Conductivity measurements were obtained with a Henelec bridge over a concentration range ( $5 \times 10^{-3}M$ – $5 \times 10^{-4}M$ ) in pure acetonitrile. No solvent was found in which the complexes were sufficiently soluble for molecular weight measurements by vapour phase osmometry.

X-ray powder data were obtained using  $CuK\alpha$  radiation. Infra-red spectra were recorded for nujol mulls and KBr discs using a Perkin Elmer 457 instrument ( $4000$ – $250\text{ cm}^{-1}$ ). Far infra-red spectra  $400$ – $40\text{ cm}^{-1}$  obtained with a R.I.I.C. FS 720 interferometer and computed to a resolution of  $2\text{ cm}^{-1}$  with the University of Aston ICL 1605 computer. Samples were nujol mulls in vacuum tight polythene cells. The spectra were duplicated ( $400$ – $200\text{ cm}^{-1}$ ) on a Perkin Elmer 225 instrument.

**Results and Discussion**

Despite the fact that metal:ligand ratios were varied between 1:4 and 1:1 for each combination of reactants used, only the compounds detailed in the experimental section were formed under our experimental conditions.

Single concentration ( $10^{-3}M$ ) conductivity studies of the complexes in acetonitrile give values of the molar conductivity ( $\Lambda_m$ ) in the range  $61$ – $77\text{ mhos cm}^2\text{ mol}^{-1}$ . This represents an appreciable conductivity but is well below the value expected for a 1:1 electrolyte in this

solvent ( $120$ – $160\text{ mhos cm}^2\text{ mol}^{-1}$ ).<sup>7</sup> However doubling the empirical formulae will bring the experimental values within the 1:1 range and formulae such as  $[CuL_4]^+[CuX_2]^-$  and  $[CuL_2]^+[CuX_2]^-$  are plausible for the 1:2 and 1:1 complexes. The infra-red data show no evidence for the presence of the dihalogenocuprate(I) ions,<sup>8</sup> hence the conductivity of each complex was studied as a function of concentration (Fig. 1). The behaviour shown was typical of weak rather than of strong electrolytes thus a solvolysis reaction is the probable explanation of the observed conductivity behaviour and the compounds may reasonably be considered non-ionic in the solid state.

X-ray powder data were quite informative. The di-(*p*-tolyl)telluride series shows a common stoichiometry (1:2) for the chloro-, bromo- and iodo- complexes, and it was clear from calculation of inter planar spacings (*d* values) that the chloro- and bromo- complexes are isomorphous and probably isostructural. However the powder pattern of the iodo-complex was considerably different. The large size of the iodo- group may be responsible for removal of isomorphism as indicated by powder data but it would be dangerous to assume on this evidence alone that the complex is not isostructural with the chloro- and bromo- compounds. It was noted that infra-red data were in accord with the powder data to the extent that the higher frequency regions of the chloro- and bromo- complex spectra were completely superimposable whereas the spectrum of the iodo-compound differed in many points of detail. It was noted that 1:2 complexes of  $CuCl$  and  $CuBr$  with the other ligands ( $Ph_2Te$  and  $(p-EtOC_6H_4)_2Te$ ) gave powder photographs very similar to those of  $Cu[(p-CH_3C_6H_4)_2Te]_2X$  ( $X = Cl, Br$ ) and the assumption of a common structure is not therefore unreasonable. Also the copper(I) chloride and bromide complexes of di-(*p*-ethoxyphenyl)telluride are isomorphous but the iodo-complex gives a very poor photograph and no firm conclusions may be reached.

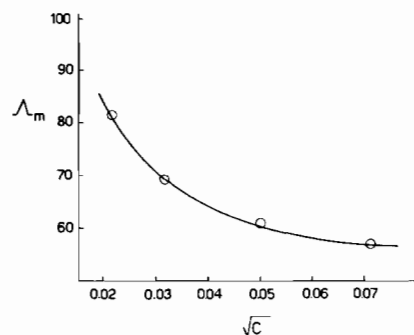


Figure 1. Plot of molar conductivity ( $\Lambda_m$ ) against (concentration)<sup>1/2</sup> for  $[Cu\{(p-tol)_2Te\}_2Cl]$ . Other compounds gave similar curves.

The low frequency infra-red spectra of the new compounds were examined with a view to assigning copper-halogen stretching frequencies and to draw inferences about the stereochemical environment of the metal ion where this was possible. Two attempts were made to obtain the Raman spectra of the complexes using Coderg (University of Leicester) and Cary 81 (University of Nottingham) instruments. In neither case was it possible to obtain useful spectra below  $200\text{ cm}^{-1}$ , thus the following discussion must be based on i.r. data only.

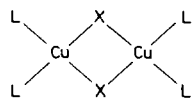
There is some information available concerning the position of Copper(I)-halogen stretching vibrations. Thus  $(\text{CuCl})_n$  exhibits a broad band at  $170\text{ cm}^{-1}$ <sup>9</sup> whereas the complex  $(\text{CuCl})_2(\text{DPPA})_3$  (DPPA = bis(diphenylphosphine)acetylene) gives a single band at  $267\text{ cm}^{-1}$  in accord with the proposed tetrahedral arrangement about copper(I),<sup>10</sup> the corresponding bromide gave a band at  $202\text{ cm}^{-1}$ . The trigonal planar  $\text{Cu}(\text{PCy}_3)_2\text{Cl}$  gives a strong absorption at  $255\text{ cm}^{-1}$ <sup>11</sup> and the halogen bridged (*o*- $\text{Me}_2\text{NC}_6\text{H}_4\text{AsMe}_2$ ) $\text{CuX}$  gives two bands at  $232$  and  $162\text{ cm}^{-1}$  ( $\text{X} = \text{Cl}$ ) or  $202$  and  $145\text{ cm}^{-1}$  ( $\text{X} = \text{Br}$ ) or  $175$  and  $128\text{ cm}^{-1}$  ( $\text{X} = \text{I}$ ).<sup>12</sup> Thus copper(I)-halogen vibrations may be expected over a fairly wide range of frequencies, indeed Cook *et al.*<sup>13</sup> have suggested lower limits of  $110\text{ cm}^{-1}$  (chloride) and  $100\text{ cm}^{-1}$  (bromide).

### 1:3 Complex, $[(\text{Ph}_2\text{Te})_3\text{CuCl}]$

A strong composite band between  $270$  and  $260\text{ cm}^{-1}$  is probably assignable as  $\nu(\text{Te-Ph})$ <sup>14</sup> +  $\nu(\text{CuCl})$ . Vibrations of terminal copper(I)-chlorine bonds are expected in this region of the spectrum, hence a tetrahedral structure is likely for this non-ionic complex.

### 1:2 Complexes, $[(\text{R}_2\text{Te})_2\text{CuX}]$

X-ray powder data are consistent with a common structure for the 1:2 chloro- and bromo- complexes. The far infra-red spectra are in accord with this conclusion since, in each case, two copper halogen stretching vibrations may be assigned. For  $[\text{Cu}(\text{R}_2\text{Te})_2\text{Cl}]$  ( $\text{R} = p$ -tolyl or *p*- $\text{EtOC}_6\text{H}_4$ ) both bands are below  $200\text{ cm}^{-1}$  and are unlikely to be attributable to terminal Cu-Cl bonds such as would occur in a trigonal planar structure. The data are however consistent with copper-chlorine bridge bonds such as would be present in a dimeric structure with a tetrahedral arrangement of ligands about individual copper(I) ions,



also two infra-red active copper-chlorine stretching vibrations are anticipated for such a structure. The failure to obtain good Raman spectra is particularly unfortunate in this case since the two Raman active bands expected should be non-coincident with the infra-red frequencies, however all available data are consistent with the proposed structure. The bromo-complexes  $[(\text{R}_2\text{Te})_2\text{CuBr}]$  ( $\text{R} = \text{Ph}$ , *p*-tolyl or *p*- $\text{EtOC}_6\text{H}_4$ ) give analogous spectra (Table I) to the above chloro-complexes, i.e. two infra-red active copper-bromine stretching vibrations. This fact, together with the X-ray data discussed above, suggests them to be isostructural with the chloro-compounds.

Although a trigonal planar structure was not seriously considered for the 1:2 complexes of  $\text{CuCl}$  and  $\text{CuBr}$  with telluride ligands, it is not clear that it may be eliminated from consideration in the case of  $\{[(p\text{-CH}_3\text{C}_6\text{H}_4)_2\text{Te}]_2\text{CuI}\}$  since neither X-ray data nor high frequency infra-red data suggest that the structure is similar to that of the stoichiometrically related chloro- and bromo compounds. Also the far infra-red data imply that the strong band at  $163\text{ cm}^{-1}$  must be assigned as  $\nu(\text{CuI})$ . Given our assignments of  $\nu(\text{CuBr})$ , this frequency seems too high for a bridging copper-iodine bond, it would however be compatible with a terminal copper-iodine vibration in a trigonal planar molecule, a structure for which there are now many precedents.<sup>2, 11, 15</sup>

### 1:1 Complexes, $[(\text{R}_2\text{Te})\text{CuI}]$

Since ionic structures are eliminated, three plausible structures can be considered for the 1:1 complexes: (a) linear (sp hybridisation on copper), (b) tetrameric as in  $[(\text{Et}_3\text{As})\text{CuI}]_4$ <sup>16</sup> or (c) dimeric as in  $[(\text{PCy}_3)\text{CuX}]_2$ .<sup>11</sup> Our data for  $\{[(p\text{-EtOC}_6\text{H}_4)_2\text{Te}]\text{CuI}\}$  allow no firm conclusions to be drawn for that compound. However the two strong bands at  $161\text{ cm}^{-1}$  and  $111\text{ cm}^{-1}$  for  $[(\text{Ph}_2\text{Te})\text{CuI}]$  may be assigned as  $\nu(\text{CuI})$ , thus the monomeric two co-ordinate structure (a) is less probable than (b) or (c). Furthermore since we assign  $\nu(\text{CuBr})$  for  $[(\text{Ph}_2\text{Te})\text{CuBr}]$  at  $155\text{ cm}^{-1}$  and  $109\text{ cm}^{-1}$ , the higher  $\nu(\text{CuI})$  frequencies only appear plausible if the co-ordination number of copper is less in the iodothan in the bromo- complex; thus our tentative preference is for structure (c):

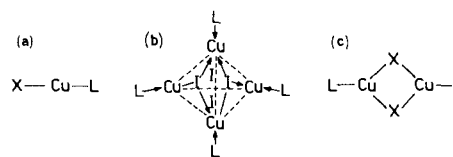


TABLE I. Low-frequency Infra-red Spectra of Copper(I) Halide-Telluride Complexes.<sup>a</sup>

[Cu(Ph <sub>2</sub> Te) <sub>3</sub> Cl]	[Cu(Ph <sub>2</sub> Te) <sub>2</sub> Br] <sub>2</sub>	[Cu(Ph <sub>2</sub> Te)I] <sub>2</sub>
382 m	383 m	390 s
270	270 s	308 s
265 s, br		270 s
260	262 s	261 s
217 m	218 m	229 m
190 m	201 vw	197 m
168 m	182 m, br	181 w
146 w	<i>155 m</i>	173 m
121 m	133 sh	<i>161 s</i>
93 s	<i>109 w</i>	<i>111 s</i>
[Cu{(p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> Te) <sub>2</sub> Cl] <sub>2</sub>	[Cu{(p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> Te) <sub>2</sub> Br] <sub>2</sub>	[Cu{(p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> Te) <sub>2</sub> I] <sub>2</sub>
382 s	382 s	382 s
312 w	315 m	308 m
276 w	274 w	243 s
258 w	238 s	237 m
240 s	182 w	193 m
213 m	<i>164 s</i>	<i>163 s</i>
<i>183 s</i>	142 m	146 m
147 sh	<i>92 m</i>	125 m
<i>117 s</i>	107 s	
87 w		
[Cu{(p-EtOC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> Te) <sub>2</sub> Cl] <sub>2</sub>	[Cu{(p-EtOC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> Te) <sub>2</sub> Br] <sub>2</sub>	[Cu{(p-EtOC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> Te) <sub>2</sub> I] <sub>2</sub>
381 s	382 s	383 s
349 m	345 m	345 s
331 m	329 m	308 m
313 m	305 m	
302 m	205 m	235 w
210 m	181 w, br	210 m
<i>185 s</i>	<i>163 m</i>	182 w
148 sh	143 m	134 w
<i>128 m</i>	<i>100 w</i>	89 m

<sup>a</sup> Bands assigned to copper-halogen stretching vibrations are given in italics.

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