New Copper(I) Derivatives of Organotellurium Compounds: Synthesis, Vibrational and ^{125}Te Mössbauer Spectra

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Introduction

Our interest in the co-ordination chemistry of organotellurium compounds with copper(I) salts arises partly from a wish to extend this area of chemistry, but also from a concern to evaluate the complexes as catalysts for some reactions of industrial interest [2]. Earlier we dealt with complexes of copper(I) salts with diaryltellurides [1], we now turn to derivatives of dialkyl- and diarylditellurides and also to a series of compounds CuTeR (R = alkyl or aryl) which may be considered derivatives of the tellurol, RTeH.

Typical reactions of ditellurides with transition metal species involve rupture of the Te–Te bond and afford products containing bridging RTe-groups [3]. This is particularly likely to happen with metal carbonyl derivatives, and we have recently reported reactions of two ditellurides with Pd(PPh$_3$)$_4$ which gave palladium(II) compounds of stoicheiometry Pd(TeR)$_2$(PPh$_3$) [4]. However, it is dangerous to assume that this behaviour is completely general since the literature contains at least three examples of complexes in which the ditelluride is said to co-ordinate intact, two with mercury(II) [5, 6] and one with uranium(V) [7]. Also Eaborn *et al.* have recently reported that species such as Pt(C$_2$H$_4$)(PPh$_3$)$_2$ may insert into the metal–carbon bond of Ph$_6$E$_2$ where E = Sn or Pb (this must be seen as a possible alternative description of our own palladium compounds [4].

We have given a preliminary account [9] of the synthesis of the compounds described in more detail in this paper. We have now measured the ^{125}Te Mössbauer spectra of many of the compounds and include data on some mercury(II) compounds for comparison.

Experimental

Preparation of Complexes

Diarylditellurides were prepared following well established literature methods [10], whereas the dialkylditellurides were prepared using the following modification of a method due to Bergson [11]. Sodium formaldehyde sulphoxylate (9.24 g) and sodium hydroxide (9.0 g) were dissolved in distilled water (200 cm^3). The apparatus was flushed with dinitrogen, and finely powdered tellurium (15.3 g) was added. The mixture was reduced under dinitrogen, with vigorous stirring, for 5 h. The alkylbromide (1.2 × 10^{-1} mol) was then added dropwise over a period of 30 min with cooling and stirring. The solution was extracted with carbon tetrachloride (3 × 100 cm^3), the extract was dried over calcium chloride and vacuum distilled to afford the dark red, foul smelling, dialkylditelluride. The material was characterised by mass and n.m.r. spectroscopy.

To synthesise the complexes, copper(I) chloride or bromide (2 mmol) was dissolved in acetonitrile (25 cm^3) under dinitrogen. To this solution was added, dropwise, a solution of the diorganoditelluride (2 mmol) in diethyl ether. The solution was warmed to 30 °C and stirred for 10 min. On cooling and setting aside for 15 min the solution afforded orange to red precipitates of compounds analysing as R$_2$Te$_2$·CuX (R = alkyl or aryl, X = Cl or Br). The compounds prepared are listed in Table I with their analytical data.

Preparation of Copper(I) Derivatives of Organotellurols

Two methods of synthesis were developed. (*a*) The diorganoditelluride (1 mmol) was dissolved in ethanol (50 cm^3). To this solution was added an excess of sodium borohydride (5 mmol) in 1*M* sodium hydroxide (10 cm^3). The solution was vigorously stirred for 15 min during which time the orange–red colour of the solution faded to pale yellow. A solution of copper(I) chloride (2 mmol) in ethanol (25 cm^3) was added to produce, immediately, a brown precipitate which was filtered and washed with ethanol and diethyl ether and dried *in vacuo*. (*b*) The preferred method was to react an organo(triphenylstannyl)telluride [12] (4 mmol) in diethylether (50 cm^3) with a vigorously stirred solution of copper (I) chloride (3 mmol) in acetonitrile (50 cm^3). The immediately formed brown precipitate of the organotellurenyl–copper(I) compound was filtered, washed with ethanol and diethyl ether and dried *in vacuo*. This method gave higher yields of an analytically purer product. The compounds prepared are given in Table I.

Carbon and hydrogen analyses were carried out within the department (University of Aston). Two methods were used to analyse for tellurium. The recent oxygen flask method evolved by Clark and Al-Turaihi [13] tended to give low results (a characteristic of the method when applied to the analysis

TABLE I. Analytical Data for New Organotellurium Derivatives of Copper(I).

Compound	Found %					Required %				
	C	H	Cu	Te	X	C	H	Cu	Te	X
$(C_2H_5)_2Te_2 \cdot CuCl$	11.8	2.49	15.3	61.4	8.11	11.7	2.43	15.4	61.8	8.60
$(C_2H_5)_2Te_2 \cdot CuBr$	10.6	2.25	14.0	56.0	17.0	10.5	2.20	13.9	55.8	17.5
$(n\text{-}C_4H_9)_2Te_2 \cdot CuCl$	20.4	3.80	13.7	54.2	7.30	20.6	3.85	13.6	54.4	7.60
$(n\text{-}C_4H_9)_2Te_2 \cdot CuBr$	18.6	3.49	12.3	49.5	16.0	18.8	3.52	12.4	49.6	15.6
$(n\text{-}C_5H_{11})_2Te_2 \cdot CuCl$	24.5	4.33	12.5	51.0	8.16	24.2	4.44	12.8	51.3	7.15
$(n\text{-}C_5H_{11})_2Te_2 \cdot CuBr$	22.4	3.44	11.6	47.0	15.1	22.2	3.34	11.8	47.1	14.8
$(C_6H_5)_2Te_2 \cdot CuCl$	28.7	2.07	12.3	50.2	6.21	28.4	1.97	12.5	50.0	7.00
$(C_6H_5)_2Te_2 \cdot CuBr$	26.2	1.88	11.8	45.9	13.2	26.1	1.81	11.5	46.1	14.5
$(p\text{-}C_2H_5OC_6H_4)_2Te_2 \cdot CuCl$	32.6	3.22	10.5	42.7	6.01	32.2	3.02	10.6	42.7	5.95
$(p\text{-}C_2H_5OC_6H_4)_2Te_2 \cdot CuBr$	29.7	2.77	9.89	40.2	12.9	30.0	2.81	9.91	39.8	12.5
$(C_2H_5)TeCu$	10.8	2.39	28.6	57.4	–	10.9	2.28	28.8	57.8	–
$(n\text{-}C_4H_9)TeCu$	20.0	3.78	26.4	52.2	–	19.4	3.64	25.7	51.3	–
$(n\text{-}C_5H_{11})TeCu$	22.7	4.35	24.0	48.8	–	22.9	4.21	24.3	48.6	–
$(C_6H_5)TeCu$	27.2	1.89	23.5	47.7	–	26.9	1.87	23.7	47.5	–
$(p\text{-}C_2H_5OC_6H_4)TeCu$	30.6	2.98	20.9	40.7	–	30.8	2.89	20.4	40.9	–

of ditellurides), however the rather more lengthy method of Thavornyutikarn [14] generally gave excellent results enabling us to improve on the data given in our preliminary communication [9]. Copper was determined by atomic absorption after removal of organic matter by Thavornyutikarn's method [14] with an improvement on the earlier data.

Physical Measurements

Where solubility permitted, the conductivities of 10^{-3} solutions of the compounds in acetonitrile were measured with a Henelec bridge. Infrared spectra were determined with Perkin Elmer 457 (4000–250 cm^{-1}) and 225 (400–200 cm^{-1}) instruments. Some compounds were also examined on a R11C FS 720/FS 200 interferometer (400–40 cm^{-1}), spectra being computed on the University of Aston computer. ^{125}Te Mössbauer spectra were recorded as previously reported [15] at Simon Fraser University.

Results and Discussion

A list of compounds prepared, together with analytical data is given in Table I. Table II reports infra-red bands of interest and Table III contains ^{125}Te Mössbauer data for the compounds.

Copper(I) Derivatives of Organotellurols, RTeCu

The stoicheiometry of the compounds is confirmed by good and complete analytical data (Table I). The compounds, both alkyl- and aryl-, are extremely insoluble in solvents of a wide range of polarity. It is therefore probable that the materials

TABLE II. For Infra-red Spectra of Some New Diorganoditelluride Complexes of Copper(I) Chloride.

Ph_2Te_2	$(Ph_2Te_2)CuCl$	Assignment	$(Et_2Te_2)CuCl$
255	250	$\nu_{as}(TePh)$	
	222 sh	$\nu(CuCl)^a$	227
188	188	phenyl x	
167			
(Raman)	170	$\nu(TeTe)$	180
146	128	phenyl x'	
		$\delta(CuCl)$	92
			85

[a]By comparison with corresponding bromide.

are highly polymeric, with the tellurium atoms bridging copper atoms. The coordination number of tellurium could be three or four. We have previously taken the view that in organotellurium(II) and organotellurium(IV) compounds, one non-bonding pair of electrons is located in an orbital of largely s-character (*i.e.* bonding is largely via tellurium p orbitals [15]. Thus if the tellurium atom were to bridge three copper atoms in RTeCu (*i.e.* should it become four co-ordinate), considerable rehybridisation at tellurium should occur resulting in direct removal of s-electron density from the tellurium nucleus. This should result in a very considerable decrease in the chemical isomer shift in the ^{125}Te Mössbauer spectrum for RTeCu, compared with R_2Te or with tellurium(IV) compounds. In fact (Table III), the chemical isomer shift of RTeCu is very similar to that of a typical telluride and also to values of δ

TABLE III. ^{125}Te Mössbauer data (4K) for Organotellurium Derivatives of Copper(I) and Mercury(II).

Compound	δ^a	Δ^b
$(C_2H_5)_2Te_2 \cdot CuCl$	0.27	9.7
$(C_2H_5)_2Te_2 \cdot CuBr$	0.36	9.3
$(n\text{-}C_4H_9)_2Te_2 \cdot CuCl$	0.40	9.4
$(n\text{-}C_4H_9)_2Te_2 \cdot CuBr$	0.37	9.4
$(n\text{-}C_5H_{11})_2Te_2 \cdot CuCl$	0.32	9.3
$(n\text{-}C_5H_{11})_2Te_2 \cdot CuBr$	0.36	9.2
$(C_6H_5)_2Te_2 \cdot CuCl$	0.32	9.5
$(C_6H_5)_2Te_2 \cdot CuBr$	0.38	8.9
$(p\text{-}C_2H_5OC_6H_4)_2Te_2 \cdot CuCl$	0.43	9.2
$(p\text{-}C_2H_5OC_6H_4)_2Te_2 \cdot CuBr$	0.24	9.2
$(CH_3)_2Te^c$	0.06	10.5
Ditelluride^c		
$(C_2H_5)TeCu$	0.15	9.7
$(n\text{-}C_4H_9)TeCu$	0.27	9.6
$(n\text{-}C_5H_{11})TeCu$	0.18	9.6
$(C_6H_5)TeCu$	0.20	9.4
$(p\text{-}C_2H_5OC_6H_4)TeCu$	0.31	9.5
$(C_6H_5)Te \cdot Sn(C_6H_5)_3{}^d$	0.15	9.2
$(p\text{-}C_2H_5OC_6H_4)Te \cdot Sn(C_6H_5)_3{}^d$	0.24	9.3
$(p\text{-}C_2H_5OC_6H_4)_2Te_2 \cdot HgCl_2{}^e$	0.18	5.1
$(p\text{-}C_2H_5OC_6H_4)_2Te_2 \cdot HgI_2{}^e$	0.20	5.1

$^a\pm0.08$ mm sec^{-1}, *vs.* ^{125}Sb/Cu. $^b\pm0.1$ mm sec^{-1}. ^{c}From reference [15]. ^{d}From reference [12]. ^{e}Compounds prepared by Dance.

observed for organo(triphenylstannyl)tellurides. Thus it is likely that the tellurium bridges two copper atoms in the structure, and that the bonds involve primarily tellurium p orbitals.

We have interpreted [15] quadrupole splitting data in terms of Townes—Dailey theory, thus we see the quadrupole splittings of tellurium(II) and tellurium(IV) compounds as being very much dominated by lone pair effects and argue that the observed values of Δ will be determined by the degree of imbalance in the occupation of the tellurium 5p orbitals. The observed splitting of around 9.6 mm sec^{-1} is rather less (by about 1 mm sec^{-1}) than that normally seen for compounds of the type R_2Te and implies less imbalance in the p orbital occupation. In fact this is consistent with the view that the p lone pair is involved to some degree in bonding, as would be the case in a three co-ordinate environment. However, the relatively large value of Δ implies the drift of electron density from tellurium to copper to be rather small. The data are, within experimental error, insensitive to the nature of the organic group.

The infra-red spectra of the compounds are rather featureless and, hence, are not tabulated. All showed a broad feature at 185 cm^{-1} which might, very tentatively, be assigned to $\nu(CuTe)$.

Diorganoditelluride Complexes of Copper(I) Halides

Both aliphatic and aromatic diorganotellurium ditellurides give compounds with CuCl or CuBr of stoicheiometry $R_2Te_2 \cdot CuX$ (Table I). The red to orange colour of the materials strongly suggest that the tellurium—tellurium bond has survived the complex forming reaction. Table II gives some far infra-red data for the two complexes for which assignments may most confidently be made. The position of $\nu(CuCl)$ close to 230 cm^{-1} is consistent with a bridging group [1]. Another band is seen at 170 cm^{-1} ($Ph_2Te_2 \cdot CuCl$) or 180 cm^{-1} ($Et_2Te_2 \cdot CuCl$). This may arise from activation of $\nu(TeTe)$ on coordination ($\nu(TeTe)$ for Ph_2Te_2 is reliably assigned [16] at 167 cm^{-1}; alternatively the mode may be $\nu(CuTe)$ (*cf.* RTeCu above). Probably, it is essentially $\nu(TeTe)$ activated by coupling with $\nu(CuTe)$; hence the label in Table II is probably a little optimistic.

Each tellurium atom in a ditelluride may, in principle, co-ordinate. The vibrational spectrum does not enable us to differentiate situations in which one tellurium atom co-ordinates from those in which both are involved since both situations may lead to activation of $\nu(TeTe)$. Mössbauer spectroscopy should be more helpful. However, the experimental line width ($\Gamma_{1/2}$) for organotellurium compounds is of the order of 5—6 mm sec^{-1}, hence two tellurium atoms of similar δ and Δ may be difficult to differentiate. However, the spectra of the complexes (Table III) gave good computer fits for one quadrupole doublet with satisfactory χ^2 values. The implication is therefore that both tellurium atoms are equivalent and, hence, both probably co-ordinated. The chemical isomer shifts (δ) are, within experimental error, insensitive to R in R_2Te_2 on to X in CuX and are similar to values expected for the parent ditellurides. Thus, following the reasoning given above in the discussion of RTeCu, we conclude that no significant change in hybridisation occurs at tellurium on co-ordination to copper(I) halides.

The quadrupole splitting data (Δ) are all fairly similar, although there is a tendency for the value for the bromo-complex to be a little lower (three out of five cases). In each case we see a lowering from values typical of free ditellurides [15], an observation consistent with co-ordination of the p-lone pair leading to a lowering of the p orbital imbalance. If we assume the bonding involving tellurium to involve only tellurium 5p orbitals, we can define U_x, U_y and U_z as occupation numbers for the tellurium $5p_x$, $5p_y$ and $5p_z$ orbitals respectively, then we may take our earlier results [15] and allow U_x ($\equiv U_{Te-Te}$) = 1.0, U_y ($\equiv U_{Te-C}$) = 1.1. Using a quadrupole splitting of 9.3 (the average of the ten determined) we calculate [15] U_z = 1.83. This implies a very small drift of electrons from tellurium to copper (U_z = 2.0 for the free ditelluride). That the quadrupole splitting can be used as some measure of the strength of the co-ordinate inter-
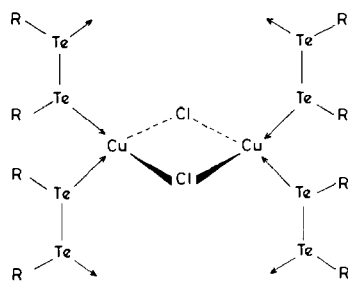
Figure. Possible structure for $R_2Te_2 \cdot CuCl$.

action is illustrated by the two mercury(II) complexes in Table III. Although δ is very comparable with values seen in the copper(I) series, Δ is reduced to 5.1 mm sec^{-1} (hence $U_z = 1.48$) illustrating the greater Lewis acid strength of HgX_2 than CuX with respect to $(p\text{-}C_2H_5OC_6H_4)_2Te_2$.

The spectroscopic data lead to the conclusion that both tellurium atoms are weakly co-ordinated to copper(I) and that the halide ligands are bridging (the complexes are not electrolytes, hence ionic formulations may be eliminated). A structure that accommodates the available data is shown schematically in the Figure.

Although the preparations of the complexes afforded crystals, these were not immediately suitable for crystallographic investigation. To date all attempts to recrystallise the complexes have led to decomposition.

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