The Reactivity of 2-(2'-Pyridyl)phenyl(*p*-ethoxyphenyl)tellurium(II) towards Copper(I) and Copper(II) Halides

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Abstract

The reaction of 2-(2'-pyridyl)phenyl(*p*-ethoxyphenyl)tellurium(II), RR'Te, with copper(I) chloride in the cold gave an air sensitive yellow product, $Cu_3Cl_3(RR'Te)_2$ (0.5 CH_3CN) (**1**). **1** under reflux in air changes to the green $Cu_2Cl(RR'Te)$ (0.5 EtOH) (**2**). The reaction of RR'Te with copper(II) chloride or bromide under mild conditions afforded the white materials CuCl(RR'Te) (**3**) and $CuBr(RR'Te)(H_2O)$ (**4**), but more forcing conditions (reflux) produced yellowish green $Cu_3Cl_3(RR'Te)(H_2O)$ (**5**) and brown $Cu_2Cl_2(RR'Te)$(0.5 EtOH) (**6**) from the $CuCl_2$ reaction.

The compounds have been studied using IR, NMR (^1H, ^{13}C), ESR and visible spectroscopies. **3** and **4** are simple copper(I) complexes, but the other materials are more complex and are discussed in terms of the labilisation of organic groups from tellurium to copper(I) centres.

Introduction

There is rapidly developing interest in the coordination chemistry of organotellurium compounds [1–4]. One of several reasons for this interest is the fact that coordination may play a role in the mechanism of the metal–organic vapour phase epitaxy (MOVPE) of tellurium semiconductors [5]. Recently, in a study of the reaction of 2-(2'-pyridyl)phenyl(*p*-ethoxyphenyl)tellurium(II) (RR'Te) with $HgCl_2$, labilisation of the *p*-ethoxyphenyl group from tellurium to mercury was noted and the phenomenon was termed 'reverse' *trans*-metallation [6]. In order to explore the generality of this reaction the behaviour of RR'Te with other metal centres is under investigation. This paper reports on reactions with copper(II) and with copper(I) both directly and produced *in situ* by reduction of copper(II).

Experimental

2-(2'-Pyridyl)phenyl(*p*-ethoxyphenyl)tellurium(II), RR'Te, was prepared by the literature method [7].

Preparation of Complexes (see Table 1 for numbering scheme)

Complex 1

To a cold solution of RR'Te (100 mg) in ethanol (10 cm^3) was added a solution of copper(I) chloride (23 mg) in a diethyl ether–acetonitrile (1:1 vol./vol.) mixture (10 cm^3) whilst passing argon. The contents of the flask were stirred at r.t. for 2 h. The removal of excess solvent with a flow of dry argon gave a pale yellow product which was filtered, washed with amounts of ethanol or acetonitrile and dried *in vacuo*.

Complex 2

To a solution of copper(I) chloride (23 mg) in an acetonitrile–ethanol mixture (1:1 vol./vol.) (10 cm^3) was added a solution of RR'Te (100 mg) in ethanol (10 cm^3). The reactants were refluxed for 1.3 h. A green coloured solution was obtained, slow evaporation of which gave a green solid which was dried *in vacuo*.

Complex 3

To a solution of copper(II) chloride (16 mg) in acetonitrile (10 cm^3) was added a solution of RR'Te (48 mg) in acetonitrile (10 cm^3). The mixture was gently warmed following which the excess solvent was removed under a stream of dinitrogen to afford a white product which was filtered, carefully washed with acetonitrile and dried *in vacuo*.

Complex 4

To a solution of copper(II) bromide (28 mg) in acetonitrile (10 cm^3) was added a solution of RR'Te (50 mg) in acetonitrile (10 cm^3). The mixture was gently warmed under dinitrogen and a white compound separated out. The product was filtered, washed with acetonitrile and dried *in vacuo*.

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TABLE 1. Analytical and ESR data for copper complexes

Complex no.	Formula[a]	C	H	N	Melting point (℃)	g
1	$Cu_3Cl_3(RR'Te)_2(0.5\ MeCN)$ (yellow)	41.2 (41.7)	3.04 (3.16)	3.07 (3.11)	120–128(d)	
2	$Cu_2Cl(RR'Te)(0.5\ EtOH)$ (green)	40.8 (40.8)	3.50 (3.40)	2.45 (2.38)	170–172(d)	2.06
3	$CuCl(RR'Te)$ (white)	47.5 (45.5)	3.47 (3.39)	2.86 (2.79)	240–242(d)	
4	$CuBr(RR'Te)$ (white)	40.3 (41.7)	3.03 (3.11)	2.94 (2.56)	203–205	
5	$Cu_3Cl_3(RR'Te)(H_2O)$ (yellow–green)	31.6 (31.8)	2.69 (2.77)	1.94 (1.95)	>270	2.15
6	$Cu_2Cl_2(RR'Te)(0.5\ MeCN)$ (brown)	38.4 (38.5)	3.09 (3.20)	2.22 (2.24)	190–192(d)	2.15

[a] RR'Te = 2-(2'-pyridyl)phenyl(*p*-ethoxyphenyl)tellurium(II).

Complexes 5 and 6

Ethanolic solutions (10 cm^3) of copper(II) chloride (16 mg) and RR'Te (48 mg) were mixed to give an initially colourless solution which, on refluxing for 2 h, became yellowish green. Slow evaporation gave a green product at the bottom of the container and a brown product on the walls. Mechanical separation followed by recrystallisation from ethanol yielded the green (5) and brown (6) products.

Analytical and Physical Data

Elemental analyses were performed by Elemental Microanalysis Ltd., Exeter Road, Oakhampton, Devon, EX20 1QA.

Melting points (uncorrected) were determined with a Gallenkamp electrically heated apparatus. Infrared spectra for KBr discs and nujol mulls in CsI supports were obtained with a Perkin-Elmer FTIR 1710 instrument. NMR data were obtained with a Bruker AC 300 spectrometer at 300 and 35.4 MHz for ^1H and ^{13}C, respectively. The internal reference was Me_4Si in both cases. Some X-band ESR data were obtained with a JEOL JES-FE 3X9 spectrometer (field range 3000 ± 2500 gauss). Absorption electronic spectra were obtained with a Shimdazu UV–Vis recording spectrophotometer, SP-300.

Results

Table 1 presents analytical data for the complexes **1**–**6**, together with ESR data where appropriate. Table 2 compares ^1H NMR data for the copper(I) complexes with those for the free ligand, RR'Te, and the recently reported R'HgCl·2RTeCl [6].

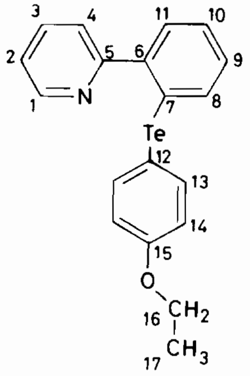

Fig. 1. Atom numbering scheme relating to Tables 2 and 3.

Discussion

The reaction of 2-(2'-pyridyl)phenyl(*p*-ethoxyphenyl)tellurium(II), RR'Te with solutions of copper(I) chloride in mixed solvents gives an ESR silent yellow complex of stoicheiometry $Cu_3Cl_3(RR'Te)_2(0.5\ CH_3CN)$ (**1**). The material is of limited stability in air, particularly when in solution. The CH_3CN content (required to give a good analytical fit) is confirmed by IR analysis; the IR spectrum also confirms the presence of both R and R' groups. By contrast, the reaction of RR'Te with acetonitrile solutions of copper(II) salts gave the compounds **3** and **4** in Table 1 which have the stoicheiometry of simple copper(I) complexes, CuX(RR'Te) (X = Cl, Br); these compounds are also ESR silent and colourless.

The comparison of ^1H NMR data (Table 2) for compounds **1**, **3** and **4** with that for RR'Te and for the recently reported [6] R'HgCl·2RTeCl reveal that

TABLE 2. ^{1}H NMR data for copper(I) complexes[a]

Compound (solvent)		δ Values (ppm, vs. TMS)		
RR′Te	1.45 (t, C17)	4.08 (q, C16)	6.85 (d, C14)	
($CDCl_3$)	7.05 (t, C3)	7.25 (m, C4, C5, C8)	7.78 (d, C2)	
	7.85 (d, C13)	7.95 (2t, C9, C10)	8.74 (d, C11)	
$Cu_3Cl_3(RR'Te)_2$ (**1**)	1.40 (t, C17)	4.00 (q, C16)	6.75 (d, C14)	
($CDCl_3$)	7.05 (t, C4)		7.25 (m, C2, C3, C)	
	7.45 (d, C5)	7.55 (d, C8)	7.65 (d, C13)	
	7.70 (t, C10)	8.80 (d, C11)		
CuCl(RR′Te) (**3**)	1.25 (t, C17)	3.95 (q, C16)	6.95 (d, C14)	
(dmso-D_6)		7.65 (d, C13)	7.85 (t, C3)	8.00 (t, C9)
	8.25 (t, C9)	8.35 (d, C5)	8.45 (t, C10)	8.55 (d, C8)
	8.65 (m, C4, 5, 8)	8.95 (d, C2)	9.55 (d, C11)	
CuBr(RR′Te) (**4**)	1.25 (t, C17)	3.95 (q, C16)	6.95 (d, C14)	
(dmso-D_6)	7.55 (d)	7.65 (d, C13)	7.90 (t, C3)	8.05 (t, C9)
	8.25 (t, C9)	8.35 (d, C5)	8.50 (t, C10)	8.44 (d, C8)
	8.65 (m, C4, 5, 8)	8.75 (d, C2)	9.00 (d, C2)	9.45 (d, Cl1)
(R′HgCl)(RTeCl)[b]	1.40 (t, C17)	4.04 (q, C16)	6.95 (d, C14)	
($CDCl_3$)	7.18 (d, C13)	7.35 (t, C3)	7.50 (t, C4)	
	7.60 (t, C10)	8.00 (t, C9)	8.20 (d, C5)	
	8.25 (d, C8)	8.60 (d, C2)	8.8 (d, C11)	

[a] See Fig. 1 for atom numbering. [b] Ref. 6.

TABLE 3. ^{13}C NMR data (ppm) for copper(I) complexes[a]

Compound (solvent)	Chemical shift values, δ					
	C1	C2	C3	C4	C5	C6
	C7	C8	C9	C10	C11	C12
	C13	C14	C15	C16	C17	
RR′Te	126.30		128.10		126.30	138.80
($CDCl_3$)	156.70	121.50	136.20	119.90	149.10	109.70
	141.30	115.70	159.70	63.20	14.70	
CuCl(RR′Te) (**3**)		132.17–133.15(m)	128.19	132.17–133.15(m)	126.30	133.60
(dmso-D_6)	152.55	121.11	132.17–133.15(m)	132.17–133.15(m)	145.57	
	143.94	115.91	160.66	63.40	14.44	
CuBr(RR′Te) (**4**)	126.48	132.17–133.15(m)	128.18	123.17–132.17	126.51	134.32
(dmso-D_6)	151.95	122.53	132.17–133.15(m)	133.15(m)	145.20	126.54
	144.02	115.96	160.70	63.42	14.35	
$(R'HgCl)(RTeCl)_2$[b]	134.24	138.45	123.88	130.97	127.47	142.02
	153.72	127.77	139.88	120.47	143.64	
	137.81	114.42	158.37	62.76	14.88	

[a] See Fig. 1 for atom numbering. [b] Ref. 6.

compound **1** is remarkably similar to the mercury derivative and rather different to **3** and **4**. The spectra of **3** and **4** (in dmso-D_6) show doubling of resonances compared with the spectrum of RR′Te; the data are consistent with some dissociation of the complexes in solution

$$CuX \cdot RR'Te + dmso\text{-}D_6 \rightleftharpoons CuX \cdot dmso\text{-}D_6 + RR'Te$$

i.e. the behaviour is that expected of copper(I) complexes in a coordinating solvent. The ^{13}C NMR data (Table 3) for **3** and **4** are also consistent with the presence of coordinated and free RR′Te in dmso-D_6 solution.

The data for **1** cannot be accounted for in this way. It is known that the reaction of RR′Te with $HgCl_2$ leads to a redistribution of organic groups between the metal centres and the isolation of R′HgCl·2RTeCl. The great similarity of the ^1H NMR data for **1** and the mercury complex lead us to speculate that the compound should be formulated $(R'Cu)_2(RTeCl)_2(CuCl)$, i.e. we suggest that the labilisation of groups from tellurium to, particularly, d^{10} ions may be general. The data available are insufficient to merit further speculation concerning the crystal and molecular structure of **1**. The known yellow colour of RTeCl [8] may explain the yellow colour of **1**. A novel synthesis of organo–copper(I) complexes is indicated.

Complex **1** (very readily) and complex **3** (reflux in air) may be oxidised to ESR active copper(II) species, two products **5** and **6** arising from (**3**) and one product **2**, from compound **1**. These materials are not well characterised and little comment is possible. They were sufficiently soluble in chloroform for UV spectra to be measured. RR′Te in chloroform gives a major peak at 225 nm which is essentially unshifted in the copper(II) complexes. A shoulder at 270 nm for RR′Te is not discernable in the complex spectra and the ligand band at 360 nm undergoes a significant blue shift to 308 nm in the complex spectra. Thus **2**, **5** and **6** give identical UV spectra which differ significantly from that of free RR′Te. The ESR spectra of **5** and **6** (Table 1) are identical and broad, so broad that no g anisotropy can be resolved. The spectrum of **2** is less broad and some suggestion of g anisotropy is seen, but perpendicular and parallel components are not clearly resolved (the g value for the centre of the spectrum is cited in Table 1). The broadly similar UV and ESR data for **5** and **6** suggest the stoicheiometries of Table 1 would be met by formulations (CuCl)(R′CuCl)(RTeCuCl), i.e. '$Cu_3Cl_3RR'Te$' (**5**) and (R′CuCl)(RTeCuCl), i.e. '$Cu_2Cl_2RR'Te$', (**6**). Unfortunately, the materials are not of good crystalline structure and crystallographic confirmation of these speculations is not possible, however variations of RR′Te may provide more crystalline materials from which further evidence for the 'reverse *trans*-metallation' reaction of organyl tellurium ligands may be forthcoming.

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