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UNSYMMETRICAL DITELLURIDES AS LIGANDS: REACTIONS WITH COPPER(I) AND MERCURY(II) HALIDES

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Summary

Reactions between copper(I) halides or mercury(II) halides and equimolar mixtures of diphenylditelluride (R_2Te_2) and bis(*p*-ethoxyphenylditelluride (R'_2Te_2) give materials of stoichiometry $[RR'Te_2 \cdot 2MX_n]$ (M = Cu, X = Cl, Br, $n = 1$; M = Hg, X = Cl, Br, $n = 2$). Change of solvent from propionitrile to ethanol gives $[(RTe)(R'Te)Hg_2Cl_2]_m$. Mass spectroscopic data and Raman spectra are presented and discussed in terms of the probability that the unsymmetrical ditelluride is present as a ligand. ν(TeTe) for PhTeTe(C_6H_4OEt-*p*) occurs at 170.5 cm^{-1} in benzene solution.

Introduction

Some years ago we reported on unsuccessful efforts to isolate unsymmetrical ditellurides, RTeTeR′ [1], but subsequently suggested that mixtures of symmetrical ditellurides (R_2Te_2, R'_2Te_2) are in an entropy controlled equilibrium [2]:

$$R_2Te_2 + R'_2Te_2 \rightleftharpoons 2\ RTeTeR' \qquad (K \simeq 4)$$

This view was subsequently confirmed by ^{125}Te NMR studies [3,4], which also revealed that the presence of dioxygen in the solutions gave side reactions to afford new radical species. Another group has also commented on these equilibria [5] and a claim to have isolated small quantities of an unsymmetrical ditelluride exists i.e. $C_4F_9TeTeC_2F_5$ (identified by mass spectroscopy) [6]. However, compounds such as (aryl)TeTe(aryl′), although defined in solution [4] and recognised in the mass spectrometer [2], have defied isolation as solids.

Ditellurides will form complexes with those metal ions e.g. copper(I), mercury(II), which may be described as soft acids [7,8] and in some, but not all, instances the tellurium—tellurium bond remains intact. It occurred to us that

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the unsymmetrical ditellurides might show different Lewis basicity to soft acids than their symmetrical counterparts. In this paper, therefore, we describe experiments in which salts of copper(I) and of mercury(II) are reacted with solutions containing equimolar mixtures of Ph_2Te_2 and $(p\text{-EtO}\cdot C_6H_4)_2Te_2$.

Experimental

Ph_2Te_2 [9] and $(p\text{-EtO}\cdot C_6H_4)_2Te_2$ [10] were prepared by literature methods. Copper(I) chloride and bromide were freshly prepared and all reactions described below were carried out under dinitrogen.

Copper(I) complexes. Diphenylditelluride (2 m*M*) and bis(*p*-ethoxyphenyl) ditelluride (2 m*M*) were dissolved in dry diethyl/ether and added, dropwise, to a solution of copper(I) chloride (or bromide) (2 m*M*) in propionitrile. The temperature was raised to 30—40°C and the solution stirred for 15 min. On cooling the reaction mixtures, orange to red precipitates of the complexes were obtained.

Mercury(II) complexes. Diphenylditelluride (0.5 m*M*) and bis(*p*-ethoxyphenyl)ditelluride (0.5 m*M*) were dissolved under dinitrogen in the minimum volume of propionitrile. To this solution was added a solution of mercury(II) chloride (or bromide) (1 m*M*) in propionitrile and the mixture was heated under reflux for 30 min. The resulting yellow complex was filtered, washed with ethanol and dried in vacuum.

The above preparations involving mercury(II) salts were repeated in ethanol, yellow materials were obtained.

Physical measurements. Infra-red spectra were recorded using Perkin—Elmer 457 and 599 B spectrometers. Mass spectra were recorded at 70 eV with an AE1 MS9 instrument. Raman data (300—26 cm^{-1}) were obtained with the Coderg RS100 at the Chemistry Department, University of Leicester, using 6471 Å (15453 cm^{-1}) Kr laser excitation. Samples were examined as microcrystalline solids or as solutions in de-oxygenated benzene. (We are grateful to Dr. D.M. Adams for access to the Raman spectrometer).

Results

Elemental analysis (C, H, Te) for the complexes are gathered into Table 1. The major features of the mass spectra are gathered into Table 2 and vibrational spectroscopic data at low frequency are presented in Table 3.

Discussion

The complexes reported have a stoichiometry $RR'Te_2\cdot 2MX_n$ ($M = Cu$, $n = 1$; $M = Hg$, $n = 2$) in contrast to those reported earlier [7] which were $R_2Te_2\cdot MX_n$. Preparative conditions were slightly different (change of solvent) and, in the mercury(II) chloride case, use of ethanol as solvent afforded a different type of complex $[(RTe)(R'Te)Hg_2Cl_2]_m$, a type which has been discussed by Dance and Jones [8]. It would seem that, as preparative conditions are varied, the sequence

$$MX_n + R_2Te_2 \rightarrow [MX_n\cdot R_2Te_2] \xrightarrow{MX_n} [(MX_n)_2R_2Te_2] \rightarrow [RTeMX_{n-1}]_m \qquad (1)$$

is observed. The preliminary coordination of two metal atoms prior to Te—Te bond rupture is not unreasonable. It should be pointed out that ethanolic solutions of ditellurides are unstable to light and dioxygen [4], hence all preparations described were carried out under dinitrogen.

The analytical data (Table 1) support the isolation of unsymmetrical ditelluride complexes and IR data (4000—200 cm^{-1}) confirm that the groups phenyl- (R) and *p*-ethoxyphenyl- (R') are present. The mass spectra (Table 2) likewise confirm this.

The mass spectra of the copper(I) complexes resemble those obtained for simple ditelluride mixtures [2] and are thus probably precisely that i.e. we are observing ligand spectra subsequent to thermolysis. The mercury(II) data are more interesting. The chloro-complex in particular seems more volatile and mercury containing fragments are seen. Doubtless some thermolysis is also seen, which will account for $R_2Te_2^+$ and $R'_2Te_2^+$ but the relative intensity of $RR'Te_2^+$ is encouragingly high suggesting that (2) occurs:

$$[HgCl_2 \cdot RR'Te_2]\ (g) + e \rightarrow HgCl_2\ (g) + RR'Te_2^+\ (g) + 2e \qquad (2)$$

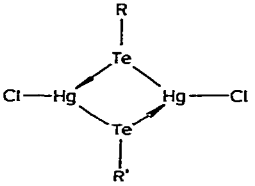
In the case of the less volatile bromide the fact that $[OH \cdot C_6H_4 \cdot Ph]^+$, derived from sequence 3, is observed as the base peak is also significant:

$$RR'Te_2^+ \xrightarrow{-Te} RR'Te^+ \xrightarrow{-Te} RR'^+ \xrightarrow{-C_2H_4} [OH \cdot C_6H_4 \cdot Ph]^+ \qquad (3)$$

Thus, despite complications arising from associated thermal decomposition, the data provide encouraging support for the view that the unsymmetrical ditellurides have been isolated as complexes.

TABLE 1

ANALYTICAL DATA FOR COPPER(I) AND MERCURY(II) COMPLEXES OF MIXED DITELLURIDES ($R = Ph$, $R' = p\text{-}EtO \cdot C_6H_4$)

Complex	Found (calcd. (%))		
	C	H	Te [a]
$RR'Te_2 \cdot 2CuCl$	24.1 (25.8)	2.50 (2.20)	—
$RR'Te_2 \cdot 2CuBr$	22.9 (22.7)	2.00 (1.90)	33.7 (34.5)
$RR'Te_2 \cdot 2HgCl_2$	16.7 (16.8)	1.50 (1.42)	24.9 (25.6)
$RR'Te_2 \cdot 2HgBr_2$	13.9 (14.3)	1.00 (1.20)	20.4 (21.7)
[b,c] 	18.3 (18.2)	1.60 (1.50)	26.6 (27.5)

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[a] Tellurium was analysed by the method of Suttle [11]. [b] Prepared from ethanol. [c] Found Cl, 8.10%, calcd. Cl, 7.67%.

TABLE 2

MASS SPECTROSCOPIC DATA FOR COMPLEXES OF COPPER(I) CHLORIDE AND BROMIDE, MERCURY(II) CHLORIDE AND BROMIDE WITH UNSYMMETRICAL DITELLURIDES ($R' = p\text{-EtO}\cdot C_6H_4$, $R = Ph$)

Ions	*m/e* [a]	$RR'Te_2\cdot 2CuCl$ (rel. int. (%))	$RR'Te_2\cdot 2CuBr$ (rel. int. (%))	$RR'Te_2\cdot 2HgCl_2$ (rel. int. (%))	$RR'Te\cdot 2HgBr_2$ (rel. int. (%))
$R'_2Te_2^+$	502	1,2	1,0	24,6	1,0
$RTeTeR'^+$	458	7,0	4,5	47,5	2,2
$R_2Te_2^+$	414	2,2	2,1	13,1	2,0
R'_2Te^+	372	80	100	100	42
$R'TeR^+$	328	100	100	100	4
R_2Te^+	284	—	3,0	—	1,8
$(p\text{-}CH_3OC_6H_4)_2^+$	214	100		100	
$R{-}R'^+$	198	77	77	100	
$(p\text{-}OH\cdot C_6H_4)_2^+$	186	100	85	100	
$(CH_3OC_6H_4{-}Ph)^+$	184	100	100	100	54
$OH\cdot C_6H_4\cdot Ph^+$	169	100	100	100	100
R_2^+	154	100	45		14
R^+	77	95	100	100	5
R_2Hg^+	356			32,8	
$RHgCl^+$	315			26,8	
RHg^+	279			50,8	
$HgCl_2^+$	277			57,8	
$R'HgBr^+$	404				1,8
$HgBr_2^+$	363				10,5
$RHgBr^+$	359				5

[a] Relative to ^{1}H, ^{12}C, ^{130}Te, ^{35}Cl, ^{81}Br, ^{203}Hg.

TABLE 3

RAMAN DATA ($\Delta\nu < 210$ cm^{-1}) FOR DITELLURIDES AND THEIR MERCURY COMPLEXES ($R = Ph$, $R' = p$-EtO·C_6H_4)

$\Delta\nu$ (cm^{-1})					
$RR'Te_2 \cdot 2HgCl_2$	$RR'Te_2 \cdot 2HgBr_2$	R_2Te_2 (benzene)	R'_2Te_2 (benzene)	$R_2Te_2 + R'_2Te_2$ (benzene)	Assignment
206w	204w				
	186vw				
				185	ν(TeTe)
		173m	188m	175	
				170.5	
144w					
	133vs				ν(HgTe) + ν(TeTe)
119vs					
60m	53w				
35s	38.5m				

Given that a solution of two symmetrical ditellurides will also contain the unsymmetrical ditelluride [2,4]:

$$R_2Te_2 + R'_2Te_2 \rightleftharpoons RTeTeR' \qquad (4)$$

Raman studies of such solutions should show three ν(TeTe). This is indeed the case (Table 3). [p-EtO·C_6H_4TeTePh] shows ν(TeTe) at 170.5 cm^{-1}, a slightly lower frequency than the corresponding modes for Ph_2Te_2 (175 cm^{-1}) and (p-EtOC_6H_4)$_2Te_2$ (185 cm^{-1}).

The copper(I) complexes decomposed in the laser beam but the yellow mercury(II) complexes gave good spectra. These were dominated by intense bands at 119 cm^{-1} (chloride) and 133 cm^{-1} (bromide). We assign those to a mixture of ν(TeHg) [8] and ν(TeTe) i.e. we postulate that ν(TeTe) undergoes a shift to lower wave number on coordination. The implied bond weakening helps to explain the relative ease of the final stage of equation 1. The band at 186 cm^{-1} for $RR'Te_2 \cdot HgBr_2$ is likely to be ν(HgBr) but the low intensity is surprising. Unfortunately, the fact that ν(TeTe) is not distinguishable as such removes the possibility of characterising the ligand as unambiguously the unsymmetrical ditelluride.

In conclusion, the new data do not conflict with the view that complexes of unsymmetrical ditellurides have been isolated, but they do not totally eliminate the possibility of fortuitous equimolar mixtures. The Raman data do not lend convincing support to large differences between the tellurium atoms in RTeTeR', thus any success in preferentially isolating complexes of the unsymmetrical ligand is likely to arise from solubility differences.

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References

1 W.R. McWhinnie and P. Thavornyutikarn, J. Organometal. Chem., 35 (1972) 149.
2 N.S. Dance, W.R. McWhinnie and C.H.W. Jones, J. Organometal. Chem., 125 (1977) 291.
3 P. Granger, Proc. 3rd Int. Symposium on Organic Se and Te Compounds (Université de Metz, 1979) p. 305.
4 P. Granger, S. Chapelle, W.R. McWhinnie and A.Z. Al-Rubaie, J. Organometal. Chem., 220 (1981) 149.
5 P.H.A. Laur, Proc. 3rd. Int. Symposium on Organic Se and Te compounds (Université de Metz, 1979) p. 217.
6 C.D. Dejardins, H.L. Pagie, B.J. Passmore and P.J. Taylor, J. Chem. Soc. (Dalton Trans), (1975) 488.
7 I. Davies, W.R. McWhinnie, N.S. Dance and C.H.W. Jones, Inorg. Chim. Acta, 29 (1978) L217.
8 N.S. Dance and C.H.W. Jones, J. Organometal. Chem., 152 (1978) 175.
9 W.V. Farrar, Research (London), 4 (1951) 177.
10 G.T. Morgan and H.D.W. Drew, J. Chem. Soc., (1925) 2307.
11 F.H. Kruse, R.W. Sauftner and J.F. Suttle, J. Anal. Chem., 25 (1953) 500.