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A SPECTROSCOPIC INVESTIGATION OF SOME ORGANOTELLURIUM-MERCURY(II) COMPLEXES

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Summary

Organotellurium—mercury(II) complexes of the form $R_2Te \cdot HgX_2$ (R = Ph, p-EtOC₆H₄, X = Cl, Br, I), α -Me₂TeI₂ \cdot HgBr₂, Ph₂Hg \cdot (Me₂TeI₂)₂, (p-EtOC₆H₄Te)₂-Hg, p-EtOC₆H₄Te \cdot HgCl, $R_2Te_2 \cdot$ HgX₂ (R = p-EtOC₆H₄, X = Cl, Br, I), have been studied using ¹²⁵Te Mössbauer spectroscopy and infrared and Raman spectroscopy. The spectroscopic data are interpreted in terms of possible structures for the complexes.

Introduction

A number of complexes formed from organotellurium compounds and mercury(II) halides are reported in the literature [1]. Many of these complexes were prepared originally to aid in the identification of the organotellurium compounds, and have not been further investigated. ¹²⁵Te Mössbauer spectroscopy has proved a valuable tool in previous studies of organotelluriums [2,3] by providing information on the stereochemistry and bonding at tellurium, and sufficient data are now available in the literature for tentative structural assignments to be made from comparison with Mössbauer parameters of compounds of known structures.

In the present paper structural assignments are made for a number of organotellurium—mercury(II) complexes, a number of which have not previously been described in the literature. A facile method for the preparation of dialkyltellurium dibromides and dichlorides from the readily available dialkyltellurium diiodides [4] is also described.

Results and discussion

¹²⁵Te Mössbauer parameters and vibrational spectroscopic data are collected in Tables 1 and 2, respectively. 176

TABLE 1

¹²⁵Te MÖSSBAUER DATA

Compound	δ (±0.1 mm s ⁻¹) ^{<i>a</i>}	Δ (±0.1 mm s ⁻¹)	$\Gamma (mm s^{-1})$	
(p-EtOC ₆ H ₄) ₂ TeHgCl ₂	0.32	5.96	7.3	
Ph2TeHgCl2	0.33	6.05 ·	5.8	
(p-EtOC ₆ H ₄) ₂ TeHgBr ₂	0.37	6.0	5.3	
Ph2TeHgBr2	0.34	6.1	5.7	
(p-EtOC ₆ H ₄) ₂ TeHgI ₂	0.28	6.25	4.8	
Ph ₂ TeHgI ₂	0.27	6.04	5.4	
a-Me ₂ TeBr ₂ • HgI ₂	0.64	8.44	5.0	
a-Me ₂ Tel ₂ · HgBr ₂	0.58	8.36	5.2	
(Me2Tel2)2 - Ph2Hg	0.14	5.51	5.4	
p-EtOC ₆ H ₄ TeHgCl	0.30	4.86	6.0	
(p-EtOC6H4Te)2Hg	0.18	5.88	6.4	
p-EtOC6H4TeHgCl2	0.27	6.04	7.4	
(p-EtOC ₆ H ₄) ₂ Te ₂ HgCl ₂	0.18	5.14	5.7	
(p-EtOC6H4)2Te2HgBr2 (yellow)	0.23	5.82	6.6	
(p-EtOC ₆ H ₄) ₂ Te ₂ HgBr ₂ (brown)	0.35	8.75	7.6	
(p-EtOC ₆ H ₄) ₂ Te ₂ HgI ₂ (brown)	0.41	8.70	7.6	
$(p-EtOC_6H_4)_2Te_2HgI_2$ (yellow)	0.20	5.10	4.5	

^a δ with respect to I/Cu, with the source and absorbers at 4.2 K.

Complexes formed between diorganotellurides and mercury(II) halides

All complexes investigated were of the stoichiometry $R_2Te \cdot HgX_2$, (R = Ph, p-EtOC₆H₄, X = Cl, Br, I). The ¹²⁵Te Mössbauer parameters for the six complexes indicate that in all cases the tellurium atom is present in an environment similar to that in a triorganotellurium salt (cf. Ph₃Te⁺Cl⁻, δ 0.35 mm s⁻¹, Δ 5.83 mm s⁻¹) [5]. The parameters do not appear to be influenced by the choice

TABLE 2

Assignment	$Ph_2Te \cdot HgCl_2$		Ph2TeHgBr2		Ph ₂ TeHgI ₂		(p-EtOC ₆ H ₄) ₂ TeHgCl ₂	
	IR	R	IR	R	IR.	R	IR	R .
ν(TeC)	272s 261s	271(sh) 262m	270(sh) 261s	268(sh) 258s	269s 262(sh)	266s 256s	-278s	284s
v(Te—Br)								
v(HgX)	286s	283s	200s	197s		118vs or 95s	278s	284s
2 X v(Hg—X)						01000		
v(Te—Hg)		133vs		124vs		118vs		120s
(v')phenyl		236m		231w		231m		
Unassigned				2021		2011	344s 385m	344w
							208m	214m
		166w				196w		
						81s		

INFRARED AND RAMAN ASSIGNMENTS FOR ORGANOTELLURIUM—MERCURIC HALIDE COMPLEXES

of halogen, indicating that the type of bonding at tellurium is largely invariant within the series.

Diorganosulphides are known to form complexes in which the sulphur is trigonally coordinate [6]; such complexes are generally polymeric in the solid phase, being made up of $[R_2S^+ \cdot HgX] X^-$ units linked through bridging halide groups to give infinite chains. In view of the apparent presence of R_2Te^+ groups within these complexes, it is reasonable to suggest that they are of the type $[R_2Te^+-HgX] X^-$. Within the lattice it is probable that the mercury is surrounded by up to four distant groups, in a manner analogous to the organosulphide complexes [6]. The low solubility of the complexes in common organic solvents indicates that they are polymeric. Vapour pressure osmometric molecular weight determinations were unsuccessful because of low solubility.

In the analogous sulphide complexes the S-Hg-halogen bond angle in the $[R_2SHgX]^+$ units generally departs from linearity, typical values being 155° [6] and 135° [7]. It is probable that the telluride complexes are similarly distorted,

in which case the skeletal symmetry of the R Te⁺-Hg X unit is C_s . All vibra-

tional modes will thus be infrared and Raman active. Assignments for a number of modes in the infrared and Raman spectra are given in Table 2, but the bending modes below 100 cm⁻¹ are not assigned because of the presence of lattice vibrations. Of particular interest are the $\nu(Hg-Te)$, $\nu(Hg-X)$ and $\nu(Te-C)$ modes. Spectroscopic studies of the analogous sulphide complexes indicate that the Hg-S bond strength varies in the series $R_2SHgCl_2 > R_2SHgBr_2 > R_2SHgI_2$, with the strongest Hg-S bonds being formed for the more electronegative halogens [8]. The variations in $\nu(Hg-S)$ are however not large, and the variation in bond strength is probably small. Thus, if the same effect is observed for the telluride

EtOPh ₂ TeHgBr ₂		$EtOPh_2TeHgI_2$		$Me_2TeI_2 \cdot HgBr_2$		Me ₂ TeBr ₂		$Ph_3Hg \cdot 2Me_2TeI_2$	
IR	R	IR	R	IR	R	IR	R	IR	R
295s		295(br)			533w		533w	· · · · · · · · · · · · · · · · · · ·	533w 262s 248(sh)
					168s		188s		
					147s		158s		
	196m		101s		112vs				125s
					231w				
	116s		101s						
341e		341e	337.07						
380s		384m	007.4						
210s	211m	212m	202m						
	192w		150m						
	178w								

complexes, it might be expected to be apparent in the vibrational spectra, but not in the relatively insensitive Mössbauer parameters. From mass considerations and the assignment of $\nu(\text{Hg-S})$ in analogous complexes [9] to bands $\simeq 300$ cm⁻¹, the $\nu(\text{Hg-Te})$ mode might be expected in the region 100–150 cm⁻¹. In all complexes a strong band is present in the Raman spectrum at Δ 100–140 cm⁻¹, and is assigned as $\nu(\text{Hg-Te})$. There is a small decrease in $\nu(\text{Hg-Te})$ passing along the series R₂TeHgCl₂, R₂TeHgBr₂, R₂TeHgI₂, which would be consistent with the degree of positive charge at the tellurium atom, and thus the Te-Hg bond strength, being a function of the electronegativity of the halogen.

The ν (Te-C) modes are readily assigned to moderately strong bands in the region 250-280 cm⁻¹ for the phenyl derivatives. The Whiffen notation [10] is used to describe these vibrations, and the ν (Te-C) modes are designated as t and t' modes. A ring mode, "u", is also expected in this region, but is of variable intensity, and may be masked by the more intense bands. The positions of the two observed bands are in close agreement with those observed for Ph₂Te⁺-MeI⁻.

The $\nu(\text{Hg}-X)$ bands are assigned following Dalziel et al. [8]. Thus $\nu(\text{Hg}-\text{Cl})$ is expected in the region 250–300 cm⁻¹, $\nu(\text{Hg}-\text{Br})$ in the region 150–200 cm⁻¹ and $\nu(\text{Hg}-I)$ in the region 80–140 cm⁻¹. In all cases the bands assigned were the most intense bands in that region of the spectrum, and in all cases only a

single sharp band was observed, as expected for $R_2Te^+-Hg^-$; if the complexes were of the type $R_2Te-HgX_2$, then a more complex series of absorptions would be expected, as is observed for mercuric halide-diorganosulphide complexes [11]. In the case of Ph₂Te · HgI₂, two bands at Δ 118 and 95 cm⁻¹ are candidates for $\nu(Hg-Te)$ and $\nu(Hg-I)$, and it is not possible to give definitive assignments.

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α -Me₂TeI₂ + HgBr₂

The Mössbauer parameters for this complex are identical to those of α -Me₂TeBr₂ $(\delta 0.65 \text{ mm s}^{-1}, \Delta 8.5 \text{ mm s}^{-1})$ [2]. On prolonged storage samples of the complex decomposed, forming mercuric iodide and α -Me₂TeBr₂. The original complex can be regenerated by dissolving in ethanol and evaporating. The ease and mode of decomposition, and the Mössbauer parameters, indicate that the compound is a weak molecular complex of the type $Me_2TeBr_2 \cdot HgI_2$, in which halogen exchange has taken place between the starting materials; the same complex is formed from α -Me₂TeBr₂ and HgI₂ in ethanol. The formulation is also supported by the Raman spectrum, which contains strong bands at Δ 168 and 147 cm⁻¹, characteristic of ν (Te–Br) [12]. Some samples decomposed in the laser, producing Me_2TeBr_2 and HgI_2 , characterized by strong bands at Δ 188 and 158 cm⁻¹. The Mössbauer parameters indicate that the tellurium atom is in a similar environment to that for α -Me₂TeBr₂; in both cases the local environment is presumably ψ -trigonal bipyramidal [13], with axial bromine and equatorial methyl ligands. The values of ν (Te–Br) in α -Me₂TeBr₂ and the complex differ by about 20 cm⁻¹, implying that in the complex appreciable Hg--Br interactions are present, rather than a Hg---Te interaction.

No information is available on the molecular complexity of the compound; molecular weight determinations in benzene indicate complete dissociation, presumably to give Me_2TeBr_2 and HgI_2 .

The observation that halogen exchange has taken place during formation of .

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the complex, and that the complex readily dissociates in solution, prompted further investigation; if the complex is refluxed for a few minutes in a solvent in which α -Me₂TeBr₂ is soluble, but HgI₂ is insoluble, then pure Me₂TeBr₂ is obtained in quantitative yield. This novel preparative route is also applicable to: (1) Me₂TeI₂ and HgCl₂, in which case a complex is not isolable, but exchange takes place, producing Me₂TeCl₂ and HgI₂, and to: (2) Ph₂TeBr₂ and HgCl₂, producing Ph₂TeCl₂ and HgBr₂. The route is of particular interest for the dialkyltellurium halides; α -Me₂TeI₂ is readily prepared, but previous methods of conversion to Me₂TeBr₂ or Me₂TeCl₂ involve either reduction to the unpleasant dimethyl telluride, and oxidation to the appropriate dihalide, or formation of the dialkyltellurium base and addition of the appropriate halogen acid [4]; samples prepared in this way are difficult to dry, and invariably have low melting points. It is felt that the method described could be applied to the preparation of a large number of organotellurium halides and pseudohalides.

$2 Me_2 TeI_2 + Ph_2 Hg$

The ¹²⁵Te Mössbauer parameters indicate that there is only one type of tellurium site, and that the tellurium atoms are essentially in a trigonal environment, with other contacts being weak; thus a major disruption of the original four-coordinate Me_2TeI_2 molecules has taken place. From molar conductivity measurements, the complex approaches a 2/1 electrolyte in DMF, and the mass spectrum indicates that transfer of a phenyl group to tellurium has taken place. The ion peaks observed (Table 3) are consistent with the following ion decomposition routes:



The complete absence of Me_2Te^+ and the presence of PhMeTe⁺ would not be expected for a complex containing the dimethyltellurium group, while the absence of Ph_2Hg^+ and $PhHg^+$ implies that both phenyl groups have been trans-

TABL	E 3				
MASS	SPECTROSCOPIC	DATA	FOR	Ph2Hg(Me	2TeI2)2

m/e	Relative intensity	Species	
456	2	HgI2 ⁺	
406	8	PhHgI ⁺	
279	3	PhHg ⁺	
222	84	PhMeTe ⁺	
207	76	PhTe ⁺	
154	3	Ph ₂ ⁺	
142	100	MeI ⁺	
127	60	I+	
77	90	Ph ⁺	

ferred to tellurium. The above evidence is consistent with the presence of $PhMe_{2}Te^{+}$ in the complex. Within the mass spectrometer thermolysis apparently takes place producing cleavage of a Te—CH₃ bond; there is evidence that methyl groups are cleaved preferentially to phenyl groups [14], for example:

Ph₂MeTe⁺I⁻ \xrightarrow{e} Ph₂Te⁺ + MeI⁺ \swarrow PhMeTe⁺ + PhI⁺

and thus the observation of PhMeTe⁺ in the spectrum of the complex could result from the following sequence:

 $PhMe_{2}Te^{+} \xrightarrow{e} PhMeTe^{+}$

The low intensity peaks corresponding to Ph_2Hg^{+} , $PhHg^{+}$ and $PhHgI^{+}$ presumably arise from a secondary ion decomposition scheme, involving thermolysis.

The ${}^{13}C$ NMR spectrum of the complex in DMSO, prepared from isotopically enriched Me₂ 125 TeI₂, contains the resonances listed in Table 4. The resonances arising from the phenyl carbons are of particular interest. Two singlets of intensity 2 can be assigned to C(2) and C(3), while a singlet of intensity 1 is assigned



to C(4). C(1) produces a doublet, $J(^{125}\text{Te-C})$ 171.6 Hz, which is of lower intensity than expected because of the lower rate of relaxation for the non-proton bearing carbon atom. The observation of a doublet, resulting from $^{13}\text{C}-^{125}\text{Te}$

TABLE 4

¹³C PROTON DECOUPLED NMR DATA FOR Ph₂Hg(Me₂¹²⁵Tel₂)₂ in DMSO



aromatic resonances

Resonance	δ (ppm)	Height	Assignment	J(¹²⁵ Te-1 ³ C) (Hz)
8	142.66	98	C(2)	
Ъ	140.86	6	C(1)	171.6
	134.05	6		
c	132.54	106	C(3)	
đ	131.87	52	C(4)	

coupling is proof that the phenyl group is tellurium bonded; if it were bonded to mercury a singlet with characteristic (¹⁹⁹Hg—¹³C) side bands would be observed. The spectrum of the complex prepared from naturally abundant tellurium contained the expected single resonance for the tellurium-bonded carbon atom.

The Raman spectrum contains peaks corresponding to $\nu(\text{Te-CH}_3)$ at Δ 533 cm⁻¹, $\nu(\text{Te-Ph})$ at 248 and 262 cm⁻¹, assigned by comparison with Me₂TeI₂ [14] and various Ph₂TeX₂ compounds [15]. A strong band at Δ 125 cm⁻¹ is assigned to $\nu(\text{Hg-I})$. Although it is apparent that the complex contains [PhMe₂Te]⁺ units, it is not known whether the complex is best formulated as [PhMe₂Te⁺I⁻]₂ · HgI₂ or as [PhMe₂Te⁺]₂HgI₄²⁻. The band at Δ 125 cm⁻¹ in the Raman spectrum could be $\nu(\text{Hg-I})$ for either species; $\nu(\text{Hg-I})$ for red HgI₂ is found at Δ 114 cm⁻¹, and at Δ 150 cm⁻¹ in ethanol [16], while $\nu(\text{Hg-I})$ for [HgI₄]²⁻ is found at Δ 126 cm⁻¹ [17].

The conclusion that the complex is a telluronium salt provides the first evidence that organometallic reagents, such as Ph_2Hg , Ph_4Sn and Ph_4Pb , which have been extensively used in the preparation of organotellurium trihalides and diorganotellurium dihalides [18], can also be used to proceed one stage further to give triorganotelluronium salts. Attempts to proceed further, to form tetraorganotelluriums in a simple one step process failed:

 $Ph_2TeBr_2 + Ph_2Hg \rightarrow Ph_4Te + HgBr_2$

This may result from the insolubility of the supposed intermediate, $Ph_3Te^+Br^-$, in the solvent benzene.

The mass spectrum of the product indicated that the Ph_3Te^+ group had been formed, but an analytically pure sample of $Ph_3Te^+Br^-$ was not obtained because of contamination by HgBr₂.

$(EtOC_6H_4Te)_2Hg$

The ¹²⁵Te Mössbauer parameters indicate that the tellurium atom is trigonally coordinate. Molecular weight measurements in benzene indicate that the complex is dimeric in solution, but because of the low solubility of the complex, and the observation of some degree of decomposition in solution, this result may be erroneous. The visible spectrum of the solution contained a broad, weak absorption at 27000 cm⁻¹, a region in which a charge transfer band arising from Te—Te interactions has previously been observed [19]. The Raman spectrum also contains a band at Δ 176 cm⁻¹, but decomposition within the laser beam was observed, and the band could possibly arise from ν (Te—Te) for (p-C₂H₅-OC₆H₄Te)₂ [19]. The complex is only weakly conducting in DMF solution.

The available information indicates that this complex does not have a structure similar to that of the mercury ethyl mercaptide [20], which contains distinct R-S-Hg-S-R molecules within the lattice. The fact that the tellurium is trigonally coordinate is consistent with the presence of a structure similar to that of mercury methyl mercaptide [21], which is polymeric with bridging mercaptide groups. Alternatively the parent ditelluride moiety may be retained, with mercury atoms bridging between two tellurium atoms on adjacent ditelluride molecules.

p-*E*tOC₆H₄TeHgCl

The Mössbauer parameters indicate that for this complex the tellurium atom is again trigonally coordinate. The Raman spectrum contains an intense peak at Δ 119 cm⁻¹, which is assigned to ν (Te-Hg). Weak bands at Δ 279 and 288 cm⁻¹ may represent ν (Hg-Cl) but are of very low intensity. The extreme insolubility of the complex in common organic solvents indicates that it is probably polymeric, while in DMF it is weakly conducting. There is no evidence of ν (Te-Te) in the Raman spectrum, and the most reasonable structure consistent with the data is shown below:



This structure is similar to those suggested for $(p-\text{EtOC}_6\text{H}_4\text{Te})_2\text{Hg}$; the presence of the electronegative Cl ligand would aid in the transfer of some degree of positive charge to the tellurium, resulting in a stronger Te—Hg bond in this compound than in $(\text{EtOC}_6\text{H}_4\text{Te})_2\text{Hg}$; the compound may more closely represent

+ Te⁺ Hg⁺ -- Hg⁻⁺ Cl⁻. Consistent with a stronger Te⁻⁻ Hg bond, the ¹²⁵Te Mössbauer

quadrupole splitting is 4.86 mm s⁻¹ compared with 5.88 mm s⁻¹ for $(EtOC_6H_4Te)_2$ -Hg.

Complexes of diorganoditellurides with mercuric halides

There appear to be two distinct classes of compounds. The majority are light yellow solids of stoichiometry RTeHgX₂ or R₂Te₂HgX₂ (R = p-EtOC₆H₄, X = Cl, Br, I). The ¹²⁵Te Mössbauer parameters indicate that there is only one distinct tellurium site, and that the tellurium is trigonally coordinate. There is no evidence of a strong Te—Te bond in the Raman spectrum, but ν (Te—Te) would be affected by coordination of tellurium to another atom and it is possible that there still exists a Te—Te bond within the complexes. The complexes of the type RTeHgX₂ may be formed by the inclusion of a further mole of mercuric halide within the R₂Te₂HgX₂ lattice. Such complexes are well documented in organosulphide systems [11].

The presence of trigonally coordinate tellurium is consistent with the presence of $(R_2Te_2)^{2+}Hg \cdot 2 X^{-}$ units linked in a polymeric arrangement through Te-Hg-Te bridges. It is not possible to comment on the environment of the mercury atom within the lattice.

The second group of ditelluride—mercuric halide complexes are dark brown and exhibit different ¹²⁵Te Mössbauer parameters to the stoichiometrically equivalent yellow complexes. Thus Δ values of $\simeq 9$ mm s⁻¹ and low values of δ indicate that the tellurium atoms are two-coordinate. The line widths of the spectra indicate that all tellurium sites are equivalent. The RTe—TeR molecule can be considered to be either very weakly bonded to the mercuric halide, remaining essentially two-coordinate; or cleavage of the Te—Te bond has taken place to give RTe—M groups. In the latter case the presence of RTe—Hg^{II}—TeR groups would not be consistent with the observed stoichiometry and therefore it is probable that these complexes are best formulated as $R_2Te_2 \cdot HgX_2$, in which both Te—Te and Hg—X bonds remain essentially similar to those present in the reactants.

Experimental

¹²⁵Te Mössbauer spectra were recorded as previously described [2,3]. Raman spectra were recorded on a Cary 81 spectrometer, utilizing a He—Ne laser. Low frequency infrared spectra were recorded on a Beckman IR12 spectrometer.

The following complexes were prepared following literature procedures. Ph₂TeHgCl₂, m.p. 158–160°C, lit. [1] m.p. 160–161°C. Ph₂TeHgBr₂, m.p. 150–152°C, lit. [1] m.p. 148°C. Ph₂TeHgI₂, m.p. 150–151°C, lit. [1] m.p. 146°C. (*p*-EtOC₆H₄)₂TeHgCl₂, m.p. 157–158°, lit. [1] m.p. 150–152°C. (*p*-EtOC₆H₄)₂TeHgBr₂, m.p. 157–158°C, lit. [1] m.p. 155–156°C. (*p*-EtOC₆H₄)₂TeHgI₂, m.p. 123–124°C. Ph₂Hg · 2Me₂TeI₂, m.p. 127–128°C, lit. [22] m.p. 125°C.

The following new compounds were also prepared.

$Me_2TeI_2 \cdot HgBr_2$

Equimolar portions of α -Me₂TeI₂ and HgBr₂ were dissolved in the minimum volume of absolute ethanol and mixed. The yellow Me₂Tel₂ solution became clear, and on standing in a stream of nitrogen, produced yellow needles of Me₂TeI₂ · HgBr₂, m.p. 127–128°C (Found: C, 3.34; H, 0.79. C₂H₆HgI₂Te calcd.: C, 3.11; H, 0.48%). This compound was also formed, following the same procedure, from α -Me₂TeBr₂ and HgI₂. Reaction of α -Me₂TeI₂ with HgCl₂ in hot ethanol produced an unstable complex which readily decomposed on standing. Boiling the complexes $Me_2TeI_2 \cdot HgBr_2$ or $Me_2TeI_2 \cdot HgCl_2$ in dry chloroform caused rapid decomposition; filtration produced insoluble red HgI_2 and evaporation of the filtrate, followed by recrystallization from chloroform/ petroleum ether yielded up to 95% of α -Me₂TeBr₂, m.p. 90–92°C, lit. [1] m.p. 92°C, and α -Me₂TeCl₂, m.p. 88–90°C, lit. [1] m.p. 92°C, respectively. Evaporation of an alcoholic solution of equimolar portions of Ph_2TeBr_2 and $HgCl_2$, followed by extraction with hot chloroform, similarly afforded a high yield of Ph₂TeCl₂, m.p. 159–160°C, lit. [1] m.p. 162–163°C. The compounds were identified by infrared and Raman spectroscopy and by mixed melting points with previously characterized samples.

$(p-EtOC_6H_4Te)_2Hg$

 $(p-\text{EtOC}_6H_4)_2\text{Te}_2$ (0.25 g, 0.5 mmol) and metallic mercury (5.0 g, 25 mmol) were shaken with 20 ml of dry benzene for 48 h. The resulting deep red solid was ground to a powder and the resulting suspension in benzene was decanted from unreacted mercury. Filtration produced 0.20 g (57% yield) of a red powder. 184

m.p. 110–112°C (Found: C, 26.56; H, 2.67. $C_{16}H_{18}O_2Te_2Hg$ calcd.: C, 27.54; H, 2.58%). The compound could not be recrystallized because of its low solubility in common organic solvents.

p-EtOC₆H₄TeHgCl

Equimolar quantities of $(p-\text{EtOC}_6\text{H}_4\text{Te})_2\text{Hg}$ and HgCl_2 were refluxed for 30 min in a small volume of ethanol. The deep red solid was rapidly replaced by a fine yellow powder which was filtered and washed with ethanol: m.p. 160–161°C (Found: C, 20.01; H, 2.00. C₈H₉OTeHgCl calcd.: C, 19.83; H, 1.86%).

p-EtOC₆H₄TeHgCl₂

 $(p-\text{EtOC}_6\text{H}_4)_2\text{Te}_2$ (1 mmol) and HgCl₂ (2 mmol) were dissolved in the minimum quantities of hot ethanol and mixed. On cooling the yellow precipitate was filtered and washed with cold ethanol, m.p. 110–112°C (Found: C, 18.68; H, 1.48. C₈H₂OTeHgCl₂ calcd.: C, 18.5; H, 1.7%).

The methyl analogue p-MeOC₆H₄TeHgCl₂ was similarly prepared from (p-MeOC₆H₄Te)₂ and HgCl₂, m.p. 114–115°C (Found: C, 17.2; H, 1.48. C_7H_7 -OTeHgCl₂ calcd.: C, 16.6; H, 1.39%).

$(p-EtOC_6H_4)_2Te_2HgBr_2$

Equimolar portions of $(p-\text{EtOC}_6\text{H}_4)_2\text{Te}_2$ and HgBr_2 were dissolved in the minimum of hot ethanol and mixed. On cooling the precipitate was filtered, washed with ethanol, and dried under vacuum, m.p. 120–122°C (Found: C, 19.36; H, 1.86. $\text{C}_{16}\text{H}_{18}\text{O}_2\text{Te}_2\text{HgBr}_2$ calcd.: C, 22.4; H, 2.1%). On repeating the preparation it was found that the stoichiometry of the complex formed was dependent on the ratio of reactants and on the rate and order of mixing. The stoichiometry was in all cases intermediate between $p-\text{EtOC}_6\text{H}_4\text{TeHgBr}_2$ and $(p-\text{EtOC}_6\text{H}_4)_2\text{Te}_2 \cdot \text{HgBr}_2$. A sample of a brown complex, of stoichiometry $(p-\text{EtOC}_6\text{H}_4)_2\text{Te}_2\text{HgBr}_2$, m.p. 109–110°C, prepared following a literature procedure [1] was provided by Prof. W.R. McWhinnie.

$(p-EtOC_6H_4)_2Te_2 \cdot HgI_2(I)$

Equimolar portions of (p-EtOC₆H₄)₂Te₂ and HgI₂ in hot ethanol were mixed and a brown flocculent precipitate formed. This was filtered, washed with ethanol and dried, m.p. 125–126°C (Found: C, 20.37; H, 1.98, C₁₆H₁₈O₂Te₂HgI₂ calcd.: C, 20.08; H, 1.88%).

1

$(EtOC_6H_4)_2Te_2HgI_2$ (II)

When $(p\text{-EtOC}_6H_4)_2\text{Te}_2$ (1 mmol) and HgI₂ (2 mmol) were mixed in hot ethanol, a yellow precipitate was formed on cooling. This was washed with cold ethanol and dried, m.p. 202–204°C (Found: C, 19.68; H, 1.91. C₈H₉OTeHgI₂ calcd.: C, 13.66; H, 1.28%; C₁₆H₁₈O₂Te₂HgI₂ calcd.: C, 20.08; H, 1.88%).

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