

Tellurium Tetrahalides in Rubber Chemistry: Some New Tellurium(IV) Complexes with an S_2X_4 (X = Halogen) Ligand Environment

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Abstract

The reaction of tellurium tetrahalides with natural rubber parallels closely reactions with model compounds such as cyclohexene and 2-methylpent-2-ene carried out under similar conditions. In both cases an α -elimination reaction of an 'organic halide' with deposition of elemental tellurium is a dominant process, but some evidence for cross-linking of natural rubber is obtained. If methyl cyanide is the solvent for cyclohexene, or if a nitrile rubber is used, elimination of tellurium is inhibited.

Tellurium tetrachloride enhances the rate and density of cross-link formation when added to tetramethylthiuram disulphide (TMTD) based natural rubber vulcanisates, but this effect is negated in the presence of triphenylphosphine. $TeCl_4$ reacts with TMTD to eliminate an atom of sulphur and to form a complex of tetramethylthiuram monosulphide (TMTM) *viz.* $[Te(TMTM)Cl_4]$. Corresponding bromo- and iodo-complexes have been prepared, the iodo-complex is a 1:1 electrolyte. ^{125}Te Mössbauer data for the complexes are briefly discussed.

Further reactions of the complexes are described which lead to the formation of: $[Te(TMTM)Cl_2(O)(pyridine)]$, $[Te(TMTM)X_2(O)]$ (X = Br, I), and $[Cu(TMTM)_2][TeCl_5]_2$. Organyltellurium(IV) trihalides also react with TMTD to release sulphur and give complexes of TMTM, *i.e.* $[(p-EtO \cdot C_6H_4)TeX_3]_2(TMTM)$ (X = Cl, Br, I).

Introduction

The use of tellurium in the rubber industry has been reviewed [1, 2]. The picture that emerges is that of a rapid decline in the use of the element, despite the fact that the addition of small amounts to vulcanisates may reduce the curing time and, with natural rubber or styrene-butadiene rubber, produce vulcanisates of enhanced toughness and heat resistance. It has been shown [2, 3] that partial replace-

ment of sulphur by tellurium in natural rubber cured by conventional high sulphur: low accelerator systems give an important improvement in thermal stability and a very great improvement in thermal oxidative stability at 100 °C.

Tetrakis(diethyldithiocarbamato)tellurium(IV) ('diethyl tellurac') continues to be used as a vulcanisation accelerator for isobutylene-isoprene rubbers and ethene-propene terpolymers. It produces fast curing stocks that can be extruded at high rates, and offers unique advantages in other applications which should ensure its continued use [2].

The literature records virtually no attempts to understand the chemistry of tellurium compounds in contact with rubber. Given the well-known ability of tellurium tetrahalides to react with alkenes, we decided to explore reactions of TeX_4 (X = Cl, Br) with natural rubber (NR) both direct and as additives to vulcanisation mixtures. The results of these experiments, which include data from model compound studies, are given in this paper and include a report of some new coordination compounds of tellurium(IV).

Experimental and Results

(i) Reactions of Tellurium Tetrahalides with Model Compounds

A number of simple alkenes are sometimes used to model the reaction of natural rubber, two are selected in this instance – cyclohexene and 2-methylpent-2-ene.

(a) Cyclohexene

Reaction of cyclohexene (20 mmol) with tellurium tetrachloride (20 mmol) in chloroform (r.t., 0 °C, or –10 °C); carbon tetrachloride (r.t.); ethanol (r.t.); or acetonitrile (r.t.) resulted in a yellow precipitate which turned black after a few minutes. The black material was identified as tellurium and GLC analysis of the filtrate showed the presence of 1,2-dichlorocyclohexane. Use of acetonitrile at 0 °C gave a product containing a tellurium to carbon

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bond. A definitive preparation has been given [4]. Analysis showed the product to be 2-chlorocyclohexyltellurium(IV) trichloride, $(C_6H_{10}Cl \cdot TeCl_3)$. *Anal.* Found: C, 20.8; H, 2.90; Cl, 39.8; Te, 35.9. Calc. for $C_6H_{10}Cl_4Te$: C, 20.5; H, 2.80; Cl, 40.4; Te, 36.4%.

(b) *2-Methylpent-2-ene*

Under all conditions tried a black residue was obtained when $TeCl_4$ was reacted with the alkene in chloroform or acetonitrile. Examination of the filtrate after removal of the black material (Te) by GLC showed the presence of 2,3-dichloro-2-methylpentane.

(ii) *Reaction of Tellurium Tetrahalides with Natural Rubber (NR)*

A standard Malaysian rubber (SMR 10) was used in this work. SMR (10 g) was masticated in a two roll mill and dissolved in dry chloroform (100 cm^3). Tellurium tetrachloride (5.38 g, 20 mmol) was dissolved in dry chloroform (50 cm^3) under dry dinitrogen and added to the 10% rubber solution. The mixture was stirred vigorously for 3 h with the temperature maintained at 30°C . A black gel formed which was separated, washed well with dry chloroform, and vacuum dried. The same reaction with $TeBr_4$ was found to be slower.

A portion of the black gel was treated with conc. HNO_3 to remove elemental tellurium and to leave a yellow resin. *Anal.* Found: C, 38.7; H, 3.8; Cl, 8.9; Te, 14.8%, i.e. a Cl:Te ratio of 2:1.

A similar reaction of $TeCl_4$ with a 10% chloroform solution of an acrylonitrile-butadiene rubber ('nitrile rubber') was carried out at 30°C . No tellurium was deposited and a yellow emulsion was formed. Evaporation of the solvent by passage of dry dinitrogen left a thin rubber-like film.

(iii) *Reactions of Tellurium Tetrahalides with Solid Natural Rubber*

This set of experiments involved the addition of TeX_4 (X = Cl, Br) to SMR 10 using the following vulcanising formula

	Parts by weight
NR	100
ZnO	5
Stearic acid	2.5
TMTD	3.0

(TMTD = tetramethylthiuram disulphide, $Me_2N \cdot C(S)S \cdot S(S) \cdot C \cdot NMe_2$.)

Tellurium tetrachloride was added in varying parts by weight, namely: 1.0 (3.7×10^{-3} mol), 1.5 (5.6×10^{-3} mol), 2.0 (7.4×10^{-3} mol), 2.5 (9.2×10^{-3} mol), 3.0 (1.1×10^{-2} mol), and 4.0 (1.5×10^{-2} mol). $TeBr_4$ was also tried at 1.5 parts by weight.

TABLE I. Data from Monsanto Rheograph Studies of NR Vulcanisates to which Tellurium Tetrahalides Have Been Added

Parts by weight TeX_4^a	R_∞^b	Rate constant (min^{-1})	Induction time (min)
0	41.0	0.27	6.0
1.5 (X = Cl)	73.4	0.21	5.2
1.5 (X = Br)	52.5	0.32	4.0

^a Added to standard vulcanisate.

^b Rheometer units.

The vulcanisates were examined with the Monsanto Rheometer and typical curves are illustrated in Fig. 1a and b. The Monsanto oscillating disc rheometer consists of a biconical disc surrounded by the compound specimen contained in a cavity. The temperature of the experiment may be controlled to within 0.5°C . The instrument measures torque as a function of time. Typically there is an initial drop in torque as the temperature rises and the rubber becomes less viscous, this is followed by an induction period after which the torque increases steadily as the cross-linking reaction proceeds. Eventually a maximum torque is reached (R_∞). If the torque at time t is R_t , plots of $\log(R_\infty - R_t)$ vs. t give the induction time and the first order rate constant which is the negative slope of the straight line obtained for values of $t >$ induction time. Some data are given in Table I.

(iv) *Reactions of Tellurium Tetrahalides with Tetraalkylthiuram Disulphides (alkyl = methyl, TMTD or ethyl, TETD)*

(a) *With Tellurium Tetrachloride*

Disulphide (TMTD or TETD) (20 mmol) dissolved in dry chloroform (50 cm^3) was added to a clear solution of tellurium tetrachloride (5.38 g, 20 mmol) dissolved in dry chloroform (50 cm^3) under dinitrogen. The mixture was vigorously stirred and a yellow precipitate formed. The product was filtered, washed with carbon tetrachloride and (TMTD only) recrystallised from acetonitrile.

The complex derived from TMTD underwent metathesis with KBr or KI in methanol solution to give the corresponding bromo- and iodo-complexes. Analysis showed the complexes to be of the monosulphide, i.e. $[R_2N \cdot C(S) \cdot S \cdot (S)C \cdot NR_2TeX_4]$.

The reaction of $TeCl_4$ and TMTD was repeated in the presence of redistilled pyridine (25 cm^3). A yellow, moisture sensitive, product was obtained, $[Me_2N \cdot C(S) \cdot S \cdot C(S) \cdot NMe_2Te(py)(O)Cl_2]$. This material, when freshly prepared, underwent metathesis with KBr or KI in methanol to give $[(TMTM) \cdot Te(O)X_2]$ (X = Br or I).

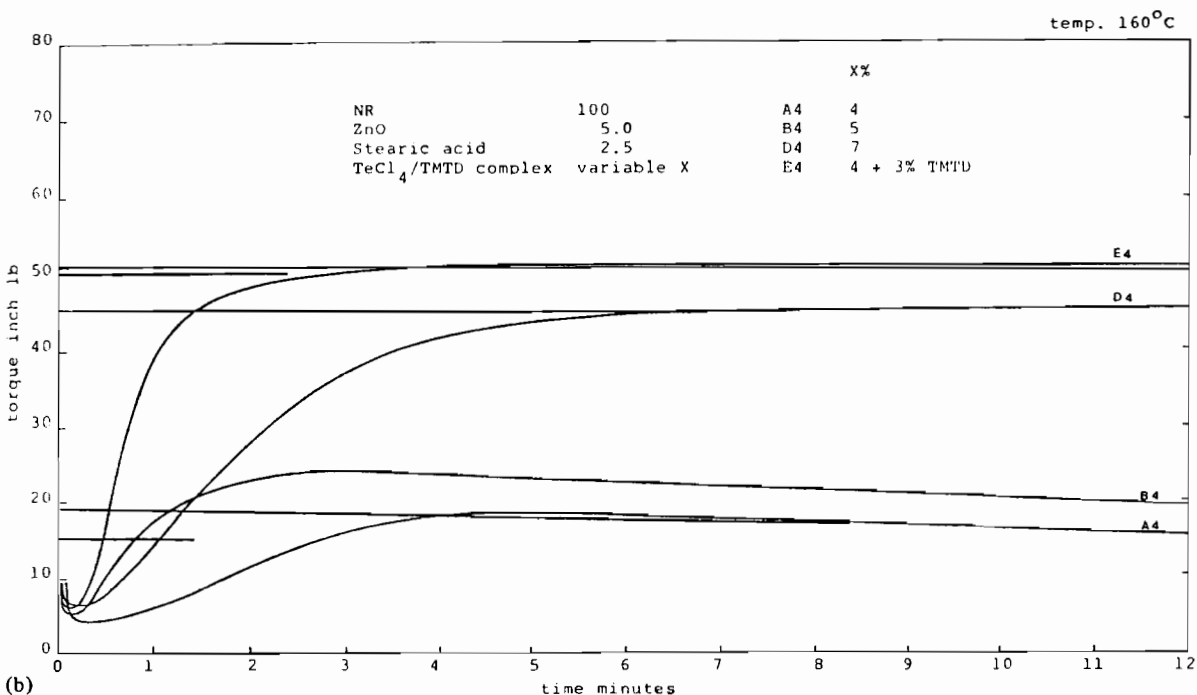
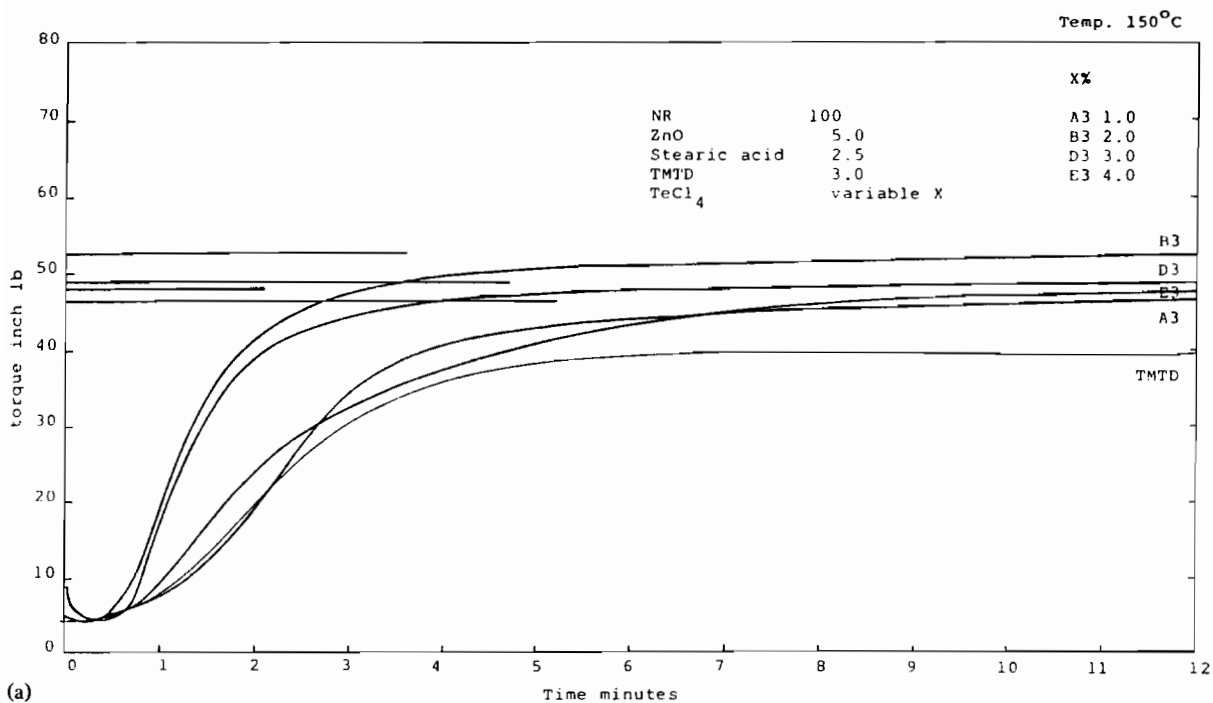


Fig. 1. Monsanto rheographs for natural rubber vulcanised by the indicated mixture.

(b) Reaction of TMTD, Triphenylphosphine and Tellurium Tetrachloride

To a clear solution of tellurium tetrachloride (5.35 g, 20 mmol) in dry benzene (25 cm³) was added dropwise a mixture of TMTD (2.4 g, 10 mmol) and triphenylphosphine (2.62 g, 10 mmol) in dry benzene. The yellow precipitate which formed was filtered and washed with benzene.

(c) Reaction of TMTD with (*p*-Ethoxyphenyl)-tellurium Trichloride

(*p*-Ethoxyphenyl)tellurium trichloride [5] (7.10 g, 20 mmol) in dry chloroform (50 cm³) was treated under dinitrogen with TMTD (2.40 g, 10 mmol) with vigorous stirring. The fine powdery precipitate was filtered after the addition of ether.

TABLE II. Analytical Data for New Complexes

Formula	Melting point (°C)	C(calc.)	H(calc.)	N(calc.)	X ^a (calc.)	Te ^b (calc.)	S(calc.)
1 TMTM ^c ·TeCl ₄ (yellow)	198	14.8 (15.0)	2.50 (2.50)	5.75 (5.85)	29.0 (29.7)	28.1 (27.6)	21.2 (20.1)
2 TMTM·TeBr ₄ (orange-brown)	173	10.9 (10.9)	1.85 (1.83)	4.27 (4.27)	47.4 (48.8)	— —	14.9 (14.6)
3 TMTM·TeI ₄ (red-brown)	193	8.60 (8.53)	1.43 (1.42)	3.32 (3.31)	— —	16.0 (15.1)	11.8 (11.4)
4 TETM ^d ·TeCl ₄ (yellow)		22.1 (22.5)	3.60 (3.74)	5.00 (5.24)	26.2 (26.6)	— —	17.2 (17.9)
5 TMTM·Te(O)(Py)Cl ₂ ^e (yellow)		26.0 (26.3)	3.29 (3.38)	7.85 (8.37)	13.6 (14.2)	— —	18.7 (19.1)
6 TMTM·Te(O)Br ₂ (orange)		14.2 (14.1)	2.37 (2.34)	5.17 (5.47)	30.9 (31.3)	— —	18.4 (18.7)
7 TMTM·Te(O)I ₂ (purple)	152	11.9 (11.9)	1.95 (1.98)	4.55 (4.62)	— —	— —	16.0 (15.9)
8 [(<i>p</i> -EtOC ₆ H ₄)TeCl ₃] ₂ TMTM (yellow)	178	28.6 (28.8)	3.15 (3.26)	3.01 (3.04)	24.0 (23.2)	— —	10.7 (10.6)
9 [(<i>p</i> -EtOC ₆ H ₄)TeBr ₃] ₂ TMTM (orange-brown)	153	22.0 (22.3)	2.52 (2.53)	2.14 (2.36)	38.9 (40.5)	— —	— —
10 [(<i>p</i> -EtOC ₆ H ₄)TeI ₃] ₂ TMTM (red-brown)	181	17.8 (17.9)	2.01 (2.04)	1.91 (1.90)	— —	— —	6.34 (6.54)
11 TMTM(SPPh ₃)(TeCl ₄) ₂ (yellow)	156	27.1 (27.6)	2.58 (2.59)	2.70 (2.68)	— —	12.0 (12.3)	— —
12 [TMTM ₂ Cu][TeCl ₅] ₂ (green)	132	13.5 (13.2)	2.15 (2.20)	5.08 (5.14)	5.33 ^f (5.79) ^f	23.0 (23.5)	18.0 (17.7)

^aCl or Br. ^bSee ref. 5 for method. ^cTMTM = (Me₂NC(S)SC(S)NMe₂). ^dTETM = (Et₂NC(S)SC(S)NEt₂). ^eAnalysis of freshly prepared sample. ^f% Cu(calc.).

The product underwent metathesis with KBr or KI in methanol to give the corresponding bromo- and iodo-complexes.

(v) Reaction of [(Me)₂NC(S)·S·C(S)·N(Me)₂TeCl₄] with Copper(II) Chloride

Copper(II) chloride dihydrate (0.08 g, 5 mmol) was dissolved in acetone (15 cm³) and to the resultant solution was added the complex TMTM·TeCl₄ (1, Table II) (4.77 g, 10 mmol) in acetone with vigorous stirring. A dark green product separated which was filtered and washed with acetone and ether and dried *in vacuo* over P₄O₁₀. (Melting point (m.p.) 132 °C).

Analytical data are presented in Table II.

Physical Measurements

Infrared spectra in the range 4000–250 cm⁻¹ were recorded on a Perkin-Elmer 457 instrument, and in the range 400–200 cm⁻¹ on a Perkin-Elmer 599 spectrometer.

Mass spectra were measured at 70 eV (1 eV = 1.60 × 10⁻¹⁹ J) with an AEI MS9 instrument.

GLC analyses were with Pye-Unicam equipment and conductivity data were determined with a Mullard bridge using a standard cell (type E7591 B); data in Table III.

TABLE III. Conductivity Data of dmf Solutions of Some New Tellurium(IV) Complexes

Complex number ^a	Λ _M (10 ⁻³ M) ^b (25 °C)	Comment ^c
1	49	weak electrolyte
2	52	weak electrolyte
3	103	strong electrolyte
5	39	weak electrolyte
7	45	weak electrolyte
8	46	weak electrolyte
9	98	approaches 1:2
10	160	1:2 electrolyte
11	58	1:1 electrolyte

^aSee Table II. ^bOhm⁻¹ cm⁻² mol⁻¹. ^cFrom plots of M vs. (concentration)^{1/2}.

A ^{125}Te Mössbauer spectrum of the black gel obtained from the reaction of NR with TeCl_4 was measured at 78 K, as were data* for compounds 1, 2 and 3 (Table II).

Discussion

Tellurium Tetrahalides and Rubber

Alkenes such as cyclohexene and 2-methylpent-2-ene are often used to model the reaction of NR with various reagents. The literature covering the reaction of cyclohexene with TeCl_4 is in a confused state. Thus one early report [6] suggests that no reaction occurs, whilst others [7–9] claim cyclohexyltellurium(IV) trichloride as the only product. However at least two groups [10, 11] have prepared bis(cyclohexyl)tellurium(IV) dichloride, the crystal structure of which has been determined [12]. In our laboratory great difficulty was experienced in isolating anything other than $(\text{C}_6\text{H}_{10}\text{Cl})\text{TiCl}_3$, and that only when acetonitrile and low temperatures were used. This is consistent with the report of Backvall *et al.* [4] who show that the concerted stereospecific syn addition of TeCl_4 to alkenes such as cyclohexene is in competition with a radical chain mechanism. The radical pathway is disfavoured when acetonitrile is used [4]. In other cases, and invariably with 2-methylpent-2-ene, tellurium metal was deposited but GLC examination of the filtrate revealed in all cases the presence of organic dihalides (1,2-dichlorocyclohexane or 2-methyl-2,3-dichloropentane).

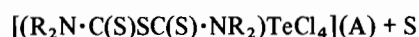
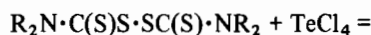
The recent work of Backvall *et al.* [4], and of Uemura [13] does help to suggest an explanation for the confusion. Uemura and Fukuzawa [13] point out that α -elimination of organic halides from organytellurium(IV) halides may be promoted oxidatively, photolytically or thermally. Although the conditions used by the Japanese workers seem much more severe than those to which the compounds in the present work were subjected, it is pertinent to note that our work is carried out in a laboratory lit with fluorescent lighting and, further, higher temperatures were found to assist the elimination of tellurium. Others have commented on the photosensitivity of organytellurium compounds [14], but we have only experienced regular difficulty with alkyl- and with some alkyl/aryl compounds.

The reaction of TeCl_4 with NR closely parallels the model compound work. Thus the black gel produced by reaction of SMR(10) with TeCl_4 in chloroform contained free tellurium. This was demonstrated by determination of the ^{125}Te Mössbauer spectrum at 78 K when a quadrupole doublet ($\Delta = 7.36 \pm 0.3 \text{ mm s}^{-1}$) was seen at $\delta = 0.08 \pm 0.2 \text{ mm}$

s^{-1} (vs. $^{125}\text{I}/\text{Cu}$). Data for Te metal have been reported [15]: $\delta = 0.5 \pm 0.2$, $\Delta = 7.77 \pm 0.06 \text{ mm s}^{-1}$ which, given the large errors on the 78 K data, renders the presence of free tellurium very probable. Interestingly, if the experiment is repeated with a nitrile rubber replacing NR, no tellurium is deposited and removal of the solvent leaves a film with good rubber-like properties suggesting some degree of cross-linking. IR examination of the film suggested that $\nu(\text{CN})$ at 2100 cm^{-1} had shifted 5 cm^{-1} to a higher frequency on treatment with TeCl_4 . This leads to the speculation that coordination of nitrile to tellurium might inhibit the α -elimination reaction (the model compound reactions that were successful were those carried out in acetonitrile, also it was subsequently shown that solutions of $\text{TeCl}_4/\text{cyclohexene}$ in THF were stable).

Chemical removal of the tellurium from the SMR(10) black gel afforded a yellow resin with $\text{Cl}:\text{Te} = 2:1$. The severe chemical treatment produced some nitration (IR) and, in common with expectation for organytellurium compounds, the recoil free fraction at 78 K was too low for a Mössbauer spectrum to be recorded. This otherwise unpromising material appears to be the only one described where reasonable evidence exists that such cross-links as it contains are based on tellurium.

The action of TeX_4 ($X = \text{Cl}, \text{Br}$) as an additive to a normal low sulphur vulcanising formulation based on an organic disulphide leads to an increase in the rate of cross-link formation ($X = \text{Cl}$) and to an increase in ultimate cross-link density ($X = \text{Cl}, \text{Br}$). Further no sign of deposition of elemental tellurium is noted. We argued that the tetrahalide reacted synergistically with another ingredient of the vulcanisate rather than directly with the rubber and quickly established that TeX_4 reacts with TMTD to produce the monosulphide and sulphur



($X = \text{Cl}, \text{Br}$; $\text{R} = \text{Me}, \text{Et}$)

The release of elemental (possibly 'nascent') sulphur explains the enhancement of rate and density of cross-link formation by TeCl_4 (Table I). The tellurium complexes (A) do themselves show some vulcanising effect which in the case of $[(\text{TMTM})\text{TeCl}_4]$ is comparable to that of TMTD on a mole to mole basis (Fig. 1b).

New S_2X_4 Complexes of Tellurium(IV) and Their Derivatives

The reaction of TeX_4 with tetramethylthiuram disulphide (TMTD) gives complexes of the monosulphide, *i.e.* $[(\text{TMTM})\text{TeX}_4]$. IR examination reveals, in the case of $[(\text{Te}(\text{TMTM})\text{Cl}_4)]$ for instance, that $\nu(\text{CN})$ for TMTM at 1506 cm^{-1} shifts to 1578

*We are grateful to Dr. F. J. Berry at the University of Birmingham for these data.

TABLE IV. ^{125}Te Mössbauer Data (77 K) for Complexes of TeX_4 ($X = \text{Cl, Br, I}$) with $\text{Me}_2\text{N}\cdot\text{C}(\text{S})\cdot\text{S}\cdot\text{C}(\text{S})\cdot\text{NMe}_2$ (TMTM)

Complex number (Table II)	δ^a (isomer shift) (mm s^{-1})	Δ (quadrupole splitting) (mm s^{-1})	$\Gamma^{1/2}$ (line width) (mm s^{-1})
1	0.84 ± 0.55	6.33 ± 0.90	6.69 ± 0.70
2	0.70 ± 0.41	6.79 ± 0.82	6.37 ± 0.70
3	1.26 ± 0.30	5.39 ± 0.60	7.20 ± 0.60

^a δ with respect to I/Cu source.

cm^{-1} on complex formation which is consistent with coordination through sulphur. The formation of the six membered TeSCSCS ring, in which some delocalisation is expected, is likely to modify significantly $\nu(\text{C}=\text{S})$ (965 cm^{-1}) and $\nu(\text{CS})$ (582 cm^{-1}) in the free ligand. Consistent with this is the observation of a new band, characteristic of the complex, at 755 cm^{-1} which is assigned as $\nu(\text{CS})$. Coordination of the ligand via two sulphur atoms is thus supported and is in accord with the 'soft' acid nature of $\text{Te}(\text{IV})$. A possible S, N model of coordination is eliminated by ^1H NMR which shows all protons in the TMTM complex to be equivalent.

The far IR spectrum of the tetrachloro-complex shows the expected four $\nu(\text{TeCl})$ bands for a [(chelate) TeCl_4] system ($298, 287, 282, 277 \text{ cm}^{-1}$), however these data give no information on the distortion of the bond angles from 90° .

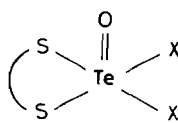
Conductivity data in DMF indicate some solvolysis of the chloro- and bromo-complexes, but studies over a concentration range indicated weak electrolyte behaviour [16]. By contrast the iodo-complex showed strong electrolyte (1:1) behaviour, suggesting the material should be formulated $[\text{Te}(\text{TMTM})\text{I}_3]\text{I}$.

Perhaps the major point of interest in these complexes is the question of the steric activity of the lone pair. Strenuous efforts have been made to produce suitable single crystals for X-ray examination, but to date without success. ^{125}Te Mössbauer spectroscopy was therefore used in the hope that s-electron density at the tellurium nucleus could be probed and hence the role of the lone pair assessed. Data obtained with difficulty at 78 K are given in Table IV. The data are best fitted to quadrupole doublets whose line widths are comparable to those seen for $[\text{TeX}_6]^{2-}$ salts [17]. The large errors in Table IV make it difficult to argue in any convincing way for significant variation of s-electron density at tellurium with change of halogen, although it is probably in order to suggest that density is greatest for the iodo-complex. This is surprising since the implication from the conductivity data is a five coordinate $[\text{Te}(\text{TMTM})\text{I}_3]^+$ ion in which directional lone pair character should be more developed (with the resultant removal of s-electron density from the nucleus) than for the six coordinate chloro- and bromo-complexes. Thus association in the solid state

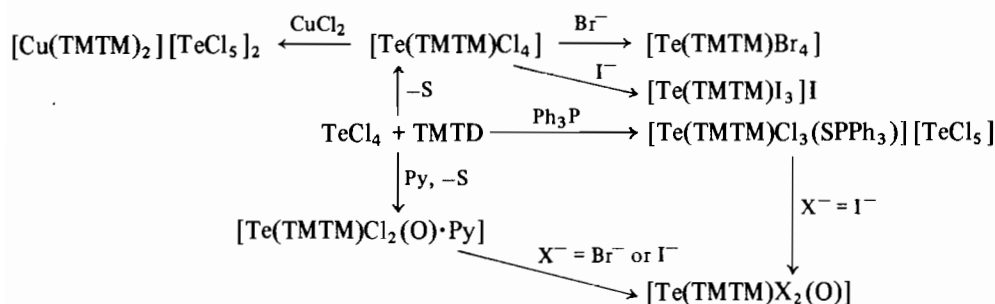
cannot be ruled out for the iodo-complex. The observation of quadrupole split spectra contrasts with the single line data for $[\text{TeX}_6]^{2-}$ and even for $[\text{TeX}_4\text{Y}_2]^{2-}$ ($X, Y = \text{halogen}$) [17], thus the splitting may arise from either the non-cubic ligand field or from a directed lone pair; or even from a combination of both factors.

The addition of triphenylphosphine to the NR vulcanisate based on TMTD and TeCl_4 cancelled the beneficial effect of the tellurium compound. When TeCl_4 , TMTD and PPh_3 are reacted together a yellow complex (11, Table II) is formed. It behaves as a 1:1 electrolyte in DMF and a ^{31}P NMR spectrum of a dilute DMSO solution shows only one phosphorus resonance. The IR spectrum is consistent with coordinated TMTM and also confirms the presence of Ph_3PS ($\nu(\text{PS}) = 642 \text{ cm}^{-1}$) [18]. Metathesis of the complex with methanolic KI gives a compound identical with 7 (Table II). A plausible, but unconfirmed, structure would be $[\text{Te}(\text{TMTM})\text{Cl}_3(\text{SPPH}_3)][\text{TeCl}_5]$. The significant observation is the capture of sulphur by phosphorus which explains why no enhancement of cross-link density by TeCl_4 for SMR(10) is promoted in the presence of triphenylphosphine.

When the reaction of TeCl_4 and TMTD is carried out in the presence of pyridine, complex 5 is obtained (Table II). The pyridine is labile but rapid elemental and IR analysis suggest the pyridine to be weakly coordinated. Thus no bands characteristic of protonated pyridine are seen despite the fact that hydrolysis of TeCl_4 to $\text{Te}(\text{O})\text{Cl}_2$ has occurred ($\nu(\text{Te}=\text{O})$ at 600 cm^{-1}). Small shifts of pyridine frequencies consistent with Lewis base behaviour are seen. The mass spectrum shows no parent ion, but the fragments py^+ and $[\text{Te}(\text{TMTM})\text{Cl}_2(\text{O})]^+$ are observed. Metathesis of 5 with KBr or KI gives $[\text{Te}(\text{TMTM})\text{X}_2(\text{O})]$ ($X = \text{Br}$ or I ; 6 and 7, Table II). Mass spectra show parent ions, IR confirms the presence of $\text{Te}=\text{O}$ (600 cm^{-1}), and of sulphur coordinated TMTM. Complexes 5, 6, and 7 are weak electrolytes in dmf. All data are consistent with the structure I.



I, $X = \text{Br}$ or I



Scheme 1. (TMTD = tetramethylthiuram disulphide, $\text{Me}_2\text{N}\cdot\text{C}(\text{S})\cdot\text{S}-\text{SC}(\text{S})\cdot\text{NMe}_2$; TMTM = tetramethylthiuram monosulphide, $\text{Me}_2\text{NC}(\text{S})\cdot\text{S}\cdot\text{C}(\text{S})\cdot\text{NMe}_2$).

It proved possible to displace coordinated TMTM from tellurium by reaction of compound **1** with copper(II) chloride to give compound **12** (Table II), which has Λ_M (10^{-3} M) of $179 \text{ cm}^2 \text{ ohm}^{-1} \text{ mol}^{-1}$ in acetonitrile, a value acceptable for a 1:2 electrolyte. The value of μ_{eff} (Gouy, room temperature) is 1.91 ± 0.05 BM. The electronic spectrum (out to 750 nm) shows a band at 634 nm. The formulation $[\text{Cu}(\text{TMTM})_2][\text{TeCl}_5]_2$ is probable. The reactions of the complexes described are summarised in Scheme 1.

Finally reactions between RTeX_3 ($\text{R} = p\text{-EtO}\cdot\text{C}_6\text{H}_4-$, $\text{X} = \text{Cl}, \text{Br}, \text{I}$) and TMTD gave compounds **8**, **9**, and **10** (Table II). The stoichiometry (RTeX_3)₂(TMTM) suggests a bridging TMTM group to give the anticipated 5-coordinate tellurium atoms; however conductivity data, particularly for **9** and **10** (Table III), imply a more complex situation. For $\text{X} = \text{Cl}$, $\nu(\text{TeCl})$ were identified at 318 and 298 cm^{-1} ; this is the region associated with RTeCl_3 or $\text{RTeCl}_3(\text{ligand})$ [19]. Re-examination of the IR spectrum after some months showed decomposition to RTeCl_3 and TMTM to have occurred.

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