Dimethyltellurium(IV) derivatives with mixed 1,1-dithio ligands. Crystal structures of Me₂Te[S₂CNMe₂][S₂COEt] and Me₂Te[S₂CNEt₂][S₂COMe]

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Abstract: Mixed ligand derivatives of Me₂TeLL'₂, where L = *N*,*N*-dialkyl dithiocarbamate or *O*,*O*-alkylene dithiophosphate and L' = *O*-alkyl dithiocarbonate, have been synthesized and characterized by elemental analysis, ¹H, ¹³C, ³¹P, and ¹²⁵Te NMR spectroscopy and infrared and Raman spectroscopy, and X-ray crystallography. Me₂Te[S₂CNMe₂][S₂COEt], **8**: $P\overline{1}$ (no. 2), with cell parameters a = 10.073(3) Å, b = 10.139(2) Å, c = 9.108(2) Å, $\alpha = 92.36(2)^{\circ}$, $\beta = 115.55(2)^{\circ}$, $\gamma = 111.19(2)^{\circ}$, V = 760.7(4) Å³, Z = 2, R = 0.0343, $R_w = 0.0296$. Me₂Te[S₂CNEt₂][S₂COMe], **9**: $P2_1/c$ (no. 14) with cell parameters a = 9.881(4) Å, b = 17.671(3) Å, c = 10.149(4) Å, $\beta = 113.65(3)^{\circ}$, V = 1623.3(10) Å³, Z = 4, R = 0.0567, $R_w = 0.0514$. The immediate environment about tellurium in both molecules is essentially that of a saw-horse structure in which the lone pair is apparently stereochemically active and occupying an equatorial position in a distorted trigonal bipyramid. The S-Te-S angles in the two molecules are 166.87(6)^{\circ} and 162.0(1)^{\circ} for **8** and **9**, respectively. In both molecules, the Te—S bonds to the dithiocarbamate groups are slightly shorter than those to dithiocarbonates. The dithiocarbamate groups are oriented to give secondary interactions involving the apparently terminal sulfur atoms resulting in Te—S distances of 3.205(2) and 3.277(4) Å, respectively, in **8** and **9**. However, only in **9** is there a similar Te—S distance of 3.346(5) Å involving the S₂COMe group because in **8**, the OEt group of S₂COEt, rather than the terminal S atom, is oriented toward Te.

Key words: structure, tellurium, methyl, dithiocarbamates, dithiocarbonates, dithiophosphates.

Résumé : On a synthétisé des dérivés à ligands mixtes du Me₂TeLL'₂ dans lesquels L = dithiocarbamate de N,Ndialkyle ou dithiophosphate de O_iO_i -alkylène et L' = dithiocarbonate de O_i -alkyle et on les a caractérisés par analyse élémentaire, spectroscopie RMN du ¹H, ¹³C, ³¹P et ¹²⁵Te, spectroscopie infrarouge et Raman et par diffraction des rayons X. Me₂Te[S₂CNMe₂][S₂COEt], **8**, $P\overline{1}$ (no. 2), avec a = 10,073(3), b = 10,139(2) et c = 9,108(2) Å, $\alpha = 10,073(3)$, b = 10,139(2) et c = 9,108(2) Å, $\alpha = 10,073(3)$, b = 10,139(2) et c = 9,108(2) Å, $\alpha = 10,073(3)$, b = 10,139(2) et c = 9,108(2) Å, $\alpha = 10,073(3)$, b = 10,139(2) et c = 9,108(2) Å, $\alpha = 10,073(3)$, b = 10,139(2) et c = 9,108(2) Å, $\alpha = 10,073(3)$, b = 10,139(2) et c = 9,108(2) Å, $\alpha = 10,073(3)$, b = 10,139(2) et c = 9,108(2) Å, $\alpha = 10,073(3)$, b = 10,139(2) et c = 9,108(2) Å, $\alpha = 10,073(3)$, b = 10,139(2) et c = 9,108(2) Å, $\alpha = 10,073(3)$, b = 10,139(2) et c = 9,108(2) Å, $\alpha = 10,073(3)$, b = 10,139(2) et c = 9,108(2) Å, $\alpha = 10,073(3)$, b = 10,139(2) et c = 9,108(2) Å 92,36(2), $\beta = 115,55(2)$ et $\gamma = 111,19(2)^{\circ}$, V = 760,7(4) Å³, Z = 2, R = 0,0343, $R_w = 0,0296$. Me₂Te[S₂CNEt₂][S₂COMe], **9**, $P2_1/c$ (no. 14), avec a = 9,881(4), b = 17,671(3) et c = 10,149(4) Å, $\beta = 113,65(3)^\circ$, V = 1623,3(10) Å³, Z = 4, R = 0,0567, $R_w = 0,0514$. Dans les deux molécules, l'environnement immédiat autour du tellure est essentiellement celui d'une structure cavalière dans laquelle la paire d'électrons libres est apparemment stéréochimiquement active et elle occupe une position équatoriale dans une bipyramide trigonale déformée. Dans les deux molécules, les angles S-Te-S sont de 166,87(6) et 162,0(1)° pour les molécules 8 et 9 respectivement. Dans chacune des molécules, les liaisons Te-S vers les groupes dithiocarbamates sont légèrement plus courtes que celles dans les dithiocarbonates. Les groupes dithiocarbonates sont orientés de façon à donner des interactions secondaires impliquant les atomes de soufre apparemment terminaux; il en résulte des distances Te-S de 3,205(2) et 3,277(4) Å pour les composés 8 et 9 respectivement. Toutefois, seul le composé 9 donne lieu à une distance Te—S semblable, 3,346(5) Å, impliquant le groupe S_2 COMe; cette situation résulte du fait que, dans le composé 8, c'est le groupe OEt du S2COEt qui est orienté vers le Te et non l'atome S terminal.

Mots clés : structure, tellure, méthyle, dithiocarbamates, dithiocarbamates, dithiophosphonates.

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Introduction

Several reports have appeared on organotellurium(IV) compounds with a variety of 1,1-dithio ligands including

O-alkyl dithiocarbonates (1-6), *N*,*N*-dialkyl dithiocarbamates (5-14), and *O*,*O*-dialkyl (alkylene) dithiophosphates (4-6, 13-20), but relatively few refer to the formation of mixed ligand moieties, such as those of the general type

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RTeL₂L' (14) or R₂TeLL' (21). We report on the synthesis of nine dimethyltellurium(IV) compounds with mixed 1,1dithio ligands along with their characterization by ¹H, ¹³C, ³¹P, and ¹²⁵Te NMR spectroscopy, infrared and Raman spectroscopy, and elemental analysis. X-ray crystal structures of Me₂Te[S₂CNMe₂][S₂COEt], **8**, and Me₂Te[S₂CNEt₂][S₂COMe], **9**, confirm that these are mixed ligand species and not 1:1 mixtures of the bis derivatives.

Experimental

Materials

TeCl₄, Me₄Sn, NaS₂CNMe₂, and NaS₂CNEt₂ were obtained from Aldrich, and the latter two were dried in vacuo for 4–5 days prior to use. Me₂TeCl₂ was prepared by the reaction of TeCl₄ and Me₄Sn in toluene at 60°C under reflux for 4 h by adaptation of the method used for the preparation of Ph₂TeCl₂ (22). Me₂TeCl[S₂CNMe₂] and Me₂TeCl[S₂CNEt₂] were prepared as described in the literature (12) as were the sodium and ammonium salts of *O*,*O*-alkylene dithiophosphatic acids and the potassium salts of *O*-alkyl dithiocarbonic acids (23, 24). All solvents were dried and distilled prior to use, and all reactions carried out under anhydrous conditions.

Preparation of dimethyl(*N*,*N*-alkyl dithiocarbamato)(*O*,*O*-alkylene dithiophosphato)tellurium(IV) compounds

Typically, NaS₂POCMe₂CMe₂O (ca. 1.4 mmol) was added to a solution of an equimolar amount of Me₂TeCl₂ in dried dichloromethane (20 mL). The mixture was stirred for 2 h and then filtered to remove NaCl and unreacted dithiophosphate salt. The solvent was reduced to 5 mL under vacuum, n-hexane (5 mL) was added, and the solution left overnight in the refrigerator at -6° C. The resulting crystals were washed with *n*-hexane and dried in vacuum to give Me2TeCl[S2POCMe2CMe2O] as white crystals. Me2TeCl- $[S_2POCMe_2CMe_2O]$ (0.470 g, 1.16 mmol) was then dissolved in dichloromethane (20 mL), NaS₂CNMe₂ (0.168 g, 1.17 mmol) added with constant stirring, and the colorless solution turned yellow. The mixture was stirred for 2 h at ambient temperature and then filtered to remove NaCl or any unreacted dithiocarbamate salt. The volume of the solvent was reduced to 5 mL, n-hexane (5 mL) was added, and the solution was left overnight in the refrigerator at -6° C. The solvent was decanted off the crystals, which were then pumped on to dryness on the vacuum line to give $Me_2Te[S_2CNMe_2][S_2POCMe_2CMe_2O]$, 1, as yellow crystals (0.459 g, yield 81%; mp 129°C). Anal. calcd. for C₁₁H₂₄NO₂PS₄Te: C 27.01, H 4.95; found: C 26.85, H 4.75. Similarly, using NaS₂CNEt₂ was formed Me₂Te[S₂CNEt₂] [S₂POCMe₂CMe₂O], 2, as yellow crystals (yield 86%, mp 127-128°C). Anal. calcd. for C13H28NO2PS4Te: C 30.20, H 5.46; found: C 29.74, H 5.28. Similarly, starting with Me₂TeCl[S₂POCH₂CMe₂CH₂O] was formed Me₂Te- $[S_2CNMe_2][S_2POCH_2CMe_2CH_2O]$, 3, as yellow crystals (yield 83%, mp 114–115°C). Anal. calcd. for Č₁₀H₂₂NO₂PS₄Te: Ĉ 25.28, H 4.67; found: C 25.58, H 4.54. Me₂Te[S₂CNEt₂][S₂POCH₂CMe₂CH₂O], 4, as yellow crystals (yield 87%, mp 88-89°C). Anal. calcd. for C₁₂H₂₆NO₂PS₄Te: C 28.64, H 5.21; found: C 28.43, H 5.27. Unfortunately, no crystals suitable for X-ray diffraction studies were obtained for compounds 1–4 despite extensive efforts at recrystallization.

Preparation of dimethyl(*O*-alkyl dithiocarbonato)(*O*,*O*-alkylene dithiophosphato)tellurium(IV) compounds

In a manner essentially the same as described above, the reaction of Me₂TeCl[S₂POCMe₂CMe₂O] (0.234 g, 0.58 mmol) in dichloromethane (20 mL) with KS₂COMe (0.087 g, 0.59 mmol) gave Me₂Te[S₂COMe][S₂POCMe₂CMe₂O], **5**, as pale-yellow crystalline material: 0.223 g, yield 81%, mp 87–88°C. Anal. calcd. for C₁₀H₂₁O₃PS₄Te: C 25.23, H 4.45; found: C 25.30, H 4.85. Similarly, using KS₂COEt was formed Me₂Te[S₂COEt][S₂POCMe₂CMe₂O], **6**, as pale-yellow crystals: yield 83%, mp 72°C. Anal. calcd. for C₁₁H₂₃O₃PS₄Te: C 26.96, H 4.73; found: C 27.07, H 4.83. Unfortunately, attempts to grow X-ray quality crystals of **5** and **6** were not successful.

Preparation of dimethyl(*N*,*N*-dialkyl dithiocarbamato) (*O*-alkyl dithiocarbonato)tellurium(IV) compounds

Typically, KS₂COMe (0.154 g, 1.05 mmol) was added, with constant stirring, to a solution of Me₂TeCl[S₂CNMe₂] (0.324 g. 1.03 mmol) in dichloromethane (20 mL). The colorless reaction mixture changed to yellow after a few minutes. The stirring was continued for 1 h after which KCl and unreacted dithiocarbonate salt were filtered off before the solvent was pumped off under vacuum to yield a yellow powder. The crude product was recrystallized from dichloromethane-*n*-hexane to give $Me_2Te[S_2CNMe_2][S_2COMe]$, 7, as yellow crystals: 0.176 g, yield 88%, mp 95-97°C. Anal. calcd. for C₇H₁₅NOS₄Te: C 21.84, H 3.93; found: C 22.22, H 3.85. Similarly were obtained Me₂Te[S₂CNMe₂][S₂COEt], 8, as yellow crystals: yield 88%, mp 106-108°C. Anal. calcd. for C₈H₁₇NOS₄Te: C 24.08, H 4.29; found: C 24.15, H 4.18. Me₂Te[S₂CNEt₂][S₂COMe], 9, as yellow crystals: yield 89%, mp 75–77°C. Anal. calcd. for C₉H₁₉NOS₄Te: C 26.17, H 4.62; found: C 25.56, H 4.71. X-ray quality crystals were obtained for compounds 8 and 9, but not for 7 despite extensive attempts at recrystallization.

Alternative synthesis of Me₂Te

[S₂CNMe₂][S₂POCMe₂CMe₂O], 1, and compounds 2-6

In essentially the same manner as described above, $NH_4S_2POCMe_2CMe_2O$ (0.124 g, 0.54 mmol) was added, with constant stirring, to a solution of Me_TeCl[S_2CNMe_2] (0.165 g, 0.53 mmol) in dichloromethane (20 mL). The colorless reaction mixture immediately changed to yellow. The reaction mixture was stirred for 2 h, filtered to remove NH_4Cl or any unreacted dithiophosphate salt, and then *n*-hexane (approximately 5 mL) was added after the solvent had been reduced to 5 mL by pumping. Crystals were formed when the solution was left overnight in the refrigerator at $-6^{\circ}C$. The solvent was decanted and the crystals pumped to dryness to give $Me_2Te[S_2CNMe_2][S_2POCMe_2CMe_2O]$, **1**, as yellow crystals: 0.218 g, yield 85%, mp 129°C. Similarly were formed compounds **2–6**.

Alternative in situ preparation of Me₂Te[S₂CNMe₂][S₂COMe], 7

Typically, NaS₂CNMe₂ (0.147 g, 1 mmol) was added to a solution of Me₂TeCl₂ (0.228 g, 1 mmol) in dried carbon

Parameter	8	9
<i>a</i> , Å	10.073 (3)	9.881 (4)
b, Å	10.139 (2)	17.671 (3)
c, Å	9.108 (2)	10.149 (4)
α, deg	92.36 (2)	90.00
β, deg	115.55 (2)	113.65 (3)
γ, deg	111.19 (2)	90.00
$V, Å^3$	760.7 (4)	1623.3 (10)
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> 1 (no. 2)	$P2_1/c$ (no. 14)
Mol. wt., g mol ⁻¹	399.07	413.10
Ζ	2	4
Crystal dimensions, mm	$0.31 \times 0.19 \times 0.12$	$0.28 \times 0.23 \times 0.15$
ρ (calcd.), g cm ⁻¹	1.742	1.690
μ , cm ⁻¹	24.66	23.3
Transmission factors	0.67-1.00	0.62-1.00
Temperature, °C	23	23
Radiation, Å	ΜοΚα 0.71069	ΜοΚα 0.71069
Monochromator	Highly oriented graphite	Highly oriented graphite
Scan method	ω-2θ	ω-2θ
Scan speed, °/min	16.0	16.0
Max. 20	50	50
Total reflections measured	2850	6052
No. of unique data	2682	2207
No. of obsd. data $(I > 3.00 \sigma(I))$	1824	1339
No. of parameters (NP)	136	145
$R = \Sigma \ F_{\rm o}\ - F_{\rm c} \Sigma F_{\rm o} $	0.0343	0.0567
$R_{w} = [(\Sigma w (F_{o} - F_{c})^{2} / \Sigma w F_{o}^{2})]^{1/2}$	0.0296	0.0514
Goodness of fit	1.29	2.33
Largest shift/esd, final cycle	0.001	0.001
Largest residual electron density, e Å ⁻³	0.51	0.72
Atom associated with residual density	Те	Те

Table 1. Summary of crystal data, intensity collection, and structural refinement for $Me_2Te[S_2CNMe_2][S_2COEt]$, **8**, and $Me_2Te[S_2CNEt_2][S_2COMe]$, **9**.

disulfide or dichloromethane (20 mL). The reaction mixture was stirred for 2 h, and then KS₂COMe (0.146 g, 1 mmol) was added before the mixture was stirred for a further 2 h. The resulting mixture was filtered to remove NaCl, KCl, and unreacted materials, and the solvent reduced to 5 mL under vacuum before *n*-hexane (5 mL) was added. A yellow powder resulted, which was dried under vacuum after the solvent was decanted. The compound was recrystallized from dichoromethane–*n*-hexane to give Me₂Te[S₂CNMe₂][S₂COMe], **7**, as yellow crystals: 0.280 g, yield 72%, mp 95–97°C. All of the compounds **1–9** were also prepared in this manner.

Physical measurements

Elemental analyses were performed at Guelph Chemical Laboratories, Guelph, Ontario. The ¹H and ¹³C NMR spectra were recorded on a Bruker 300 FT/NMR spectrometer in CDCl₃ using Me₄Si as internal standard. The ³¹P and ¹²⁵Te NMR spectra were recorded on a Bruker 200 FT/NMR spectrometer in CDCl₃ using 85% H₃PO₄ andMe₂Te, respectively, as external standard. The infrared spectra were recorded on a Nicolet 5DX FT spectrometer as KBr pellets and far infrared spectra on a Bomem IR spectrometer between polyethylene films as Nujol mulls. Raman spectra

were recorded using samples in sealed capillary tubes on a Spectra-Physics 164 spectrometer using the 5145 Å exciting line of an argon ion laser. The melting points were determined on a Fisher–Johns apparatus.

X-ray crystallographic analysis

Pale yellow block-shaped crystals of $Me_2Te[S_2CNMe_2]$ -[S₂COEt], **8**, and $Me_2Te[S_2CNEt_2][S_2COMe]$, **9**, were sealed in thin-walled glass capillaries and mounted on a Rigaku AFC6S diffractometer, with graphite-monochromated MoK α radiation.

Cell constants corresponded to triclinic and monoclinic cell for 8 and 9, respectively, whose dimensions are given in Table 1, along with other experimental parameters. Based on the appropriate systematic absences for 9, statistical analyses of intensity distributions, and the successful solution and refinement of the structures, the space groups were determined to be $P\overline{1}$ (no. 2) for 8 and $P2_1/c$ (no. 14) for 9. The data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied.

The structures were solved by direct methods (25), and all calculations were performed using the TEXSAN (26) crystallographic software package of Molecular Structure Corp.²

² Least-squares function minimized: $\Sigma w(|F_0| - |F_c|)^2$, where $w = 4F_0^2(F_0^2)$, $\sigma^2(F_0^2) = [S^2(C + R^2B) + (pF_0^2)^2]/(Lp)^2$, S = scan rate, C = total integrated peak count, R = ratio of scan time to background counting time, Lp = Lorentz-polarization factor, and p = p factor.

The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included in their idealized positions with C—H set at 0.95 Å and with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they were attached.

The weighted and unweighted agreement factors and standard deviation of an observation of unit weight³ are given in Table 1. Plots of $\Sigma w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, sin θ/λ , and various classes of indices showed no unusual trends. Interatomic distances and bond angles are given in Table 2, and the molecular structures of the two compounds are displayed as ORTEP diagrams in Figs. 1–4. The final atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms, anisotropic thermal parameters for non-hydrogen atoms, and final fractional coordinates and thermal parameters for hydrogen atoms, have been deposited.⁴

Calculation of Pauling partial bond order

The formula proposed by Pauling (27) for calculating the bond orders of partial bonds is given by $d_n - d = -0.60 \log n$, where d_n is the bond length for bond number, n, and d is the length of the single bond of the same type. Based on the C—C single bond of 1.54 Å, Pauling's formula gives bond lengths of 1.36 Å for n = 2; 1.72 Å for n = 0.5; and 1.90 Å for n = 0.25. These give percentage increases in bond length for the partial bonds of approximately 12 and 23%, respectively, for n = 0.5 and 0.25. It is reasonable to assume that similar relationships relating bond order to interatomic distances for the much longer secondary interactions or partial bonds involving Te and S should utilize percentage differences.

Pauling's relationship, which can be written as $n = 10^X$, where $X = (d - d_n)/0.6$, can be modified to allow for percentage differences normalized to 1.54 to give $X = [1.54(d - d_n)/d]/0.6$ or $X = 2.5(d - d_n)/d$. Based on a Te—S single bond length of 2.63 Å, typical calculated values of the lengths of partial bonds for various values of *n* are as follows: 1.0, 2.63; 0.75, 2.76; 0.50, 2.95; 0.25, 3.26; 0.10, 3.68; *n*, bond length (Å). This scale appears to be compatible with the sum of the van der Waals radii of 3.86 Å for Te and S (28).

Results and discussion

The preparation of a variety of dimethyltellurium(IV) compounds with two different 1,1 dithio ligands is achieved in 80–90% yield by the action of approximately equimolar amounts of the sodium or potassium salt of a dithiocarbamic or dithiocarbonic acid with an *O*,*O*-alkylene dithiophosphate or *N*,*N*-dialkyl dithiocarbamate derivative of chlorodimethyltellurium(IV) such as Me₂TeCl[S₂POCMe₂CMe₂O], Me₂TeCl[S₂POCH₂CMe₂CH₂O], or Me₂TeCl[S₂CNMe₂] in dichloromethane, in accord with the eqs. [1]–[3]:

$$Me_{2}TeCl[S_{2}\overrightarrow{POGO}] + NaS_{2}CNR_{2}$$
$$\rightarrow Me_{2}Te[S_{2}CNR_{2}][S_{2}\overrightarrow{POGO}]$$

$$[2] Me_2TeCl[S_2POCMe_2CMe_2O] + KS_2COR'$$

$$[3] \qquad Me_2TeCl[S_2CNR_2] + KS_2COR'$$

[1]

$$\rightarrow$$
 Me₂Te[S₂CNR₂][S₂COR']

$$(G = -CMe_2CMe_2-, -CH_2CMe_2CH_2-; R = Me, Et; R' = Me, Et)$$

These mixed ligand dimethyltellurium(IV) compounds can also be formed in similar yields by the addition of the ammonium salt of the dithiophosphoric acid to chlorodimethyl (N,N-dialkyl dithiocarbamato)tellurium(IV) as exemplified by eq. [4]:

$$[4] \qquad Me_2 TeCl[S_2CNMe_2] + NH_4S_2POCMe_2CMe_2O \rightarrow Me_2Te[S_2CNMe_2][S_2POCMe_2CMe_2O] \rightarrow Me_2Te[S_2CNMe_2][S_2POCMe_2CMe_2O]$$

The Me₂TeClL species can also be prepared in situ in which case the reaction involves the complete addition of an equimolar amount of the salt of one 1,1-dithio acid to dimethyltellurium dichloride, the removal of insoluble salts, and the addition of an equimolar amount of the salt of a different 1,1-dithio acid, as exemplified by eqs. [5] and [6]. The overall yield based on Me₂TeCl₂ is close to 70%

[5]
$$Me_2TeCl_2 + KS_2COR'$$

 \rightarrow Me₂TeCl[S₂COR'] + KCl

$$[6] Me_2TeCl[S_2COR'] + NaS_2CNR_2$$

$$\rightarrow$$
 Me₂Te[S₂CNR₂][S₂COR'] + NaCl

Solid samples of compounds 1–9 are stable over extended periods, particularly when stored in the refrigerator, as can be confirmed by the fact that NMR spectra recorded after several months show no changes from the spectra recorded immediately after the formation of the compounds. All of the compounds are soluble in common organic solvents such as benzene, toluene, carbon disulfide, dichloromethane, and chloroform, the later being used as the solvent for spectroscopic studies. The vibrational spectra as well as the NMR spectra of the freshly prepared samples provide definitive evidence that these compounds are indeed the mixed ligand species, Me₂TeLL', and not 1:1 mixtures of the bis species Me_2TeL_2 and $Me_2TeL'_2$. This is of course further confirmed by the X-ray structures of 8 and 9. The NMR spectra recorded over time also indicate that eventually all derivatives, Me2TeLL', slowly disproportionate to the two bis derivatives, Me_2TeL_2 and $Me_2TeL'_2$. The three species appear to be in equilibrium because the addition of more Me₂TeL₂ to a solution brings about the expected changes in the relative

³Standard deviation of an observation of unit weight: $\sum w(|F_0| - |F_c|)^2 / (N_0 - N_v)^{1/2}$, where N_0 = number of observations and N_v = number of variables.

⁴ Copies of material deposited may be purchased from: The Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, Canada, K1A 0S2. Tables of atomic coordinates have also been deposited with the Cambridge Crystallographic Data Centre and can be obtained on request from: The Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, 12 Union Road, Cambridge, CB2 1EZ, U.K. Structure factor amplitudes are no longer being deposited and may be obtained directly from the author.

Me ₂ Te[S ₂ CNM	le ₂][S ₂ COEt], 8	Me ₂ Te[S ₂ CNEt ₂]	[S ₂ COMe], 9
Te(1)—S(1)	2.620(2)	Te(1)—S(1)	2.608(5)
Te(1) - S(3)	2.650(2)	Te(1) - S(3)	2.620(5)
Te(1) - C(1)	2.128(6)	Te(1)-C(1)	2.11(1)
Te(1) - C(2)	2.132(7)	Te(1)-C(2)	2.10(2)
S(1)—C(3)	1.762(7)	S(1)—C(3)	1.75(1)
S(2)—C(3)	1.682(7)	S(2)—C(3)	1.67(2)
N(1)—C(3)	1.311(8)	N(1)—C(3)	1.38(2)
N(1)—C(4)	1.435(9)	N(1)—C(4)	1.46(2)
N(1)—C(5)	1.445(9)	N(1)—C(6)	1.46(2)
S(3)—C(6)	1.729(7)	S(3)—C(8)	1.74(2)
S(4)—C(6)	1.633(7)	S(4)—C(8)	1.66(2)
O(1)—C(6)	1.343(8)	O(1)—C(8)	1.32(2)
O(1)—C(7)	1.451(9)	O(1)—C(9)	1.43(2)
C(7)—C(8)	1.46(1)	C(4)—C(5)	1.51(2)
		C(6)—C(7)	1.52(2)
S(1)—S(2)	2.994(3)	S(1)—S(2)	2.987(6)
S(3)—S(4)	2.956(3)	S(3)—S(4)	3.007(7)
Te(1) - S(2)	3.205(2)	Te(1) - S(2)	3.277(4)
Te(1) - S(4)	5.085(2)	Te(1) - S(4)	3.346(5)
Te(1)—O(1)	3.145(5)	Te(1) - O(1)	4.64(1)
Te(1) - S(2)'	3.567(2)	Te(1) - S(2)''	3.585(5)
Te(1)—Te(1)'	4.0251(9)	Te(1)— $Te(1)''$	4.072(2)
S(1)-Te(1)-S(3)	166.87(6)	S(1)-Te(1)-S(3)	162.0(2)
S(1)-Te(1)-C(1)	88.5(2)	S(1)-Te(1)-C(1)	87.1(5)
S(1)-Te(1)-C(2)	83.4(2)	S(1)-Te(1)-C(2)	81.3(5)
S(3)-Te(1)-C(1)	87.8(2)	S(3)-Te(1)-C(1)	88.2(5)
S(3)-Te(1)-C(2)	84.4(2)	S(3)-Te(1)-C(2)	82.0(4)
C(1)-Te(1)-C(2)	95.3(3)	C(1)-Te(1)-C(2)	96.4(7)
Te(1)-S(1)-C(3)	98.1(2)	Te(1)-S(1)-C(3)	99.3(6)
S(1)-C(3)-S(2)	120.8(4)	S(1)-C(3)-S(2)	122(1)
S(1)-C(3)-N(1)	117.0(5)	S(1)-C(3)-N(1)	114(1)
S(2)-C(3)-N(1)	122.2(6)	S(2)-C(3)-N(1)	124(1)
C(3)-N(1)-C(4)	124.9(7)	C(3)-N(1)-C(4)	124(1)
C(3)-N(1)-C(5)	121.5(7)	C(3)-N(1)-C(6)	120(1)
C(4)-N(1)-C(5)	113.6(6)	C(4)-N(1)-C(6)	116(1)
		N(1)-C(4)-C(5)	115(1)
		N(1)-C(6)-C(7)	114(1)
Te(1)-S(3)-C(6)	103.0(3)	Te(1)-S(3)-C(8)	99.6(6)
S(3)-C(6)-S(4)	123.1(5)	S(3)-C(8)-S(4)	124(1)
S(3)-C(6)-O(1)	111.9(5)	S(3)-C(8)-O(1)	110(1)
S(4)-C(6)-O(1)	125.0(5)	S(4)-C(8)-O(1)	126(1)
C(6)-O(1)-C(7)	118.9(6)	C(8)-O(1)-C(9)	119(1)
O(1)-C(7)-C(8)	107.7(7)		
S(1)-Te(1)S(2)	60.89(5)	S(1)-Te(1)S(2)	59.7(1)
S(3)-Te(1)-O(1)	51.5(1)	S(3)-Te(1)S(4)	59.1(1)
S(3)-Te(1)S(2)	130.83(5)	S(3)-Te(1)S(2)	136.7(1)
S(1)-Te(1)-O(1)	139.7(1)	S(1)-Te(1)S(4)	136.3(1)
S(2)Te(1)O(1)	79.4(1)	S(2)Te(1)S(4)	77.7(1)
C(1)-Te(1)S(2)	82.1(2)	C(1)-Te(1)S(2)	83.2(5)
C(2)-Te(1)S(2)	144.1(2)	C(2)-Te(1)S(2)	141.0(5)
C(1)- $Te(1)$ $O(1)$	79.5(2)	C(1)-Te(1)S(4)	78.3(5)
C(2)-Te(1)-O(1)	135.6(2)	C(2)-Te(1)S(4)	140.7(4)
C(1)-Te(1)-S(2)'	170.5(2)	C(1)-Te(1)S(2)"	169.2(5)
S(2)-Te(1)S(2)'	107.28(4)	S(2)-Te(1)S(2)"	107.37(9)
Te(1)-S(2)Te(1)'	72,72(4)	Te(1)-S(2)Te(1)''	72.63(9)

Table 2. Interatomic distances (Å) and angles (deg) for $Me_2Te[S_2CNMe_2][S_2COEt]$, 8, and $Me_2Te[S_2CNEt_2][S_2COMe]$, 9.^{*a*}

^aSymmetry equivalent position (1 - x, -y, -z) and (-x, -y, -z) by a double prime.

Fig. 1. ORTEP plots of the molecules (*a*) $Me_2Te[S_2CNMe_2][S_2COEt]$, 8, and (*b*) $Me_2Te[S_2CNEt_2][S_2COMe]$, 9. Atoms are drawn with 30% probability ellipsoids and spheres with hydrogen atoms omitted for clarity.



amounts of Me₂TeLL' and Me₂TeL'₂. However, all three species, simultaneously also undergo reductive elimination to Me₂Te and the diligands, so that the spectra become very complicated. Qualitatively, the reductive elimination does not appear to be a reversible process so eventually the solution becomes depleted of tellurium(IV) species. Qualitatively, the disproportionation and reductive elimination appear to be most evident for derivatives containing dithiocarbonate ligands and least evident for those containing the cyclic dithiophosphate ligands.

Crystal structures of Me₂Te[S₂CNMe₂][S₂COEt], 8, and Me₂Te[S₂CNEt₂][S₂COMe], 9

 $Me_2Te[S_2CNMe_2][S_2COEt]$, 8, crystallizes in the space group $P\overline{1}$ and Me₂Te[S₂CNEt₂][S₂COMe], **9**, in $P2_1/c$. The ORTEP diagrams in Fig. 1a and 1b illustrate that in both compounds the immediate environment about tellurium is that of the sawhorse structure typical of tellurium(IV) compounds in which the lone pair is assumed to be active stereochemically and occupying an equatorial position in a distorted trigonal bipyramid, approximately in the position of the Te(1) label. The two methyl groups occupy the other two equatorial positions; the C-Te-C bond angles of 95.3(3)° and $96.4(7)^{\circ}$ in 8 and 9, respectively, being close to the value of 96(1)° in Me₂Te[S₂CN(CH₂)₃CH₂][S₂CN(CH₂)₄CH₂] (21), and similar to those of $93.9(2)^{\circ}$, $96.6(2)^{\circ}$, and $96.2(2)^{\circ}$ in related bis derivatives, $Me_2Te[S_2CNMe_2]_2$ (12), Me₂Te[S₂COMe]₂ (1),and Me₂Te[S₂COEt]₂ (2), respectively. The average Te—C bond length of 2.12(1) Å in 8 and 9 is essentially the same as that in $Me_2Te[S_2NCMe_2]_2$ and the two Me₂Te[S₂COR]₂ species. The S-Te-S bond angle of 166.87(6)° for the axial sulfur atoms in **8** is close to that in the mixed species, Me₂Te[S₂CN(CH₂)₃CH₂][S₂CN(CH₂)₄CH₂] $(166.1(2)^{\circ})$, as well as in Me₂Te[S₂NCMe₂]₂ and $Me_2Te[S_2COR]_2$ (167.58(7)° and 166.2(2)° avg., respectively). By contrast, the value of $162.0(1)^{\circ}$ in 9 is the same as in Me₂Te[S₂CN(CH₂)₃CH₂]₂ (21), so it is difficult to detect an obvious pattern or trend. The two Te-S bonds in the **Fig. 2.** ORTEP plots of the molecules (*a*) $Me_2Te[S_2CNMe_2]$ [S₂COEt], **8**, and (*b*) $Me_2Te[S_2CNEt_2][S_2COMe]$, **9**, showing the stereochemistry about tellurium when the intramolecular interactions leading to unsymmetrical ligands are included. The atoms are drawn with 30% probability ellipsoids and spheres. Hydrogen atoms are omitted for clarity.



bis species $Me_2Te[S_2NCMe_2]_2$, $Me_2Te[S_2COMe]_2$, and $Me_2Te[S_2COEt]_2$ have an average value of 2.63(1) Å, even though in all three cases the two Te—S bonds have quite different lengths ranging from 2.566(1) to 2.680(1) Å. In **8** and **9**, the Te—S bonds to the S_2CNR_2 groups, 2.620(2) in **8** and 2.608(5) Å in **9**, are shorter than those to the S_2COR groups, 2.650(2) in **8** and 2.620(5) Å in **9**. In the absence of any Te--S associations involving the bonded S atom at contact distances less than the sum of the van der Waals radii of 3.86 Å (28), bonding to dithiocarbamates is apparently slightly favored.

The pendant sulfur atoms in the dithiocarbamate groups are oriented toward the tellurium center to give Te-S anisobonds of 3.205(1) in 8 and 3.277(4) Å in 9 (see Fig. 2a and 2b). These values are typical for analogous dithiocarbamates and correspond to normalized Pauling partial bond orders of about 0.25, which is compatible with their being part of the coordination sphere. Similar Te-S anisobonds, varying from 3.274(2) to 3.521(1) Å, occur in $Me_2Te[S_2COMe]_2$ and $Me_2Te[S_2COEt]_2$ (2) as well as in the two independent molecules of Me2TeCl[S2COEt] with values of 3.210(3) and 3.292(3) Å (29). Similarly, in Me₂Te[S₂CNEt₂][S₂COMe], 9, there is an anisobond between Te(1)—S(4) of 3.346(5) Å involving the S_2 COMe group (see Fig. 2b). Surprisingly, the orientation of the S₂COEt group in Me₂Te[S₂CNMe₂][S₂COEt], 8, is such that the second sulfur atom is turned away from tellurium so that Te(1)—S(4) is 5.085(2) Å and so clearly not bonded (see Fig. 2a). The intramolecular association now involves the oxygen of the OEt group with a Te(1)-O(1) distance of 3.145(5) Å. In a study of analogous monothiocarbonates (30), the terminal oxygen atom is oriented toward the tellurium center in Me₂Te[SCO₂(i-Pr)]₂ and Me₂TeCl[SCO₂Me], with Te—O (terminal) distances averaging 3.05(8) Å in the former and 2.948(8) Å in the latter. However, in Ph₂Te[SCO₂(i-Pr)]₂, one of the SCO₂(i-Pr) groups has a Te—O

Fig. 3. Plot of the molecule $Me_2Te[S_2CNMe_2][S_2COEt]$, **8**, showing the intermolecular interactions involving the anisobonded sulfur atoms leading to a dimer. Hydrogen atoms and the carbon atoms of the phenyl rings other than those attached to phosphorus are omitted for clarity.



(terminal) distance of 3.050(5) Å, but the other is oriented so that the Te—O(i-Pr) distance is 3.150(5) Å. This orientation is repeated in Me₂TeBr[SCO₂(i-Pr)] where the Te—O(i-Pr) distance is 2.930(6) Å. Thus, again it is difficult to detect a consistent trend.

In $Me_2Te[S_2CNEt_2][S_2COMe]$, 9, the orientations of the dithiocarbamate and dithiocarbonate groups result in the five atoms, S(1), S(2), S(3), S(4), and C(2), as well as Te(1) forming an approximate plane (mean deviation from plane of 0.1164 Å) with C(1) above the plane (2.06(1) Å) to give an approximate pentagonal pyramidal arrangement about Te(1) or a pentagonal bipyramidal arrangement if the lone pair is assumed to be occupying the axial position trans to C(1) (see Fig. 2b). The two planar S_2CN and S_2CO cores of the dithio groups have a dihedral angle of 10.4(1)°. By contrast, in Me₂Te[S₂CN(CH₂)₃CH₂][S₂CN(CH₂)₄CH₂], the dihedral angle between the two different dithiocarbamate groups is only $1.4(1)^\circ$. Despite the fact that the oxygen atom of the OEt group is turned toward tellurium in Me₂Te[S₂CNMe₂][S₂COEt], 8, rather than the terminal sulfur atom as can be seen from Fig. 2a, there is still an approximate plane (mean deviation from plane of 0.0946 Å) around tellurium with the five atoms, S(1), S(2), S(3), C(2), and now O(1) as well as Te(1) forming the plane with C(1) above the plane (2.08(1) Å). The two planar S₂CN and S₂CO cores of the dithio groups have a dihedral angle of only 3.9(1)°. Similar pentagonal planes appear to be a com**Fig. 4.** Plot of the molecule Me₂Te[S₂CNEt₂][S₂COMe], **9**, showing the intermolecular interactions involving the anisobonded sulfur atoms leading to a dimer. Hydrogen atoms and the carbon atoms of the phenyl rings other than those attached to phosphorus are omitted for clarity.



mon feature for dimethyltellurium derivatives with sulfur ligands having been reported for $Me_2Te[S_2COR]_2$ (1, 2), $Me_2Te[SCO_2R]_2$ (30), $Me_2Te[SCONR_2]_2$ (31), and $Me_2Te[S_2CN(CH_2)_3CH_2]_2$ (21), where the two dithio groups have small dihedral angles. However, by contrast, in $Me_2Te[S_2CN(CH_2)_4CH_2]_2$, the orientation of the two dithiocarbamates results in a dihedral angle between the two planar S_2CN cores being 69.6(2)° so that the arrangement about tellurium is better described as a distorted octahedral with the lone pair apparently inactive (21). A similar arrangement is found in $Ph_2Te[S_2COEt]_2$ so again it is difficult to identify factors that determine these orientations.

An examination of possible intermolecular associations reveals that both 8 and 9 have similar Te--S' interactions involving only the anisobonded sulfur atoms of the dithiocarbamate groups as is illustrated by Figs. 3 and 4. The Te(1)—S(2)' distances are 3.567(2) and 3.585(5) Å for 8 and 9, respectively, which correspond to bond orders close to 0.15, leading to pseudo-dimers. Thus, despite the different orientations of the dithiocarbonate groups in 8 and 9, neither of which show any intermolecular distances indicative of associations, similar dimeric units are formed in 8 and 9 by bridges in which the Te(1)-S(2)--Te'(1) and S(2)-Te(1)--S'(2) angles are $72.72(4)^{\circ}$ and $107.28(4)^{\circ}$, respectively, for 8 (see Fig. 3) and 72.63(9)° and 107.37(9)°, respectively, for 9 (see Fig. 4). A similar bridging system is found in $Me_2TeI[S_2CN(CH_2)_3CH_2]$, where, in contrast with the Me₂TeX[S₂CN(CH₂)₄CH₂] analogues which all have the halogen atoms acting as bridges, a rectangular bridge again

leads to pseudo-dimers with Te(1)-S(2)--Te'(1) and S(2)-Te(1)--S'(2) angles of 76.19(9)° and 103.8(1)°, respectively (21). Surprisingly, there are no comparable Te--S--Te bridges in the bis-Me₂Te[S₂CN(CH₂)_nCH₂]₂ species. In general, dithiocarbonates apparently do not tend to form intermolecular interactions through the sulfur atoms.

As with other dithiocarbamates, the (Te)S-C-N angles are all less than 120°, at 117.0(5)° and 114(1)° for 8 and 9, respectively, whereas the (Te)S-C-S and S-C-N angles are all over 120°, averaging 122(1)°, which is consistent with the π bond delocalization within the S₂CN planar moiety being of greater importance in the S₂C—N and TeS(N)C—S bonds. The (Te)S—C bonds (1.756(9) Å avg.) are typical of an S-C bond attached to the stronger Te-S bond in anisobidentate di- and monothiocarbamate derivatives (31) and also shorter than the sum of the covalent radii of C and S of 1.81 Å, suggesting a small degree of participation in the delocalized π -bonding. The C—S bond involving the anisobonded sulfur atom is shorter, with an average length of 1.676(9) Å. This is still considerably longer than a C=S bond (ca. 1.56 Å in CS_2 , COS, or CSTe (32)) but similar to that observed in species such as (NH₂)₂CS and thus consistent with a considerable degree of partial π -bond character as well as an anisobidentate link. Not only are the dithiocarbonate groups planar in terms of the sulfur and oxygen atoms about the central carbon, with a mean deviation of 0.003 Å in 8 and 0.004 Å in 9, but so to a first approximation are the ethyl and methyl groups; C(7) and C(8) being out of plane by only 0.050 and 0.068 Å, respectively, in 8 and C(9) only 0.018 Å out of the plane in 9. The terminal C=S bond in 8 (1.633(7) Å) is apparently shorter than the anisobonded C=S(--Te) bond in 9 (1.66(2) Å), and conversely, the C—STe bond in 8 (1.74(2) Å) is longer than in 9 (1.729(7) Å). The bond lengths and angles within the S₂CO moiety are in the same range as those reported for $Me_{2}Te[S_{2}COEt]_{2}$ $Me_2Te[S_2COMe]_2$ (2),(1).and $Me_2TeCl[S_2COEt]_2$ (29), which emphasizes the rigidity of the ligand regardless of its orientation about tellurium or whether it is in a mixed ligand species, bis compound, or haloderivative.

The S(1)-Te(1)-S(2) bite angles of the two dithiocarbamate groups are $60.89(2)^{\circ}$ and $59.7(1)^{\circ}$ with "bites" of 2.994(3) and 2.987(6) Å in 8 and 9, respectively, which are typical of anisobidentate dithiocarbamates. Similarly, the S(3)--S(4) bite angle in 9 of $59.1(1)^{\circ}$ in the dithiocarbonate is close to the average of the two angles in Me₂Te[S₂COEt]₂ (2). In view of the rigidity of the planar groups, not surprisingly, the S(3)—S(4) distances in 8 and 9 are similar.

Infrared and Raman spectra

Selected features in the infrared and Raman spectra and their assignments are given in Table 3. In considering these mixed species, it is useful to establish those features among the plethora of peaks, especially those associated with the presence of the CH₃ and CH₂ groups, that most clearly identify the presence of the particular dithiocarbamate, dithiocarbonate, or alkylene dithiophosphate group. In tellurium dithiocarbamate species, a distinctive peak in the infrared spectrum between 1484 and 1508 cm⁻¹ corresponds to the v(C-NR₂) stretching vibration, and one generally of medium intensity in both effects between 963 and 985 cm⁻¹ corre-

sponds to the v(C-S) stretch of the terminal or aniso sulfur atom (7, 8, 12). In tellurium dithiocarbonates, three strong features define the presence of stretching modes involving the stretching of the CO and CS bonds within the moiety S₂COC. As was confirmed by normal coordinates analyses, there is considerable mixing amongst these modes that are seen at ca. 1200, 1120, and 1040 cm^{-1} , and hence, they are assigned as $v(S_2COC)_a$, $v(S_2COC)_b$, and $v(S_2COC)_c$, respectively (29). Strong bands in the infrared spectra in the region 995–900 cm⁻¹ provide characteristic features indicative of the presence of the alkylene dithiophophate group in Me₂Te[S₂POCMe₂CMe₂O]₂ and Me₂Te[S₂POCH₂CMe₂CH₂O]₂, which are attributable to ring vibrations that are probably coupled with C-C stretching vibrations (20, 30, 31). In compounds 1–9, the above features are seen for the appropriate groups at similar, but not identical positions, to the corresponding bis compounds. Thus, for example, for $Me_2Te[S_2CNMe_2][S_2POCH_2CMe_2CH_2O]$ (3), v(C-NR₂) and v(C-S) are seen at 1517 and 968 cm⁻¹, respectively, in the infrared and Raman spectra, compared to 1491 and 973 cm⁻¹ in $Me_2Te[S_2CNMe_2]_2$ (12), and the most distinct ring vibration in Me₂Te[S₂POCH₂CMe₂CH₂O]₂ at 994 cm⁻¹ is seen at 985 cm⁻¹ in $\overline{3}$. All of this data is indicative of the presence of a mixed species rather than a mixture of two bis compounds.

The characteristic peaks corresponding to the Te-C asymmetric and symmetric stretches are prominent in all of the Raman spectra of 1-9, in general having values for v(Te-C)asym (531-541 cm⁻¹) that are closer to those found in $Me_2Te[S_2COR]_2$ or $Me_2TeCl[S_2COR]$ (533–544 cm⁻¹) than to Me₂Te[S₂POCMe₂CMe₂O]₂ and Me₂Te[S₂POCH₂CMe₂CH₂O]₂ (ca. 529 cm⁻¹) (20). In Me₂Te[S₂CNMe₂][S₂COEt], **8**, whose structure has been described above, the two Te-S stretches are assigned to 359 and 317 cm⁻¹, compared to the asymmetric and symmetric stretches in Me₂Te[S₂CNMe₂]₂ (362 and 349 cm⁻¹) and Me₂Te[S₂COEt]₂ (382 and 301 cm⁻¹), which is of course consistent with the mixed compound rather than a mixture, as can be illustrated for all nine compounds. While the mixing between the two Te-S modes is going to still be significant in 1–9, the groups are not equivalent as in bis compounds. The Te-S bond to the dithiocarbamate is slightly shorter, so the band at 359 cm⁻¹ probably has a greater contribution from Te-S(CNR₂) and that at 317 cm⁻¹ a corresponding contribution from Te-S(COR). Both bands are seen at slightly higher wave number in $Me_2Te[S_2CNEt_2][S_2COMe]$, 9, at 369 and 328 cm⁻¹, which is at least consistent with both bonds being slightly shorter in 9 than in 8. For the compounds containing a dithiophosphate group, 1-6, it is reasonable to assign the band at higher wave number as having more contribution from Te- $S(CNR_2)$ or Te-S(COR), because in the bis compounds, Me₂Te[S₂POCMe₂CMe₂O]₂ and Me₂Te[S₂POCH₂CMe₂CH₂O]₂, the Te-S stretches were assigned at lower wave number than in the bis dithiocarbamates and -carbonates (20).

NMR spectra

The ¹³C{¹H} NMR spectral data for compounds **1–9** are presented in Table 4. Although the peaks corresponding to the S_2CN and S_2CO carbon atom are the weakest in every spectrum, they provide definitive evidence for the formation

Table 3. Selected features (cm⁻¹) and their assignments in the vibrational spectra of $Me_2Te[S_2CNMe_2][S_2POCMe_2CMe_2O]$, **1**, $Me_2Te[S_2CNEt_2][S_2POCMe_2CMe_2O]$, **2**, $Me_2Te[S_2CNMe_2][S_2POCH_2CMe_2CH_2O]$, **3**, $Me_2Te[S_2CNEt_2][S_2POCMe_2CMe_2O]$, **4**, $Me_2Te[S_2COMe][S_2POCMe_2CMe_2O]$, **5**, $Me_2Te[S_2COEt][S_2POCMe_2CMe_2O]$, **6**, $Me_2Te[S_2CNMe_2][S_2COMe]$, **7**, $Me_2Te[S_2CNMe_2][S_2COEt]$, **8**, $Me_2Te[S_2CNEt_2][S_2COMe]$, **9**. *^{a,b,c}*

1	2	3	4	5	6	7	8	9	Assignment
1504 ms	1490 s	1517 s	1483 s			1496 ms	1501 s	1483 vs	v (C-NR ₂)
				1205 vs	1200 vs	1195 ms	1187 s	1201 vs	v $(S_2COC)^a$
				1145 vs	1140 vs	1130 s	1110 s	1139 vs	$v (S_2 COC)^b$
				1048 vs	1042 vs	1045 vs	1031 vs	1050 vs	$v (S_2 COC)^c$
1009 mw	1007 m	1046 vs	1045 s	1013 sh	1010 sh				ν (PO-C)
		985 vs, br 980 [5]	992 vs, br 995 [5]						Ring
961 s 966 [35]	989 m 985 [15]	965 sh 968 [30]	983 [20]			971 s 969 [20]	968 s 968 [10]	984 ms 982 [15]	v (S=CSNR ₂)
911 vs 915 [5]	917 s 911 [10]	910 m	909 ms 914 [15]	908 vs	910 vs				Ring
818 mw 820 [10]	815 ms 820 [5]	806 m 814 [5]	805 s 810 [10]	821 mw 820 [15]	815 mw 820 [15]				v (PO ₂)sym
537 [40]	537 [40]	539 [40]	537 [60]	532 [30]	533 [30]	531 [20]	541 [30]	534 [100]	v (Te-C)asym
515 [90]	512 [80]	517 [90]	523 [100]	525 [50]	525 [50]	515 [40]	527 [40]	520 [60]	v (Te-C)sym
373 m 372 [100]	377 s 378 [100]	373 ms 372 [100]	374 ms 373 [90]	352 m 361 [30]	361 mw 361 [20]	370 ms 368 [100]	356 ms 359 [70]	358 ms 369 [80]	v (Te-S)asym
296 mw 293 [30]	330 ms 333 [25]	298 mw 303 [5]	333 ms 335 [20]	309 mw 313 [100]	310 ms 313 [100]	351 s 350 [10]	316 ms 317 [100]	326 m 328 [10]	v (Te-S)sym

"IR assignments in italic with s = strong, m = medium, w = weak, sh = shoulder, br = broad, and v = very.

^bSquare brackets denote relative intensities in the Raman effect.

^cIR spectra run between KBr plates down to 400 cm⁻¹ and between polyethylene below 400 cm⁻¹.

^{*d*}Raman spectra run neat in sealed tubes.

	Table 4.	$^{13}C,$	³¹ P,	and	¹²⁵ Te	NMR	chemical	shifts	for	the	mixed	ligand	dimethylte	llurium	derivatives	1–9 . ^{<i>a</i>}	, <i>b</i> , <i>c</i>
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Compounds 1–9	TeCH ₃	POC	POCC	NC	NCC	OC	OCC	NCS_2	OCS_2	³¹ P	¹²⁵ Te
$Me_2Te[S_2CNMe_2][S_2POCMe_2CMe_2O], 1^d$	17.32	89.25	24.40 d	44.35					196.0	109.5	525
			[17.6]								
$Me_2Te[S_2CNEt_2][S_2POCMe_2CMe_2O], 2$	17.29	89.09	24.4	49.01	12.14				194.8	110.0	525
$Me_2Te[S_2CNMe_2][S_2POCH_2CMe_2CH_2O], 3^d$	17.40	75.98 d	32.67	44.59					196	97.6	522
		[29.4]									
$Me_2Te[S_2CNEt_2][S_2POCH_2CMe_2CH_2O], 4^d$	17.55	75.81 d	32.70 d	49.22	12.69				194.2	98.1	519
		[29.4]	[18.0]								
$Me_2Te[S_2COMe][S_2POCMe_2CMe_2O]$, 5	16.89	89.70	24.32 d			61.22			222.9	107.5	539
			[19.4]								
$Me_2Te[S_2COEt][S_2POCMe_2CMe_2O], 6$	16.85	89.89	24.30			71.24	13.95		222.3	107.7	536
$Me_2Te[S_2CNMe_2][S_2COMe], 7$	16.19			44.34		60.62		198.9	222.2		491
$Me_2Te[S_2CNMe_2][S_2COEt], 8$	16.17			44.25		70.42	14.16	199.1	221.2		488
$Me_2Te[S_2CNEt_2][S_2COMe], 9$	16.34			48.88	12.59	60.29		197.2	222.0		474

^aThe spectra were recorded in CDCl₃ and reported in ppm from Me₄Si for ¹³C, from H₃PO₄ for ³¹P, and from Me₂Te for ¹²⁵Te.

^bAll peaks are singlets, the doublets arising from J(PC) coupling are marked with a d.

^cCoupling constants in Hz shown in square brackets.

^dPOCCC for 3 and 4, 21.93 and 21.95 ppm, respectively.

Table 5. ¹H NMR chemical shifts for the mixed ligand dimethyltellurium derivatives 1–9.^{*a,b,c*}

Compounds 1–9	Te-CH ₃	POC_nCH_3	PO-CH ₂	N-CH ₃ /CH ₂	NCH ₂ -CH ₃	O-CH ₃ /CH ₂	OC-CH ₃
$Me_2Te[S_2CNMe_2][S_2POCMe_2CMe_2O], 1$	2.54	1.43		3.43 (6 H, s)			
	(6 H, s)	(12 H, s)					
Me ₂ Te[S ₂ CNEt ₂][S ₂ POCMe ₂ CMe ₂ O], 2	2.54	1.43		3.83 (4 H, q)	1.25 (6 H, t)		
	(6 H, s)	(12 H, s)		[J(HH) 7.0]	[J(HH) 7.0]		
$Me_2Te[S_2CNMe_2][S_2POCH_2CMe_2CH_2O], 3^d$	2.59	1.04	4.02 (4 H, d)	3.43 (6 H, s)			
	(6 H, s)	(6 H, s)	[J(PH) 15.5]				
$Me_2Te[S_2CNEt_2][S_2POCH_2CMe_2CH_2O], 4^d$	2.59	1.03	4.02 (4 H,d)	3.82 (4 H, q)	1.26 (6 H, t)		
	(6 H, s)	(6 H, s)	[J(PH) 15.5]	[J(HH) 7.1]	[J(HH) 7.1]		
Me ₂ Te[S ₂ COMe][S ₂ POCMe ₂ CMe ₂ O], 5	2.61	1.43				4.12 (3 H, s)	
	(6 H, s)	(12 H, s)					
$Me_2Te[S_2COEt][S_2POCMe_2CMe_2O], 6$	2.58	1.41				4.55 (2 H, q)	1.39
	(6 H, s)	(12 H, s)				[J(HH) 7.1]	$(3 H, t)^{e}$
$Me_2Te[S_2CNMe_2][S_2COMe], 7$	2.47			3.42 (6 H, s)		4.07 (3 H, s)	
	(6 H, s)						
$Me_2Te[S_2CNMe_2][S_2COEt], 8$	2.49			3.44 (6 H, s)		4.55 (2 H, q)	1.39 (3 H, t)
	(6 H, s)					[J(HH) 7.1]	[J(HH) 7.1]
$Me_2Te[S_2CNEt_2][S_2COMe], 9$	2.45			3.85 (4 H, q)	1.26 (6 H, t)	4.05 (3 H, s)	
	(6 H, s)			[J(HH) 7.1]	[J(HH) 7.1]		

^aThe spectra were recorded in CDCl₃ and reported in ppm from Me₄Si.

^{*b*}Number of protons and multiplicities are in parentheses (s = singlet; t = triplet; d = doublet; q = quartet).

^cCoupling constants in Hz shown in square brackets.

^{*d*}PO-C H_2 for **3** and **4** are both 4.02 (4 H, d) (J(PH) = 15.5) ppm.

^ePartially masked by the large singlet at 1.41 ppm.

of the mixed ligand Me₂TeLL' species. Thus, for example, in the spectrum of Me₂Te[S₂CNMe₂][S₂COMe], **9**, for which we have the solid state structure, two peaks are seen at 198.9 and 222.2 ppm which correspond to the S₂CN and S₂CO peaks, respectively. These are shifted slightly but definitively from those of the corresponding bis species, Me₂Te[S₂CNMe₂]₂ at 200.0 and Me₂Te[S₂COMe]₂ at 220.9 ppm (12, 2). When the spectra are rerecorded after 24 h, two additional peaks corresponding to the two bis species are present. Identical features are seen in the spectra of compounds **7** and **8**. In compounds **1**–**4**, which contain a cyclic dithiophosphate instead of a dithiocarbonate, the shift of the S₂CN carbon is more marked.

The peak attributed to the $TeCH_3$ carbon is at 17.32 ppm in Me₂Te[S₂CNMe₂][S₂POCMe₂CMe₂O], 1, which is slightly less than the average value of the chemical shift for their bis analogues $Me_2Te[S_2POCMe_2CMe_2O]_2$ and Me₂Te[S₂CNMe₂]₂, which are at 19.2 and 16.6 ppm, respectively (12, 20). The chemical shifts in 2-4 range from 17.29 to 17.55 ppm but in compounds 5 and 6 are at ca. 16.9 ppm, which is closer to the value of ca. 15.6 ppm found in the bis dithiocarbonates (2). In the mixed ligand compounds that contain dithiocarbamate and -carbonate, 7-9, the TeCH₃ shifts are essentially the average of the bis species, so the contributions appear to be additive. All of the carbon atoms in the ligands have very similar, though not identical, chemical shifts to those observed in the analogous bis compounds (2, 12, 20). The doublets arising from P-C coupling and the values of the J^{PC} coupling constants are as observed for the bis compounds and (or) related cyclic dithiophosphate derivatives (20, 33).

The ³¹P{H} NMR spectra of fresh samples show single peaks (see Table 4) in the region 107.5-110.0 ppm for compounds 1, 2, 5, and 6, relative to a peak at 105.0 ppm in Me₂Te[S₂POCMe₂CMe₂O]₂, and at 97.6 and 98.1 ppm for compounds 3 and 4, respectively, relative to 92.0 ppm in Me₂Te[S₂POCH₂CMe₂CH₂O]₂ (20). These constitute downfield shifts relative to the free cyclic dithiophosphoric acids of the order of 15.1-17.6 ppm when a dithiocarbamate is present with the dithiophosphate and of the order of 20.5-21.0 ppm when a dithiocarbonate is present. These shifts appear to favor the concept that the dithiophosphates are essentially bidentate in solution (34), presumably through rapid exchange. When the spectra were recorded again after the solutions had been left standing, peaks at 105 or 92 ppm from were observed arising the formation of Me₂Te[S₂POCMe₂CMe₂O]₂ or Me₂Te[S₂POCH₂CMe₂CH₂O]₂, respectively, as the result of disproportionation and grew over several days to be approximately equal in height with that of the Me₂TeLL' species.

The ¹²⁵Te NMR spectra of freshly prepared solutions (Table 4) show a single peak whose chemical shift is reasonably close to the average value for the related bis compounds and hence in the range 519–528 ppm for compounds 1–4, 539 and 536 ppm for 5 and 6, and 474–491 ppm for 7–9. The spectra of compounds 7–9 show evidence of the presence of the bis species, indicating that disproportionation is already significant in the time taken to run a ¹²⁵Te NMR spectrum in species that do not contain a cyclic dithiophosphate. Over a period of approximately three days, the relative peak heights of the bis species increase, although all are decreasing in in-

tensity. The peak due to $Me_2Te[S_2COR]_2$ dies away more rapidly, presumably reflecting the fact that the dithiocarbonate derivatives more readily undergo reductive elimination to Me_2Te and diligand.

The ¹H NMR spectral data for compounds 1–9 are summarized in Table 5. The splitting patterns and intensities of peaks in the ¹H NMR spectra of all of these compounds are found to be consistent with the structures of 7 and 8, and by extension to all of the other derivatives. All compounds, 1-9, show a sharp singlet assignable to the CH₃ groups attached to tellurium in the range 2.45–2.54 ppm. The CH_3 Te chemical shifts are close to but not quite additive for compounds 1–6 and essentially additive for 7–9 in that they all lie close to the average value of the two analogous bis derivatives. As was the case for the ¹³C NMR spectra, the chemical shifts of protons within the ligands are close to but not identical to those of the bis ligand species. In all derivatives containing a dithiocarbamate group, compounds 1-4 and 7-9, the two CH_3 or CH_3CH_2 groups show no signs of nonequivalence despite the fact that the nitrogen atom is clearly planar in the solid state structures of 8 and 9. There is still no sign of coalescence in low-temperature runs. Similarly, in the compounds containing the dithiophosphate groups, 1-6, only single peaks are seen for the CH₃ protons of the dithiophosphate groups even though they have the potential to be in nonequivalent positions. This is the same as was observed for the corresponding bis species, where nonequivalent positions were seen in solid state structures (20). Compounds 3 and 4 have hydrogen atoms attached to the α carbon atom of the glycoxy groups, which display geminal coupling with phosphorus with $^{J}(PH)$ values of 15.5 Hz that are the same as in the bis species and appear to be more typical of bidentate than monodentate linkages.

Concluding comments

The study demonstrates that, despite the well-known propensity of Me₂TeL₂ species, where L is a dithio ligand, to undergo exchange and reductive elimination, mixed ligand species of the type Me₂TeLL', are formed in both stepwise and in situ reactions and are not just fortuitous 1:1 mixtures of Me₂TeL₂ and Me₂TeL'₂ derivatives. Surprisingly, the orientations of the dithiocarbonate groups differ in Me₂Te[S₂CNMe₂][S₂COEt], 8, and Me₂Te[S₂CNEt₂][S₂COMe], 9; having the pendant sulfur atom turned toward tellurium in 9 as has been found for the corresponding bis dithiocarbonate species, Me₂Te[S₂COEt]₂ and Me₂Te[S₂COMe]₂, but away from tellurium in 8. This suggests that the difference in energy when aniso bonds are formed between OR groups or terminal S atoms, must be very small and easily overridden by other effects. Despite the difference in the intramolecular associations in 8 and 9, the intermolecular association to make pseudo dimers is identical in both resulting in Te-S-Te-S rectangular bridges involving the pendant sulfur atom of the dithiocarbamate groups.

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