Inorg. Chem. **1994,** *33,* 6154−6162

Synthesis and Characterization of *N,N*-Diethyl, Pyrrolidyl, and Piperidyl Monothiocarbamate Derivatives of Dimethyltellurium(IV). Crystal Structures of Me$_2$Te[SCONEt$_2$]$_2$, Me$_2$TeCl[SCONEt$_2$], Me$_2$TeBr[SCONEt$_2$], and Me$_2$TeI[SCONEt$_2$]

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Received May 10, 1994[⊗]

The dimethylbis(monothiocarbamato)tellurium(IV) compounds Me$_2$Te[SCONR$_2$]$_2$, where NR$_2$ = NEt$_2$, N(CH$_2$)$_3$CH$_2$, and N(CH$_2$)$_4$CH$_2$, and the halodimethyl(*N,N*-diethyl and pyrrolidyl monothiocarbamato)tellurium(IV) compounds Me$_2$TeX[SCONR$_2$], where X = Cl, Br, and I and NR$_2$ = NEt$_2$ or N(CH$_2$)$_3$CH$_2$, have been prepared, with yields of 80% or better, by the reaction of the sodium salts of the monothiocarbamic acids, in excess or in equimolar amounts, with dimethyltellurium dihalide. The compounds were characterized by elemental analysis and ^{1}H, ^{13}C, and ^{125}Te NMR, infrared, and Raman spectroscopy. The crystal structures of Me$_2$Te[SCONEt$_2$]$_2$, Me$_2$TeCl[SCONEt$_2$], Me$_2$TeBr[SCONEt$_2$], and Me$_2$TeI[SCONEt$_2$] were determined. Me$_2$Te[SCONEt$_2$]$_2$ (**1**), which crystallizes as monoclinic in space group $P2_1/n$ (No. 14), has the cell parameters a = 11.184(2) Å, b = 10.036(2) Å, c = 16.531(2) Å, β = 94.08(1)°, V = 2424(1) Å^3, Z = 4, R = 0.0337, and R_w = 0.0270. Me$_2$TeCl[SCONEt$_2$] (**4**), which crystallizes as monoclinic in space group $P2_1/c$ (No. 14), has the cell parameters a = 10.539(2) Å, b = 10.864(2) Å, c = 11.511(2) Å, β = 112.23(1)°, V = 1220.0(4) Å^3, Z = 4, R = 0.0319, and R_w = 0.0289. Me$_2$TeBr[SCONEt$_2$] (**5**), which also crystallizes as monoclinic in space group $P2_1/c$ (No. 14), has the cell parameters a = 10.533(4) Å, b = 10.965(2) Å, c = 11.814(4) Å, β = 113.11(2)°, V = 1254.9(7) Å^3, Z = 4, R = 0.0528, and R_w = 0.0462. Me$_2$TeI[SCONEt$_2$] (**6**), which also crystallizes as monoclinic in space group $P2_1/c$ (No. 14), has the cell parameters a = 10.702(2) Å, b = 11.241(1) Å, c = 12.280(3) Å, β = 114.51(2)°, V = 1344.2(5) Å^3, Z = 4, R = 0.0430, and R_w = 0.0343. The immediate environment about tellurium in **1** and **4**−**6** can be described as that of a sawhorse structure in which the lone pair is apparently stereochemically active and occupying an equatorial position in a distorted trigonal bipyramid. The two methyl groups occupy the other equatorial positions with the sulfur atoms of the monothiocarbamate groups occupying both axial positions in the case of **1**. In **4**−**6**, the halogen atom occupies one of the axial positions. The S−Te−S angle in **1** is 168.35(5)°, and the S−Te−X angles range from 171.34(8) to 171.62(8)°. The orientation of the monothiocarbamates is such as to suggest secondary intramolecular Te--O interactions, and if the oxygen atoms are considered as part of a coordination sphere, then the six atoms around tellurium in **1** have a distorted pentagonal pyramidal arrangement. The Te−X bond lengths are considerably longer than found in the parent Me$_2$TeX$_2$ species.

Introduction

Several reports have appeared on organotellurium(IV) derivatives with 1,1-dithio ligands including *O*-alkyl dithiocarbonates,[1−5] *N,N*-dithiocarbamates,[3,4,6−14] *O,O*-dialkyl dithiophosphates,[3−6,15−19] and *O,O*-alkylene dithiophosphates.[19−21] By contrast, there have been no reports on analogous organotellurium derivatives with monothiocarbamate ligands. In general, the coordination chemistry of monothiocarbamate ligands has received little attention and included among the few reports that have appeared involving main group metals[22−29] are complexes of the type

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[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1994.

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0020-1669/94/1333-6154$04.50/0

Tl(R_2mtc) with thallium[22] and $Me_3Sn(Me_2mtc)$,[26] $R_2Sn(R'_2$-mtc$)_2$,[28] and $Ph_3Sn(R'_2mtc)$[28] (R = alkyl, aryl; R′ = Me, Et) with tin. Most of the compounds reported to date have been synthesized by the insertion of COS gas into the M−N bonds of $M(NR_2)_n$ species, a process that appears to be somewhat unpredictable.

We report the synthesis and spectroscopic characterization of two series of dimethylltellurium(IV) *N,N*-diethyl, pyrrolidyl, and piperidyl monothiocarbamates of the types $Me_2Te[SCONR_2]_2$ (NR_2 = NEt_2, $N(CH_2)_3CH_2$, and $N(CH_2)_4CH_2$) and $Me_2TeX[SCONR_2]$ (X = Cl, Br, and I; NR_2 = NEt_2 or $N(CH_2)_3CH_2$). X-ray crystal structures are reported for $Me_2Te[SCONEt_2]_2$ (**1**), $Me_2TeCl[SCONEt_2]$ (**4**), $Me_2TeBr[SCONEt_2]$ (**5**), and $Me_2TeI[SCONEt_2]$ (**6**).

Experimental Section

Materials. $TeCl_4$ and Me_4Sn were obtained from Aldrich. $TeBr_4$ and Me_2TeI_2 were obtained from Alfa and Organometallics, Inc., respectively. Me_2TeCl_2 and Me_2TeBr_2 were prepared by the adaption of the method described in the literature for the preparation of Ph_2TeCl_2[30] by the reaction of $TeCl_4$ or $TeBr_4$ with Me_4Sn in toluene at 60 °C under reflux for 4 h. Sodium salts of *N,N*-disubstituted (diethyl,[22,31] pyrrolidyl,[32] and piperidyl[32]) monothiocarbamates were prepared by literature methods. All solvents were dried and distilled prior to use, and all reactions were carried out under anhydrous conditions. Elemental analyses were performed at Guelph Chemical Laboratories, Guelph, Ontario, Canada.

Preparation of Dimethylbis(*N,N*-diethyl, pyrrolidyl, and piperidyl monothiocarbamato)tellurium(IV), $Me_2Te[SCONEt_2]_2$ (1), $Me_2Te[SCON(CH_2)_3CH_2]_2$ (2), and $Me_2Te[SCON(CH_2)_4CH_2]_2$ (3). Typically, the sodium salt of *N,N*-diethyl monothiocarbamate (0.31 g, 2.00 mmol) was added to a solution of dimethyltellurium dichloride (0.22 g, 0.96 mmol) in dried carbon disulfide (20 mL). The reaction mixture was stirred for 2 h and filtered to remove NaCl and any unreacted materials. The solvent was reduced to 5 mL under vacuum before *n*-hexane (approximately 5 mL) was added. A white precipitate resulted, which was dried under vacuum after the solvent was decanted. $Me_2Te[SCONEt_2]_2$ (**1**) was then recrystallized from CS_2 to give white crystals: 0.34 g, yield 85%; mp 96−97 °C. Similarly were formed $Me_2Te[SCON(CH_2)_3CH_2]_2$ (**2**): white crystals; yield 86%; mp 114 °C. Anal. Calcd for $C_{12}H_{22}N_2O_2S_2Te$: C, 34.48; H, 5.30. Found: C, 34.68; H, 5.30. $Me_2Te[SCON(CH_2)_4CH_2]_2$ (**3**): white crystals; yield 86%; mp 94−95 °C.

Preparation of Chlorodimethyl(*N,N*-diethyl and pyrrolidyl monothiocarbamato)tellurium(IV), $Me_2TeCl[SCONEt_2]$ (4), and $Me_2TeCl[SCON(CH_2)_3CH_2$ (5). Typically, the sodium salt of *N,N*-diethyl monothiocarbamate (0.14 g, 0.88 mmol) was added to a solution of dimethyltellurium dichloride (0.20 g, 0.88 mmol) in dichloromethane (20 mL). The reaction mixture was stirred for 2 h and then filtered to remove NaCl or any unreacted materials. The solution was evaporated to give a white solid, which was recrystallized from a chloroform/*n*-hexane mixture to give $Me_2TeCl[SCONEt_2]$ (**4**): white block-shaped crystals; 0.23 g, yield 80%; mp 116−117 °C. Similarly was formed $Me_2TeCl[SCON(CH_2)_3CH_2]$ (**5**): white crystals; yield 82%; mp 138−140 °C. Anal. Calcd for $C_7H_{14}NOSClTe$: C, 26.00; H, 4.36. Found: C, 25.17; H, 4.41.

Preparation of Bromodimethyl(*N,N*-diethyl and pyrrolidyl monothiocarbamato)tellurium(IV), $Me_2TeBr[SCONEt_2]$ (6), and $Me_2TeBr[SCON(CH_2)_3CH_2]$ (7). Typically, the sodium salt of *N,N*-diethyl monothiocarbamate (0.12 g, 0.78 mmol) was added to a solution of dimethyltellurium dibromide (0.25 g, 0.78 mmol) in dichloromethane (20 mL). A rapid reaction ensued with the solution changing from colorless to bright yellow. The reaction mixture was stirred for 2 h and then filtered to remove NaBr or any unreacted materials. The solvent was reduced to 5 mL, and then *n*-hexane (approximately 5 mL) was added and the solution left overnight in the refrigerator at −6 °C. Pale yellow crystals were formed which were dried under vacuum after the bulk of the remaining solution had been decanted. Thus was formed $Me_2TeBr[SCONEt_2]$ (**6**): pale yellow block-shaped crystals; 0.25 g, yield 86%; decomp. 118−121 °C. Anal. Calcd for $C_7H_{16}NOSBrTe$: C, 22.74; H, 4.36. Found: C, 23.18; H, 4.51. Similarly was formed $Me_2TeBr[SCON(CH_2)_3CH_2]$ (**7**): pale yellow crystals; yield 81%, decomp. 126−128 °C.

Preparation of Iododimethyl(*N,N*-diethyl monothiocarbamato)tellurium(IV), $Me_2TeI[SCONEt_2]$ (8), and $Me_2TeI[SCON(CH_2)_3CH_2]$ (9). Typically, the sodium salt of *N,N*-diethyl monothiocarbamate (0.16 g, 1.0 mmol) was added to a solution of dimethyltellurium diiodide (0.41 g, 1.0 mmol) in dichloromethane (20 mL). The color of the solution became yellow-orange within a few minutes. The reaction mixture was stirred for 2 h and then filtered to remove NaI or any unreacted materials. The solvent was pumped off to leave a yellow-orange residue, which was redissolved in dichloromethane (5 mL) and *n*-hexane (approximately 5 mL) to form a solution that was left overnight in the refrigerator at −6 °C. Yellow crystals were formed and dried under vacuum after decanting the remaining solvent. Thus was formed $Me_2TeI[SCONEt_2]$ (**8**): yellow block-shaped crystals; 0.34 g, yield 80%; decomp. 95−97 °C. Similarly was formed $Me_2TeI[SCON(CH_2)_3CH_2]$ (**6**): yellow crystals; yield 82%; decomp. 105−107 °C. Anal. Calcd for $C_7H_{14}NOSITe$: C, 20.27; H, 3.40. Found: C, 19.98; H, 3.20.

Physical Measurements. The infrared spectra were recorded on a Nicolet 5DX FT spectrometer as KBr pellets, and far infrared spectra, on a Bomen IR spectrometer between polyethylene films. The Raman spectra were recorded on a Spectra-Physics 164 spectrometer using the 5145 Å exciting line of an argon ion laser with samples as KBr pellets or sealed in glass capillaries. The ^1H and ^{13}C NMR spectra were recorded on a Bruker 300 FT/NMR spectrometer in $CDCl_3$ using Me_4Si as internal standard. The ^{125}Te NMR spectra were recorded on a Bruker 200 FT/NMR spectrometer in $CDCl_3$ using Me_2Te as an external standard. The melting points were determined on a Fisher-Johns apparatus.

X-ray Crystallographic Analysis. Block-shaped crystals of $Me_2Te[SCONEt_2]_2$ (**1**), $Me_2TeCl[SCONEt_2]$ (**4**), $Me_2TeBr[SCONEt_2]$ (**5**), or $Me_2TeI[SCONEt_2]$ (**6**) were sealed in thin-walled glass capillaries and mounted on a Rigaku AFC6S diffractometer, with graphite-monochromated Mo Kα radiation.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $20 < 2\theta < 27°$ (for **1**), $36.49 < 2\theta < 41.67$ (for **4**), $12.65 < 2\theta < 15.54$ (for **5**), and $20.05 < 2\theta < 27.18$ (for **6**), corresponded to monoclinic cells whose dimensions are given in Table 1. On the basis of the systematic absences ($h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$ for **1** and $h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$ for **4**−**6**), packing considerations, statistical analyses of intensity distributions, and the successful solution and refinement of the structures, the space groups were determined to be $P2_1/n$ (No. 14) for **1** and $P2_1/c$ (No. 14) for **4**−**6**.

The data were collected at a temperature of 23 ± 1 °C using the $\omega-2\theta$ scan technique to a maximum 2θ value of 50.0°. The ω scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.28° for **1**, 0.29° for **4** and **5**, and 0.27° for **6**, with a takeoff angle of 6.0°. Scans of $(1.26 + 0.30 \tan \theta)°$ for **1**, $(1.73 + 0.30 \tan \theta)°$ for **4**, and $(1.37 + 0.30 \tan \theta)°$ for **5** and **6** were made at a speed of 16.0°/min (in ω) for **1**, **5**, and **6** and at 32.0°/min for **4**. The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of 2 rescans) and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm, and the crystal to detector distance was 400.0 mm.

Of the 3650 (for **1**), 2411 (for **4**), 2469 (for **5**), or 1901 (for **6**) reflections which were collected, 3467 (for **1**), 2283 (for **4**), 2338 (for

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Table 1. Crystallographic Data for $Me_2Te[SCONEt_2]_2$ (**1**), $Me_2TeCl[SCONEt_2]$ (**4**), $Me_2TeBr[SCONEt_2]$ (**5**), and $Me_2TeI[SCONEt_2]$ (**6**)

	$Me_2Te[SCONEt_2]_2$ (**1**)	$Me_2TeCl[SCONEt_2]$ (**4**)	$Me_2TeBr[SCONEt_2]$ (**5**)	$Me_2TeI[SCONEt_2]$ (**6**)
chem formula	$C_{12}H_{26}N_2O_2S_2Te$	$C_7H_{16}ClNOSTe$	$C_7H_{16}BrNOSTe$	$C_7H_{16}INOSTe$
a, Å	11.184(2)	10.539(2)	10.533(4)	10.702(2)
b, Å	10.036(2)	10.864(2)	10.965(2)	11.241(1)
c, Å	16.531(2)	11.511(2)	11.814(4)	12.280(3)
β, deg	94.08(1)	112.23(1)	113.11(2)	114.51(2)
V, Å^3	2424(1)	1220.0(4)	1254.9(7)	1344.2(5)
space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
fw, g mol^{-1}	422.07	325.32	369.77	416.77
Z	4	4	4	4
ϱ_{calcd} g cm^{-1}	1.51	1.77	1.96	2.06
μ, cm^{-1}	18.27	27.91	56.55	46.33
abs range	0.67−1.00	0.68−1.00	0.14−1.00	0.42−1.00
T, °C	23	23	23	23
λ, Å	0.710 69	0.710 69	0.710 69	0.710 69
R^a	0.0337	0.0319	0.0525	0.0425
$R_w{}^a$	0.0270	0.0289	0.0459	0.0339
GoF	1.41	1.85	2.34	2.50

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2)]^{1/2}$.

5), or 1787 (for **6**) were unique ($R_{int} = 0.055$, 0.049, 0.061, and 0.137 for **1**, **4**, **5**, and **6**, respectively). The intensities of three representative reflections that were measured after every 150 reflections remained constant throughout data collection indicating crystal and electronic stability (no decay correction were applied).

The linear absorption coefficient for Mo Kα is 18.3 cm^{-1} (for **1**), 27.91 cm^{-1} (for **4**), 56.55 cm^{-1} (for **5**), and 46.33 cm^{-1} (for **6**). An empirical absorption correction, based on azimuthal scans of several reflections, was applied which resulted in transmission factors ranging from 0.67 to 1.00 (for **1** and **4**), 0.14 to 1.00 (for **5**), and 0.42 to 1.00 (for **6**). The data were corrected for Lorentz and polarization effects.

The structures were solved by direct methods.[33] 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 final cycle of full-matrix least-squares refinement[34] was based on 1929 (for **1**), 1521 (for **4**), 1412 (for **5**), and 1276 (for **6**) observed reflections ($I > 3.00\sigma(I)$) and 173 (for **1**) and 109 (for **4**−**6**) variable parameters and converged (largest parameter shift was 0.001 times its esd in all cases) with unweighted and weighted agreement factors of $R = \sum||F_o| - |F_c|/\sum|F_o| = 0.0337$ (for **1**), 0.0319 (for **4**), 0.0528 (for **5**), and 0.0430 (for **6**) and $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o2)]^{1/2} = 0.0270$ (for **1**), 0.0289 (for **4**), 0.0462 (for **5**), and 0.0342 (for **6**).

The standard deviations of an observation of unit weight[35] was 1.41 (for **1**), 1.85 (for **4**), 2.39 (for **5**), and 2.54 (for **6**). The weighting scheme was based on counting statistics and included a factor ($p =$ 0.0006 for **1**, 0.005 for **4**, and 0.003 for **5** and **6**) to downweight the intense reflections. Plots of $\sum w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $(\sin \theta)/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.63 and −0.39 e/Å^3 for **1**, 0.46 and −0.62 e/Å^3 for **4**, 1.49 and −1.42 e/Å^3 for **5**, and 0.65 and −0.64e/Å^3, respectively, for **6**.

Neutral-atom scattering factors were taken from Cromer and Waber.[36] Anomalous dispersion effects were included in F_c;[37] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[38] All calculations were performed using the TEXSAN[39] crystallographic software package of Molecular Structure Corp.

Table 2. Final Fractional Coordinates and B(eq) Values for Non-Hydrogen Atoms of $Me_2Te[SCONEt_2]_2$ (**1**) with Standard Deviations in Parentheses

atom	x	y	z	B(eq), Å^2
Te(1)	0.37352(4)	0.17741(5)	0.01012(3)	3.01(2)
S(1)	0.4238(2)	0.3917(2)	0.0925(1)	4.3(1)
S(2)	0.3511(2)	−0.0206(2)	−0.0953(1)	3.69(9)
O(1)	0.2188(4)	0.2888(5)	0.1332(2)	4.2(3)
O(2)	0.1853(4)	−0.0238(5)	0.0115(3)	4.2(3)
N(1)	0.3046(5)	0.4343(6)	0.2246(3)	3.6(3)
N(2)	0.1822(5)	−0.2029(6)	−0.0718(3)	3.8(3)
C(1)	0.2333(7)	0.2780(8)	−0.0566(4)	5.2(4)
C(2)	0.5128(6)	0.2395(7)	−0.0618(4)	4.1(4)
C(3)	0.3002(6)	0.3658(7)	0.1546(4)	3.4(3)
C(4)	0.4044(7)	0.5159(8)	0.2564(4)	4.8(4)
C(5)	0.4938(8)	0.437(1)	0.3106(5)	7.3(6)
C(6)	0.2024(7)	0.4227(8)	0.2761(4)	5.0(5)
C(7)	0.1060(8)	0.521(1)	0.2531(5)	6.5(5)
C(8)	0.2280(6)	−0.0852(7)	−0.0448(4)	3.5(3)
C(9)	0.2335(7)	−0.286(1)	−0.1334(5)	6.5(5)
C(10)	0.178(1)	−0.272(1)	−0.2121(6)	11.6(9)
C(11)	0.0777(7)	−0.2557(8)	−0.0349(4)	4.8(4)
C(12)	0.1133(7)	−0.3466(9)	0.0364(5)	6.9(5)

Table 3. Final Fractional Coordinates and B(eq) Values for Non-Hydrogen Atoms of MeTeCl[SCONEt$_2$] (**4**) with Standard Deviations in Parentheses

atom	x	y	z	B(eq), Å^2
Te(1)	0.14641(4)	0.04369(4)	0.41246(4)	2.37(2)
Cl(1)	0.1484(2)	0.1252(2)	0.6374(2)	4.41(9)
S(1)	0.1286(2)	−0.0003(2)	0.1955(2)	3.21(7)
O(1)	0.3418(4)	−0.1131(4)	0.3626(4)	3.6(2)
N(1)	0.3127(5)	−0.1488(5)	0.1594(5)	2.8(2)
C(1)	0.3100(7)	0.1686(7)	0.4402(6)	3.7(3)
C(2)	−0.0098(7)	0.1765(6)	0.3359(7)	3.9(3)
C(3)	0.2766(6)	−0.0980(6)	0.2477(6)	2.6(3)
C(4)	0.2356(7)	−0.1291(7)	0.0247(6)	3.4(3)
C(5)	0.285(1)	−0.0165(9)	−0.0261(7)	6.1(5)
C(6)	0.4433(8)	−0.2158(8)	0.1968(7)	4.1(3)
C(7)	0.4299(9)	−0.3488(9)	0.2169(9)	6.6(5)

The final atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms are given in Tables 2 −5, important distances and bond angles are in Tables 6 and 7, and ORTEP diagrams are in Figures 1−5. Additional crystallographic data are available as supplementary material.

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(33) Sheldrick, G. M. *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Oxford University Press: Oxford, England, 1985; p 175.

(34) Least-squares: Function minimized, $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o2(F_o{}^2)$, $\sigma^2(F_o{}^2) = [S^2(C + R^2B) + (pF_o2)^2]/(Lp)^2$, 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.

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

(36) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2 A.

(37) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

(38) Cromer, D. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

(39) *TEXSAN-TEXRAY Structure Analysis Package*; Molecular Structure Corp.: The Woodlands, TX, 1985.

Table 4. Final Fractional Coordinates and *B*(eq) Values for Non-Hydrogen Atoms of $Me_2TeBr[SCONEt_2]$ (**5**) with Standard Deviations in Parentheses

atom	*x*	*y*	*z*	*B*(eq), Å^2
Te(1)	0.14811(9)	0.04286(7)	0.40745(7)	2.43(3)
Br(1)	0.1529(2)	0.1308(1)	0.6410(1)	4.21(6)
S(1)	0.1272(4)	−0.0035(3)	0.1960(3)	3.2(1)
O(1)	0.341(1)	−0.1153(7)	0.3614(7)	3.8(4)
N(1)	0.311(1)	−0.1508(8)	0.1638(8)	2.9(4)
C(1)	0.312(1)	0.164(1)	0.437(1)	3.6(6)
C(2)	−0.006(1)	0.173(1)	0.330(1)	3.8(6)
C(3)	0.278(1)	−0.101(1)	0.251(1)	2.7(5)
C(4)	0.236(1)	−0.130(1)	0.032(1)	3.8(6)
C(5)	0.285(2)	−0.019(2)	−0.015(1)	7(1)
C(6)	0.443(2)	−0.218(1)	0.203(1)	4.3(6)
C(7)	0.424(2)	−0.350(2)	0.214(2)	8(1)

Table 5. Final Fractional Coordinates and *B*(eq) Values for Non-Hydrogen Atoms of $Me_2TeI[SCONEt_2]$ (**6**) with Standard Deviations in Parentheses

atom	*x*	*y*	*z*	*B*(eq), Å^2
I(1)	0.1574(1)	0.13594(8)	0.64082(8)	5.35(5)
Te(1)	0.15088(8)	0.04104(7)	0.40012(7)	3.46(3)
S(1)	0.1254(3)	−0.0072(3)	0.1940(3)	4.5(1)
O(1)	0.337(1)	−0.1181(8)	0.3566(8)	5.4(4)
N(1)	0.308(1)	−0.1523(8)	0.1673(8)	4.2(5)
C(1)	0.317(1)	0.157(1)	0.430(1)	5.4(7)
C(2)	−0.008(1)	0.169(1)	0.321(1)	5.3(6)
C(3)	0.272(1)	−0.103(1)	0.248(1)	4.5(6)
C(4)	0.234(1)	−0.128(1)	0.038(1)	5.4(7)
C(5)	0.291(2)	−0.023(2)	−0.004(1)	9(1)
C(6)	0.436(1)	−0.218(1)	0.206(1)	5.7(7)
C(7)	0.419(2)	−0.347(2)	0.216(2)	10(1)

Calculation of Pauling Bond Order. The formula proposed by Pauling[40] 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. On the basis of a C-C single bond of 1.54 Å, Pauling's formula gives a bond length 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 "normalized" to 1.54 as follows rather than absolute differences. Pauling's relationship, which can 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 $X = 2.6(d - d_n)/d$. On the basis of the assumption that in these compounds the appropriate Te−S single bond length is the average in $Me_2Te[SCONEt_2]_2$ of 2.615 Å, typical calculated values of the lengths of Te--S partial bonds for various values of *n* are as follows: 2.615 Å ($n = 1.0$); 2.74 (0.75), 2.92 (0.50), 3.23 (0.25), and 3.63 Å ($n = 0.10$). Similarly, on the basis of a Te−O single bond length of 2.11 Å, typical calculated values of the lengths of Te--O partial bonds for various values of *n* are as follows: 2.11 Å ($n = 1.0$); 2.21 (0.75), 2.35 (0.50), 2.60 (0.25), and 2.92 Å ($n = 0.10$). Further, on the basis of the assumption that the appropriate Te−Cl, Te−Br, and Te−I single bond lengths are those found in the corresponding Me_2TeX_2 compounds of 2.51, 2.68, and 2.92 Å, respectively, for X = Cl, Br, and I, typical calculated values of the lengths of Te--X partial bonds for various values of *n* are as follows: for Te--Cl, 2.51 Å ($n = 1.0$) and 2.63 (0.75), 2.80 (0.50), 3.10 (0.25), and 3.49 Å ($n = 0.10$); for Te--Br, 2.68 Å ($n = 1.0$) and 2.81 (0.75), 2.99 (0.50), 3.31 (0.25), and 3.71 Å ($n = 0.10$); for Te--I, 2.92 Å ($n = 1.0$) and 3.06 (0.75), 3.26 (0.50), 3.60 (0.25), and 4.06 Å ($n = 0.10$).

Results and Discussion

The preparation of *N,N*-diethyl, pyrrolidyl, and piperidyl monothiocarbamate bis derivatives of dimethyltellurium(IV) is readily achieved in 85% yield by the reaction of an excess of the sodium salt of the appropriate monothiocarbamate with dimethyltellurium dichloride in accord with the equation

$$Me_2TeCl_2 + 2NaSCONR_2 \rightarrow Me_2Te[SCONR_2]_2 + 2NaCl$$

$$NR_2 = NEt_2,\ N(CH_2)_3CH_2,\ N(CH_2)_4CH_2$$

Dimethylhalo(*N,N*-diethyl and piperidyl monothiocarbamato)tellurium(IV) compounds can be similarly prepared in 80−85% yields by the reaction of equimolar amounts of the appropriate salt and dimethyltellurium dihalide

$$Me_2TeX_2 + NaSCONR_2 \rightarrow Me_2TeX[SCONR_2] + NaX$$

$$X = Cl, Br\ or\ I;\ NR_2 = NEt_2\ or\ N(CH_2)_3CH_2$$

The bis-substituted compounds, $Me_2Te[SCONR_2]_2$, were readily prepared as crystalline solids using CS_2 as solvent, whereas CH_2Cl_2 was the preferred solvent in the preparation of the partially substituted derivatives, $Me_2TeX[SCONR_2]$. With the exception of $Me_2TeBr[SCON(CH_2)_3CH_2)]$ (**7**), the compounds can be handled in the open air rather than under nitrogen and can be stored in closed vials without prior evacuation. Compound **7** decomposed in 1−2 h at room temperature but could be stored for extended periods if kept at −6 °C. Although all of the other compounds, **1**−**6**, **8**, and **9** appeared to be stable at room temperature, they were stored in the refrigerator. All of the compounds are soluble in common organic solvents such as C_6H_6, $CHCl_3$, and CH_2Cl_2 and are formed as crystalline solids, but despite considerable effort, it was only possible to obtain X-ray-quality crystals for the four *N,N*-diethyl monothiocarbamate derivatives.

Molecular Structures of $Me_2Te[SCONEt_2]_2$ (1), $Me_2TeCl[SCONEt_2]$ (4), $Me_2TeBr[SCONEt_2]$ (5), and $Me_2TeI[SCONEt_2]$ (6). Dimethylbis(*N,N*-diethyl monothiocarbamato)tellurium(IV) (**1**) crystallizes in the space group $P2_1/n$. The ORTEP diagram, Figure 1, illustrates that the immediate environment about tellurium is 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. The two methyl groups occupy the other two equatorial positions, the C−Te−C bond angle of 96.6(3)° being slightly larger than those reported for related dithiocarbamates[8,13] and the Te−C bond lengths being slightly shorter (2.109(7) and 2.119(7) Å) than in $Me_2Te[S_2CNMe_2]_2$ (2.13(1) Å).[13] The axial positions are occupied by the sulfur atoms of the monothiocarbamate groups, the S−Te−S bond angle of 168.33(6)° being similar to that observed in $Me_2Te[S_2CNMe_2]_2$. The average Te-S bond length is similar to the values reported for related dithiocarbamate derivatives,[7,8,13] although one of the Te−S bonds is distinctly longer than the other, 2.585(2) and 2.643(2) Å. The sulfur atom of the longer Te−S bond is 3.650(2) Å from the tellurium atom of an adjacent molecule, which is the only such contact less than the sum of the van der Waals radii of 3.86 Å.[41]

In dithiocarbamates, the nonbonded sulfur atoms are oriented toward the tellurium center at Te--S distances ranging from 3.16 to 3.36 Å. These correspond to normalized Pauling partial bond orders of about 0.25, which is compatible with their being part of the coordination sphere and hence aniso-bonded. In Me2-

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(40) Pauling, L. *J. Am. Chem. Soc.* **1947**, *69*, 542. Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 255.

(41) Bondi, A. J. *Phys. Chem.* **1964**, *68*, 441.

Table 6. Interatomic Distances (Å) in Compounds **1** and **4–6**

$Me_2Te[SCONEt_2]_2$ (**1**)		$Me_2TeCl[SCONEt_2]$ (**4**)		$Me_2TeBr[SCONEt_2]$ (**5**)		$Me_2TeI[SCONEt_2]$ (**6**)	
Te(1)–S(1)	2.585(2)	Te(1)–Cl(1)	2.792(2)	Te(1)–Br(1)	2.905(1)	Te(1)–I(1)	3.116(1)
Te(1)–S(3)	2.643(2)	Te(1)–S(1)	2.479(2)	Te(1)–S(1)	2.473(3)	Te(2)–S(1)	2.490(3)
Te(1)–C(1)	2.109(7)	Te(1)–C(1)	2.121(7)	Te(1)–C(1)	2.09(1)	Te(1)–C(1)	2.11(1)
Te(1)–C(2)	2.119(6)	Te(1)–C(2)	2.115(7)	Te(1)–C(2)	2.09(1)	Te(1)–C(2)	2.13(1)
S(1)–C(3)	1.799(7)	S(1)–C(3)	1.792(6)	S(1)–C(3)	1.81(1)	S(1)–C(3)	1.79(1)
O(1)–C(3)	1.227(7)	O(1)–C(3)	1.250(7)	O(1)–C(3)	1.22(1)	O(1)–C(3)	1.23(1)
N(1)–C(3)	1.343(7)	N(1)–C(3)	1.332(7)	N(1)–C(3)	1.33(1)	N(1)–C(3)	1.33(1)
N(1)–C(4)	1.452(8)	N(1)–C(4)	1.469(8)	N(1)–C(4)	1.46(1)	N(1)–C(4)	1.48(1)
N(1)–C(6)	1.478(7)	N(1)–C(6)	1.470(8)	N(1)–C(6)	1.48(2)	N(1)–C(6)	1.44(1)
C(4)–C(5)	1.52(1)	C(4)–C(5)	1.53(1)	C(4)–C(5)	1.51(2)	C(4)–C(5)	1.51(2)
C(6)–C(7)	1.49(1)	C(6)–C(7)	1.48(1)	C(6)–C(7)	1.47(2)	C(6)–C(7)	1.48(2)
S(2)–C(8)	1.782(7)						
O(2)–C(8)	1.240(7)						
N(2)–C(8)	1.350(8)						
N(2)–C(9)	1.467(9)						
N(2)–C(11)	1.456(8)						
C(9)–C(10)	1.41(1)						
C(11)–C(12)	1.52(1)						
Te(1)--O(1)	2.981(4)	Te(1)--O(1)	2.892(4)	Te(1)--O(1)	2.882(8)	Te(1)--O(1)	2.883(8)
Te(1)--O(2)	2.918(4)						
Te(1)--S(2)[a]	3.650(2)	Te(1)--Cl(1)[b]	3.465(2)	Te(1)--Br(1)[b]	3.547(2)	Te(1)--I(1)[b]	3.704(1)
Te(1)--Te(1)[a]	4.575(1)	Te(1)--Te(1)[b]	4.381(1)	Te(1)--Te(1)[b]	4.556(2)	Te(1)--Te(1)[b]	4.886(2)

[a] $1 - x, -y, -z$. [b] $-x, -y, 1 - z$.

Table 7. Interatomic Angles (deg) in Compounds **1** and **4–6**

$Me_2Te[SCONEt_2]_2$ (**1**)		$Me_2TeCl[SCONEt_2]$ (**4**)		$Me_2TeBr[SCONEt_2]$ (**5**)		$Me_2TeI[SCONEt_2]$ (**6**)	
S(1)–Te(1)–S(2)	168.33(6)	Cl(1)–Te(1)–S(1)	171.41(6)	Br(1)–Te(1)–S(1)	171.62(8)	I(1)–Te(1)–S(1)	171.34(8)
S(2)–Te(1)–C(1)	89.0(2)	Cl(1)–Te(1)–C(1)	86.3(2)	Br(1)–Te(1)–C(1)	85.9(3)	I(1)–Te(1)–C(1)	86.5(3)
S(2)–Te(1)–C(2)	83.7(2)	Cl(1)–Te(1)–C(2)	84.2(2)	Br(1)–Te(1)–C(2)	84.9(3)	I(1)–Te(1)–C(2)	84.3(3)
S(1)–Te(1)–C(1)	90.2(2)	S(1)–Te(1)–C(1)	91.3(2)	S(1)–Te(1)–C(1)	92.1(3)	S(1)–Te(1)–C(1)	92.2(3)
S(2)–Te(1)–C(2)	84.8(2)	S(1)–Te(1)–C(2)	87.8(2)	S(1)–Te(1)–C(2)	87.1(4)	S(1)–Te(1)–C(2)	87.4(3)
C(1)–Te(1)–C(2)	96.6(3)	C(1)–Te(1)–C(2)	95.0(3)	C(1)–Te(1)–C(2)	95.1(5)	C(1)–Te(1)–C(2)	97.0(5)
S(1)–Te(1)--O(1)	56.21(9)	S(1)–Te(1)--O(1)	58.32(9)	S(1)–Te(1)--O(1)	58.3(2)	S(1)–Te(1)--O(1)	58.0(2)
S(2)–Te(1)--O(1)	134.54(9)	Cl(1)–Te(1)--O(1)	128.97(9)	Br(1)–Te(1)--O(1)	129.0(2)	I(1)–Te(1)--O(1)	129.9(2)
S(1)–Te(1)--S(2)[a]	90.55(6)	S(1)–Te(1)--Cl(1)[b]	90.55(5)	S(1)–Te(1)--Br(1)[b]	90.39(9)	S(1)–Te(1)--I(1)[b]	91.67(9)
S(2)–Te(1)--S(2)[a]	88.16(5)	Cl(1)–Te(1)--Cl(1)[b]	90.78(5)	Br(1)–Te(1)--Br(1)[b]	90.73(4)	I(1)–Te(1)--I(1)[b]	88.90(3)
Te(1)–S(2)--Te(1)[a]	91.84(5)	Te(1)–Cl(1)--Te(1)[b]	89.22(5)	Te(1)–Br(1)--Te(1)[b]	89.27(4)	Te(1)–I(1)--Te(1)[b]	91.10(3)
Te(1)–S(1)–C(3)	91.9(2)	Te(1)–S(1)–C(3)	93.0(2)	Te(1)–S(1)–C(3)	92.3(4)	Te(1)–S(1)–C(3)	92.6(5)
C(3)–N(1)–C(4)	125.5(6)	C(3)–N(1)–C(4)	122.8(5)	C(3)–N(1)–C(4)	124(1)	C(3)–N(1)–C(4)	122(1)
C(3)–N(1)–C(6)	118.2(6)	C(3)–N(1)–C(6)	119.2(5)	C(3)–N(1)–C(6)	117.5(9)	C(3)–N(1)–C(6)	120(1)
C(4)–N(1)–C(6)	116.3(5)	C(4)–N(1)–C(6)	117.7(5)	C(4)–N(1)–C(6)	118(1)	C(4)–N(1)–C(6)	118(1)
S(1)–C(3)–O(1)	120.7(5)	S(1)–C(3)–O(1)	119.5(5)	S(1)–C(3)–O(1)	119.7(9)	S(1)–C(3)–O(1)	120(1)
S(1)–C(3)–N(1)	115.8(5)	S(1)–C(3)–N(1)	117.0(5)	S(1)–C(3)–N(1)	115.2(7)	S(1)–C(3)–N(1)	117(1)
O(1)–C(3)–N(1)	123.6(6)	O(1)–C(3)–N(1)	123.5(6)	O(1)–C(3)–N(1)	125(1)	O(1)–C(3)–N(1)	123(1)
N(1)–C(4)–C(5)	112.1(7)	N(1)–C(4)–C(5)	112.9(6)	N(1)–C(4)–C(5)	114(1)	N(1)–C(4)–C(5)	114(1)
N(1)–C(6)–C(7)	112.1(6)	N(1)–C(6)–C(7)	113.3(7)	N(1)–C(6)–C(7)	112(1)	N(1)–C(6)–C(7)	113(1)
Te(1)–S(2)–C(8)	90.3(2)						
C(8)–N(2)–C(9)	124.8(6)						
C(8)–N(2)–C(11)	118.5(6)						
C(9)–N(2)–C(11)	116.6(6)						
S(2)–C(8)–O(2)	121.5(5)						
S(2)–C(8)–N(2)	116.8(5)						
O(2)–C(8)–N(2)	121.7(6)						
N(2)–C(9)–C(10)	114.7(8)						
N(2)–C(10)–C(11)	111.7(6)						

[a] $1 - x, -y, -z$. [b] $-x, -y, 1 - z$.

$Te[SCONEt_2]_2$, the oxygen atoms are similarly oriented toward tellurium but at Te--O distances of 2.918(4) and 2.981(5) Å, which correspond to bond orders of 0.10 or less. However, the orientation of the two monothiocarbamates display interesting features when the oxygen atoms are included. Thus the five atoms S(1), S(2), O(1), O(2), and C(2) along with Te(1) form an approximate plane (mean deviation from plane of 0.1229 Å) with C(1) above the plane (2.0327(7) 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 one axial position and C(1) the other (see the projection used in Figure 2). The two planar SCON cores of the monothiocarbamate groups have a dihedral angle of only 20.4 (2)°.

All three of the dimethylhalo(*N*,*N*-diethyl monothiocarbamato)tellurium(IV) compounds, $Me_2TeCl[SCONEt_2]$ (**4**), $Me_2TeBr[SCONEt_2]$ (**5**), and $Me_2TeI[SCONEt_2]$ (**6**), crystallize in the space group $P2_1/c$ and are isomorphous. The ORTEP diagrams, which are presented for all three molecules in Figure 3, illustrate that, as with $Me_2Te[SCONEt_2]_2$ (**1**), the immediate environment about tellurium is the sawhorse structure with the halogen atoms occupying the position of one of the sulfur atoms in **1** and also

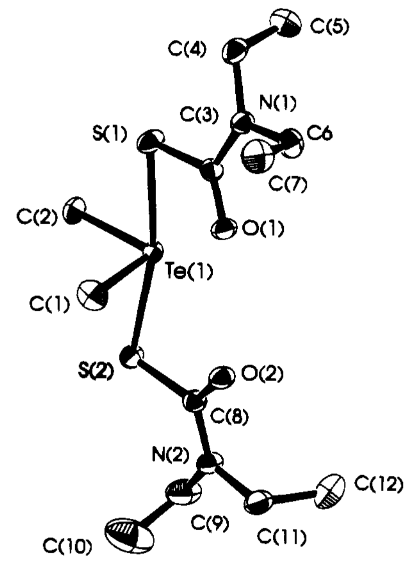

Figure 1. ORTEP plot of the molecule $Me_2Te[SCONEt_2]_2$ (**1**). The atoms are drawn with 25% probability ellipsoids. Hydrogen atoms are omitted for clarity.

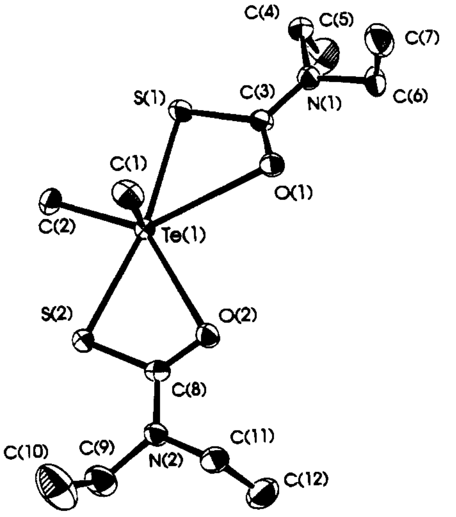

Figure 2. ORTEP plot of the molecule $Me_2Te[SCONEt_2]_2$ (**1**), showing intramolecular interactions involving the oxygen atoms. The atoms are drawn with 25% probability ellipsoids. Hydrogen atoms are omitted for clarity.

that the orientation of the monothiocarbamate group in compounds **4**–**6** is similar, though not identical, to one of the groups in the bis compound, **1**. The Te–C bond lengths in **4**–**6** are not significantly different from those observed in **1**. However, the average Te–S distance in **4**–**6** of 2.481(9) Å is shorter than even the shorter of the two Te–S bonds in **1** (Table 6) and corresponds to a bond order of 1.36, whereas the Te–X bonds are distinctly longer than in related R_2TeX_2 species, 2.792(2) Å for Te–Cl in **4** compared to 2.51(3) Å in α-Me_2TeCl_2,[42] 2.905(1) Å for Te–Br in **5** compared to 2.682(3) Å in Ph_2TeBr_2,[43] and 3.116(1) Å for Te–I in **6** compared to a range of 2.885(3)–2.994(3) Å in α-Me_2TeI_2.[44] On the basis of the bond order being 1.0 in R_2TeX_2, the bond orders for Te–Cl, Te–Br, and Te–I in **4**–**6** are 0.51, 0.61, and 0.67, respectively.

In all three compounds **4**–**6**, the halogen atom has an intermolecular interaction with an adjacent tellurium atom to form an unsymmetrical Te–X--Te′ bridge. The Te--X′ intermolecular distances of 3.465(1), 3.547(2), and 3.704(1) Å, respectively, for Te--Cl′, Te--Br,′ and Te--I′, with bond orders of 0.10, 0.15, and 0.20, respectively, are similar in the Me_2TeX_2 species where the average Te--X′ distances are 3.50 and 3.88 Å, respectively, for X = Cl and I. Also, as with the dihalides, the X–Te--X′ and Te–X--Te′ angles are both very close to 90°, so the bridging systems essentially form a rectangle with cis Te–X and Te--X′ bonds. The bridging system is demonstrated in Figure 4 in which $Me_2TeI[SCONEt_2]$ is the representative example. The similarity of the bridging interactions in the dihalides and monosubstituted species suggests that the longer, weaker Te–X bond in **4**–**6** is related to the fact that the monothiocarbamate group, rather than a second halogen atom, is now at approximately 180°. The shortening of the Te–S bond and lengthening of the Te–X bonds appears to be an example of the trans effect operating on a main group metal.

The oxygen atom is again oriented toward the tellurium atom in **4**–**6** in the same fashion as in **1** to give very similar Te--O intramolecular distances, an average of 2.886(8) Å in all three halide derivatives. In **4**–**6**, the four atoms S(1), X(1), O(1), and C(2) along with Te(1) form an approximate plane (mean deviation from plane of 0.1104, 0.1073, and 0.1088 Å for X = Cl, Br, and I, respectively) with C(1) well above the plane (2.05(1), 2.04(2), and 2.07(2) Å for Cl, Br, and I, respectively) to give a distorted approximate square pyramidal arrangement about Te(1) or a distorted pseudo-octahedral arrangement if the lone pair is assumed to be occupying one axial position and C(1) the other. This can be seen in the two projections used in Figure 6 for compounds **4** and **5**. The latter view, in particular, illustrates the fact that even when N(1) and C(3) are also included in the planes in **4**–**6**, thus including the whole of the monothiocarbamate planar core, the mean deviations from plane are virtually unchanged at 0.1036, 0.1194, and 0.1065 Å, respectively.

Thus, as with related dithiocarbamates, the monothiocarbamate groups are planar in all four compounds with S–C–N angles all less than 120° at an average of 116.8(8)° for **1** and **4**–**6**. The average S–C–O angle in all four molecules is close to 120°, while the O–C–N angles are greater, with an average angle of 123(1)°. The S–C bonds, which average 1.791(8) Å in **1** and 1.81(1) Å in **4**–**6**, are slightly longer than the TeS–C bonds in dithiocarbamates. The C–N bond lengths of 1.343(9) and 1.350(8) Å in 1 and 1.33(1) Å in **4**–**6** are similar to those reported for the dithiocarbamates, indicating that π-electron delocalization is extending to the SOC–N bond. The C=O bond lengths of 1.224(7) and 1.240(8) Å in 1 and 1.233(13) Å in **4**–**6** are comparable to those of terminal C=O bonds involved with secondary bonding such as hydrogen bonding,[45] which is consistent with a weak secondary Te--O interaction. The similarity of the monothiocarbamate groups in all four compounds suggests that the orientations of the groups are not just packing effects.

Infrared and Raman Spectra. Characteristic features of the infrared and Raman spectra of compounds **1**–**9** are summarized in Table 8. The assignments are based on those reported previously for related monothiocarbamates.[28,31,46] Of three stretching vibrations, C–O, C–N, and C–S, to be expected for the planar SCON moiety, only one, described as a coupled C–O/C–N vibration, has been reported consistently. This strong band in the infrared spectrum[31,32] is assumed to

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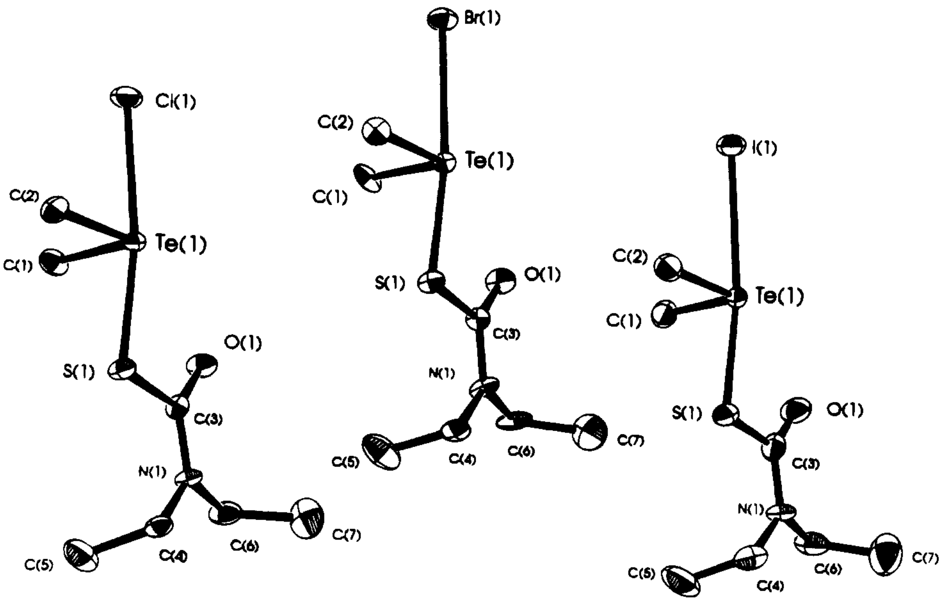

Figure 3. ORTEP plots of the molecules $Me_2TeCl[SCONEt_2]$ (**4**), $Me_2TeBr[SCONEt_2]$ (**5**), and $Me_2TeI[SCONEt_2]$ (**6**). The atoms are drawn with 25% probability ellipsoids. Hydrogen atoms are omitted for clarity.

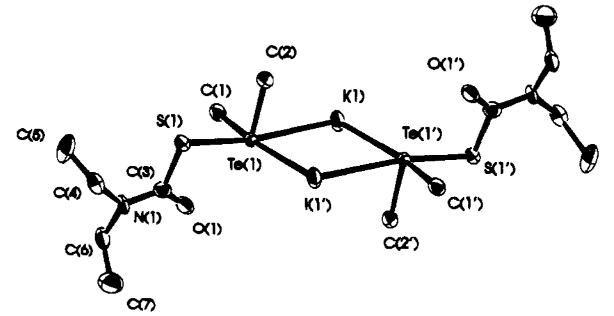

Figure 4. ORTEP plot of the molecule $Me_2TeI[SCONEt_2]$ (**6**), showing intermolecular interactions involving the halogen atoms leading to dimers. The atoms are drawn with 25% probability ellipsoids. Hydrogen atoms are omitted for clarity.

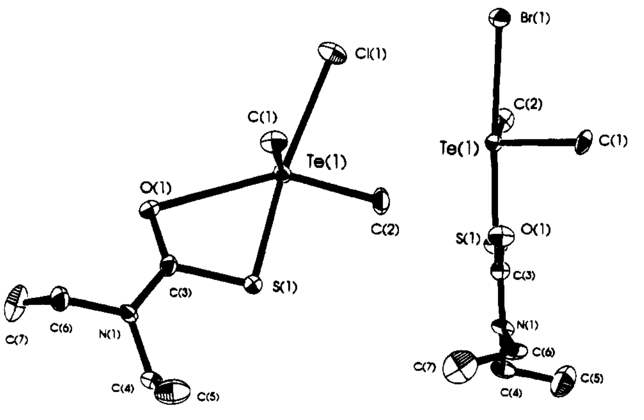

Figure 5. ORTEP plots of the molecules $Me_2TeCl[SCONEt_2]$ (**4**) and $Me_2TeBr[SCONEt_2]$ (**5**) demonstrating the coplanarity of the monothiocarbamate group with tellurium, chlorine, or bromine and one of the methyl carbon atoms. The atoms are drawn with 25% probability ellipsoids. Hydrogen atoms are omitted for clarity.

indicate a monodentate ligand if it appears above 1545 cm^{-1},[47,48] although such a distinction needs to be treated with caution.[28,46] In compounds **1**−**9** a strong peak is observed in the infrared spectrum between 1560 and 1605 cm^{-1}. The similarity of the location and appearance of the bands in all nine compounds is consistent with monothiocarbamate groups being attached in the same, essentially monodentate fashion, as observed in the crystal structures of $Me_2Te[SCONEt_2]_2$ (**1**), $Me_2TeCl[SCONEt_2]$ (**4**), $Me_2TeBr[SCONEt_2]$ (**5**), and $Me_2TeI[SCONEt_2]$ (**6**). A band assignable to the C−S stretching vibration is observed close to 663 cm^{-1}, which corresponds to the assignment made in other metal monothiocarbamates,[49] and is in a typical location for a C−S single bond, consistent with the bond lengths in **1**, **4**, **5**, and **6** being close to the sum of the covalent radii of C and S.

In the Raman spectrum of $Me_2Te[SCONEt_2]_2$ (**1**) below 600 cm^{-1}, four peaks at 543 (40), 535 (60), 385 (30), and 326 (100) cm^{-1} are dominant. None of these peaks are present in the starting salt, and so, by analogy with the Me_2TeX_2 series, where X = Cl, Br, and I,[50] these are assigned to the symmetric and asymmetric Te−C and Te−S stretching vibrations. The near accidental degeneracy of the two Te−C stretches in **1**−**9** is consistent with the observation of a C−Te−C angle close to 90° in all four structures. In the three bis compounds, **1**−**3**, the asymmetric Te−S stretch is assigned in the region 360−385 cm^{-1} and the symmetric Te−S stretch from 272 to 326 cm^{-1}. The Te−S stretching vibration in compounds **4**−**9** is seen in the region 370−381 cm^{-1}. This places it to higher wavenumber than the average of the two Te−S stretching vibrations in **1**−**3**, consistent with a shorter Te−S bond in the halo monothiocarbamates. The crystal structures of the latter also indicated that the Te−X bonds are longer and presumably weaker than those in Me_2TeX_2. The assignments of the Te−X stretch (Table 8) are made to lower wavenumbers than in Me_2TeX_2, which average 264, 169, and 129 cm^{-1}, respectively for X = Cl, Br, and I.

^{13}C NMR Spectra. The ^{13}C NMR spectral data for compounds **1**−**9** are displayed in Table 9. In $Me_2Te[SCONEt_2]_2$ (**1**) there are four sets of peaks (ppm), a singlet at 171.69 (S*C*ON), a doublet at 41.40 and 41.53 (N*C*H$_2$), a doublet at 13.27 and 13.73 (NC*C*H$_3$), and a singlet at 14.80 (Te*C*H$_3$). The presence of two sets of peaks of equal intensity assignable to the methylene and methyl carbon atoms of the two ethyl groups

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Table 8. Selected Features and Their Assignments in the Vibrational Spectra (cm^{-1}) of Compounds **1**−**9**[a,b]

no.	compd	ν(C=O,C=N): IR[c] [Raman][d]	ν(S−C: IR[c] [Raman][d]	$\nu(Te{-}C)_{asym}$: IR[c] [Raman][d]	$\nu(Te{-}C)_{sym}$: IR[c] [Raman][d]	$\nu(Te{-}S)_{asym}$: IR[c] [Raman][d]	$\nu(Te{-}S)_{sym}$: IR[c] [Raman][d]	ν(Te−X): IR[c] [Raman][d]
1	$Me_2Te[SCONEt_2]_2$	1580 s [1577 (5)]	663 m [664 (20)]	540 w [543 (40)]	540 w [535 (60)]	382 s [385 (30)]	316 m 326 (100)	
2	$Me_2Te[SCON(CH_2)_3CH_2]_2$	1584 s [1585 (5)]	663 m n.o.[e]	539 w,sh [543 (10)]	539 w,sh [532 (20)]	360 s [366 (40)]	273 ms [272 (100)]	
3	$Me_2Te[SCON(CH_2)_4CH_2]_2$	1578 s [1575 (5)]	670 m [676 (10)]	547 w,br [543 (sh)]	547 w,br [538 (40)]	362 m [361 (20)]	309 m [323 (100)]	
4	$Me_2TeCl[SCONEt_2]$	1598 vs n.o.	661 ms [661 (10)]	542 w,br [537 (100)]	542 w,br [537 (100)]		381 s [381 (90)]	180 s [190 (65)]
5	$Me_2TeBr[SCONEt_2]$	1598 vs n.o.	660 m [661 (10)]	540 w,br [542 (50)]	540 w,br [533 (100)]		381 m [380 (90)]	130 s [130 (20)]
6	$Me_2TeI[SCONEt_2]$	1597 vs n.o.	658 m [662 (5)]	530 vw,sh [535 (15)]	530 vw,sh [524 (50)]		377 m [377 (100)]	114 s [114 (90)]
7	$Me_2TeCl[SCON(CH_2)_3CH_2]$	1605 vs [1604 (1)]	663 mw n.o.	528 vw,br [542 (90)]	528 vw,br [531 (100)]		372 m [370 (40)]	210 s [190 (25)]
8	$Me_2TeBr[SCON(CH_2)_3CH_2]$	1591 vs n.o.	660 mw n.o.	534 w,br [538 (40)]	534 w,br [528 (80)]		372 m [370 (55)]	130 m,sh [130 (100)]
9	$Me_2TeI[SCON(CH_2)_3CH_2]$	1591 vs n.o.	658 m [654 (15)]	530 w,sh [538 (5)]	530 w,sh [527 (10)]		371 m [368 (15)]	114 s [114 (100)]

[a] Parentheses denote relative intensities in the Raman effect. [b] s = strong, m = medium, w = weak, v = very, sh = shoulder. [c] Run as KBr pellets to 400 cm^{-1} and as Nujol mulls below 450 cm^{-1}. [d] Run as a solid in a glass capillary. [e] n.o. = not observed.

Table 9. ^{13}C and ^{125}Te NMR Chemical Shifts for the Dimethyl- and Halodimethyltellurium Monothiocarbamates **1**−**9**[a]

		^{13}C					
no.	compd	Te−CH_3	S−*C*	N−*C*	NC−*C*	NCC−*C*	^{125}Te
1	$Me_2Te[SCONEt_2]_2$	14.80	171.69	41.20, 41.53	13.27, 13.73		444.8
2	$Me_2Te[SCON(CH_2)_3CH_2]_2$	14.72	170.24	46.61, 48.57	25.06, 25.57		448.1
3	$Me_2Te[SCON(CH_2)_4CH_2]_2$	14.83	171.10	44.21, 49.16	25.64, 25.97	24.47	448.1
4	$Me_2TeCl[SCONEt_2]$	18.87	167.48	41.90, 44.97	13.04, 13.69		554.1
5	$Me_2TeBr[SCONEt_2]$	18.22	167.35	42.05, 45.04	13.07, 13.74		539.4
6	$Me_2TeI[SCONEt_2]$	16.78	167.63	42.06, 45.04	13.03, 13.70		516.0
7	$Me_2TeCl[SCON(CH_2)_3CH_2]$	18.87	166.00	47.20, 48.57	24.98, 25.59		553.7
8	$Me_2TeBr[SCON(CH_2)_3CH_2]$	18.31	165.90	47.30, 48.63	25.02, 25.66		536.3
9	$Me_2TeI[SCON(CH_2)_3CH_2]$	17.08	166.25	47.33, 48.60	24.98, 25.63		515.6

[a] The spectra were recorded in $CDCl_3$ and reported in ppm from Me_4Si for ^{13}C and from Me_2Te for ^{125}Te.

on nitrogen is clear evidence that the restricted rotation expected from the planar arrangement about nitrogen in the crystal structure is maintained in solution. The same nonequivalence is observed for the ethyl groups in the halo-substituted derivatives **4**−**6** and also for the corresponding carbon atoms in the pyrrolidyl rings in **7**−**9**. The chemical shifts of the methyl groups attached to tellurium are similar in compounds **1**−**3**; all having values close to 14.8 ppm which are comparable to values around 16.6 and 19.2 ppm, respectively, for the corresponding $Me_2Te[S_2CNR_2]_2$[13] and $Me_2Te[S_2POGO]_2$[21] species. The starting materials Me_2TeCl_2, Me_2TeBr_2, and Me_2TeI_2 have chemical shifts of 26.9, 25.1, and 22.0 ppm, respectively, so the upfield shift as the electronegativity of the halogen substituent decreases for **4**−**9**. The similarity in the values of the Te−CH_3 chemical shifts of the halo diethyl and pyrrolidyl compounds suggests similar environments for all of these compounds in solution. The S*C*ON chemical shifts are also similar for all nine compounds, with the Me_2TeL_2 species **1**−**3**, at *ca.* 170, the $Me_2TeX[SCONEt_2]$ compounds **4**−**6**, at *ca.* 167.5, and the $Me_2TeX[SCON(CH_2)_3CH_2]$ compounds **7**−**9** at *ca.* 166 ppm, consistent with similar environments around the planar C atom.

^{125}Te NMR Spectra. The ^{125}Te NMR spectral data for compounds **1**−**9** are also presented in Table 9. All compounds give the single peak consistent with the presence in solution of one compound containing tellurium. The peak is in the region 445−448 ppm for the three bis compounds, **1**−**3**, comparable to 475 and 463 ppm for the related dithiocarbamates, $Me_2Te[S_2CNMe_2]_2$ and $Me_2Te[S_2CNEt_2]_2$,[13] and between 515 and 554 ppm for the halo monothiocarbamato derivatives, **4**−**9**. The chemical shifts of *ca.* 554 and 538 ppm for the chloro (**4**, **7**) and bromo (**5**, **8**) derivatives, respectively, are much closer to the values for the bis compounds than the dihalide starting materials Me_2TeCl_2 (733.8 ppm) and Me_2TeBr_2 (649.2 ppm), consistent with the monothiocarbamate groups having more influence on the environment than the halogens. For the iodo derivatives (**6**, **9**) the signals are seen at *ca.* 516 ppm, compared with 519.6 ppm for Me_2TeI_2, suggesting that the overall effect of the monothiocarbamate ligands is comparable to that of an iodine atom.

^{1}H NMR Spectra. The ^1H NMR spectral data for compounds **1**−**9** are summarized in Table 10. The splitting patterns and relative intensities of the peaks in the spectra of all of the compounds are consistent with the solid state structures of compounds **1**, **4**, **5**, and **6** being maintained in solution. All the derivatives show a sharp singlet assignable to the methyl group attached to tellurium, and the CH_3−Te chemical shift of 2.45 ppm for **1**−**3** is essentially the same as found for $Me_2Te[S_2CNR_2]_2$ species. In the Me_2TeXL derivatives, **4**−**9**, these singlets are seen in a narrow range from 2.75 to 2.82 ppm. There is a small but consistent upfield shift from Cl to I, which is similar to that between Me_2TeCl_2 (3.10 ppm) and Me_2TeI_2 (3.27 ppm).

The features attributable to the monothiocarbamate groups are as expected in view of the nonequivalence of the carbon atoms noted in the ^{13}C NMR spectra. Thus in the spectrum of $Me_2Te[S_2CNEt]_2$, two sets of triplets and quartets are observed for the two CH_3CH_2 groups. The quartets associated with the methylene groups are centered at 3.35 and 3.44 ppm and so only just overlap, whereas the methyl signals are seen as a 1:2:2:2:1 quintet arising from the precise overlap of the two triplets centered at 1.08 and 1.18 ppm. The corresponding peaks in $Et_2Sn[SCONEt_2]_2$ are seen at similar positions of 3.31, 3.45,

Table 10. ^{1}H NMR Chemical Shifts for the Dimethyl- and Halodimethyltellurium Monothiocarbamates **1**−**6**[a−c]

no.	compd	Te−CH_3/C$_6H_5$	N−CH_2	NC−CH_3/CCH_n
1	$Me_2Te[SCONEt_2]_2$	2.45 (6 H, s)	3.35 (4 H, q) [7.0] 3.44 (4 H, q) [7.0]	1.08 (6 H, t) [7.0] 1.13 (6 H, t) [7.0]
2	$Me_2Te[SCON(CH_2)_3CH_2]_2$	2.45 (6 H, s)	3.39 (4 H, t) [6.2] 3.41 (4 H, t) [6.2]	1.83 (4 H, q) [6.9] 1.85 (4, H, q) [6.9]
3	$Me_2Te[SCON(CH_2)_4CH_2]_2$	2.45 (6 H, s)	3.52 (8 H, br s)	1.51−1.57 (12 H, m)[d]
4	$Me_2TeCl[SCONEt_2]$	2.75 (6 H, s)	3.34 (2 H, q) [7.0] 3.38 (2 H, q) [7.0]	1.10 (3 H, t) [7.2] 1.15 (3 H, t) [7.3]
5	$Me_2TeBr[SCONEt_2]$	2.79 (6 H, s)	3.32−3.42 (4 H, m) [7.0]	1.11 (3 H, t) [7.1] 1.17 (3 H, t) [7.1]
6	$Me_2TeI[SCONEt_2]$	2.81 (6 H, s)	3.31−3.42 (4 H, m) [7.1]	1.11 (3 H, t) [7.1] 1.17 (3 H, t) [7.1]
7	$Me_2TeCl[SCON(CH_2)_3CH_2]$	2.77 (6 H, s)	3.37 (2 H, t) [6.5] 3.44 (2 H, t) [6.5]	1.90 (4 H, m) [7.0]
8	$Me_2TeBr[SCON(CH_2)_3CH_2]$	2.81 (6 H, s)	3.38 (2 H, t) [6.5] 3.45 (2 H, t) [6.5]	1.92 (4 H, m) [7.0]
9	$Me_2TeI[SCON(CH_2)_3CH_2]$	2.82 (6 H, s)	3.38 (2 H, t) [6.4] 3.44 (2 H, t) [6.4]	1.91 (4 H, m) [6.9]

[a] The spectra were recorded in $CDCl_3$ and reported in ppm from Me_4Si for ^{1}H and from Me_2Te for ^{125}Te. [b] Number of protons and multiplicities are in parentheses (s = singlet; t = triplet; q = quartet; m = multiplet; br = broad). [c] Coupling constants in Hz shown in brackets. [d] Includes overlapping peaks arising from NCCCH_2.

1.17, and 1.27.[28] The value of the ^2J(HH) coupling constant is 7.0 Hz for both sets of peaks. In the spectra of compounds **2** and **3**, two sets of overlapping triplets are again seen for the methylene protons of the carbon atoms attached to nitrogen in the $N(CH_2)_3CH_2$ and $N(CH_2)_4CH_2$ groups. The splitting patterns are more complex for the protons on the methylene groups not attached to nitrogen, but the relative intensities of all groups of peaks in compounds **1**−**3** are as expected. The same general comments apply to the Me_2TeXL series, **4**−**9**, where the splitting patterns for the monothiocarbamate groups are similar to those observed in the analogous Me_2TeL_2 derivatives just discussed.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and Imperial Oil Canada for financial support. One of us (L.N.K.) thanks the former for an NSERC Research Reorientation Associateship, and one of us (R.R) thanks Dayanand College, Ajmer, India, for granting a leave of absence.

Supplementary Material Available: Tables SI−SIX, listing experimental details, anisotropic thermal parameters for non-hydrogen atoms, and final fractional coordinates and thermal parameters for hydrogen atoms (9 pages). Ordering information is given on any current masthead page. Structure factor tables may be obtained directly from the authors.