



Synthesis and spectroscopic characterization of six new monosubstituted dithiocarbamate compounds containing organotellurium(IV) heterocycles: Single-crystal structures of $C_5H_{10}TeI[S_2CN(CH_2CH_3)_2]$, $C_4H_8TeI[S_2CN(CH_2CH_2)_2]$, $C_4H_8OTeI[S_2CN(CH_2CH_2)_2]$ and $C_5H_{10}TeI[S_2CN(CH_2CH_2)_2]$

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ARTICLE INFO

Article history:

Received 25 August 2009

Received in revised form 29 January 2010

Accepted 29 January 2010

Available online 4 February 2010

Keywords:

Dithiocarbamates
Organotellurium(IV)
Tellurium(IV)
Tellurocycles
Crystal structure

ABSTRACT

Six novel monosubstituted dithiocarbamate compounds containing organotellurium(IV) heterocycles, $C_4H_8OTeI[S_2CN(CH_2CH_3)_2]$ (**1**), $C_5H_{10}TeI[S_2CN(CH_2CH_3)_2]$ (**2**), $C_4H_8TeI[S_2CN(CH_2CH_2)_2]$ (**3**), $C_8H_8TeI[S_2CN(CH_2CH_2)_2]$ (**4**), $C_4H_8OTeI[S_2CN(CH_2CH_2)_2]$ (**5**) and $C_5H_{10}TeI[S_2CN(CH_2CH_2)_2]$ (**6**) were synthesized. The compounds were characterized by common spectroscopic methods; IR, EI-MS and multinuclear NMR (1H , ^{13}C and ^{125}Te). The structure of compounds **2**, **3**, **5** and **6** was unequivocally established by single-crystal X-ray diffraction studies. Compounds **3**, **4** and **5** exhibit dimeric arrangements achieved through secondary bonding (Te...S) and in the case of **2**, an additional Te...S interaction resulted in the formation of a self-assembled chain. Furthermore, the geometrical arrangement displayed in the tellurium atoms of all the compounds corresponds to a distorted octahedron while the coordination mode for the dithiocarbamate ligands is considered anisobidentate in all cases.

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1. Introduction

The continuous interest in tellurium compounds comprising sulfur-donor ligands is largely due to the span of structures achievable with these types of ligands. In particular, the structural diversity attained by tellurium compounds containing 1,1-dithiolate ligands (dithiocarbamate, xanthate, phosphorodithioate, phosphinodithioate, etc.) is a consequence of several factors. The ability of these ligands to exhibit a broad range of coordination patterns, the capacity of tellurium to increase its coordination number by inter- and intra-molecular interactions and the presence of stereochemically active lone pairs on the tellurium atom play a decisive role in the structure outcome of these compounds.

Indeed, several reports on organotellurium(IV) compounds containing 1,1-dithiolate ligands have appeared on the literature, albeit only a handful of such reports are related to halogen-tellurocyclic derivatives [1–5].

As an extension of our studies regarding the stereochemistry and bonding of hypervalent tellurium compounds, we now report

on the synthesis and structural characterization of six new monosubstituted compounds derived from four tellurocycles with diethyl-dithiocarbamate and pyrrolidiny-*N*-carbodithioate ligands.

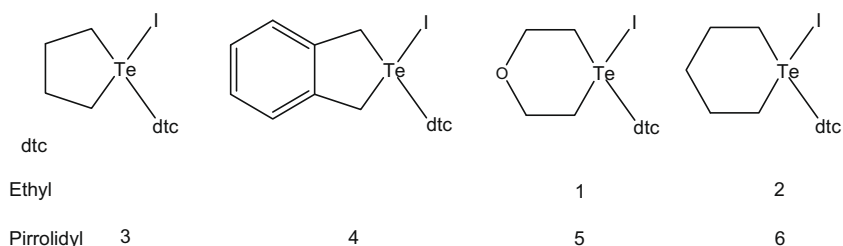
2. Results and discussion

The reaction between 1,1-diiodotelluroolane, 1,3-dihidro-2λ⁴-benzotellurool-2,2-dyildiiodo, 1-oxa-4,4-diiodo-tellurane or 1,1-diiodo-tellurane with the sodium salts of diethyl-dithiocarbamate and pyrrolidiny-*N*-carbodithioate in methanol produced the corresponding monosubstituted compounds: $C_4H_8OTeI[S_2CN(CH_2CH_3)_2]$ (**1**), $C_5H_{10}TeI[S_2CN(CH_2CH_3)_2]$ (**2**), $C_4H_8TeI[S_2CN(CH_2CH_2)_2]$ (**3**), $C_8H_8TeI[S_2CN(CH_2CH_2)_2]$ (**4**), $C_4H_8OTeI[S_2CN(CH_2CH_2)_2]$ (**5**) and $C_5H_{10}TeI[S_2CN(CH_2CH_2)_2]$ (**6**) (Scheme 1). All compounds are pale yellow solids soluble in common organic solvents such as CH_2Cl_2 , Me_2CO and C_6H_6 , and stable towards atmospheric oxygen and moisture. Furthermore, these compounds are stable as solid samples for long periods of time but slowly decompose in solution.

The compounds were characterized by IR, (EI) mass spectrometry and multinuclear NMR (1H , ^{13}C and ^{125}Te) spectroscopy and the

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Scheme 1. Monosubstituted compounds.

crystal structures of **2**, **3**, **5** and **6** were determined by single-crystal X-ray diffraction studies.

The mass spectra (EI⁺) of compounds **1–6** do not exhibit the peaks owing to their molecular ions [M⁺]. Nonetheless, fragments containing the tellurium atom bounded to ligand moieties were observed; i.e. m/z 202 [C₄H₈OTe]⁺ and m/z 329 [C₄H₈OTe]⁺ for **1** and m/z 200 [C₅H₁₀Te]⁺ and m/z 327 [C₅H₁₀Te]⁺ for **2**. In addition, **1** and **2** exhibited their base peak at m/z 148 corresponding to the [C₅H₁₀NS₂]⁺ fragment from the diethyl-dithiocarbamate ligand. For **3–5**, a base peak at m/z 114 was observed and corresponds to the C₅H₈NS⁺ fragment derived from the pyrrolidinyl carbodithioate ligand. This same fragment is present in **6** albeit with 50% of relative abundance. All the observed peaks containing tellurium atoms exhibit the proper isotopic distribution patterns.

The IR (KBr) spectra of the reported compounds were assigned by comparison with the literature data of similar compounds [1,6–8]. In all the spectra a strong band appeared in the range of 1421–1457 cm⁻¹ and was assigned to the N–CS₂ stretching mode [9,10]. This band is characteristic of a carbon–nitrogen bond with an intermediate order between a single and double bond [7], indicating a strong electron delocalization in the dithiocarbamate moiety. Furthermore, two signals with medium intensity owing to the stretching mode of the C–S bonds were observed in the regions of 930 and 1070 cm⁻¹. The difference in wave numbers of these two bands is greater than 20 cm⁻¹ and thus, according to Bonati and Ugo [8], the coordination of the dithiocarbamate ligands to the tellurium atoms corresponds to a monodentate mode.

In the ¹H NMR spectra, the corresponding signals of the tellurocycle moiety and the ligand are observed, and their integration corresponds to that expected for monosubstituted compounds. Furthermore, in these compounds two signals for the methylene protons adjacent to the tellurium atom are observed evidencing magnetic non-equivalent protons. In all the spectra the signals corresponding to the axial protons appear shifted downfield in comparison to the equatorial protons. Nevertheless, in all the cases the signals due to the tellurocycle ring appear shifted upfield with regard to the analogous diiodo derivatives. In the ¹H NMR spectra of **1** and **2**, the signals owing to the methylene protons appear in a range from 3.82 to 3.88 ppm, while those for the methyl protons are observed in the range from 1.25 to 1.30 ppm. Furthermore, the protons from the pyrrolidine ring owing to compounds **3–6** are exhibited in the regions from 3.71 to 3.78 (CH₂CH₂N) and 2.04 to 2.08 ppm (CH₂CH₂N).

The ¹³C NMR spectra of compounds **1–6** exhibit a signal in the range of 194.2–191.1 ppm owing to the methine carbon of the dithiocarbamate group. The signals of the methylene carbons attached to the nitrogen atom (CH₂N) appear in 49.5 and 49.6 ppm for compounds **1** and **2**, respectively. However, for compounds **3–6** these signals appear shifted downfield between 54.5 and 54.3 ppm. The carbon atom bounded to the tellurium atom in the tellurocycles (CH₂Te) experiences an upfield shift with regard to the starting materials with the following chemical shifts; 26.8 ppm (**1**), 26.6 ppm (**5**), 31.0 ppm (**3**), 30.8 ppm (**6**), 42.3 ppm (**3**) and 46.9 ppm (**4**). Additionally, in compounds **1** and **5** the sig-

nals corresponding to CH₂O are observed in an average of 65.7 ppm.

The ¹²⁵Te NMR data showed the presence of a single peak in compounds **1–6**, suggesting the presence of only one species containing tellurium. The chemical shifts for **1** (496 ppm), **2** (572 ppm), **3** (792 ppm), **5** (498 ppm) and **6** (573 ppm) are shifted upfield when compared to those of the corresponding diiodo-tellurocycles. Such type of shift has been observed in similar compounds [11]. However, these data contrast with the downfield shift observed for the compound O[Si(CH₃)₂CH₂]₂TeS₂CNR₂ [12], which is in agreement with that of compound **4** (695 ppm) showing a downfield shift with regard to the diiodo-tellurocycles.

3. Description of the structures

The structure of compounds C₅H₁₀Te[S₂CNET₂] (**2**), C₄H₈Te[S₂CN(CH₂CH₂)₂] (**3**), C₄H₈OTe[S₂CN(CH₂CH₂)₂] (**5**) and C₅H₁₀Te[S₂CN(CH₂CH₂)₂] (**6**) were determined by single-crystal X-ray diffraction methods. The molecular structures are shown in Figs. 1–4. The crystallographic data and selected bond distances and angles are given in Tables 1–4, respectively.

The geometry around the tellurium atom in compounds **2**, **3**, **5** and **6**, corresponds to a trigonal bipyramid with the carbon atoms adjacent to the tellurium atom and the lone pair occupying the equatorial positions. The length of the Te–C bond in these com-

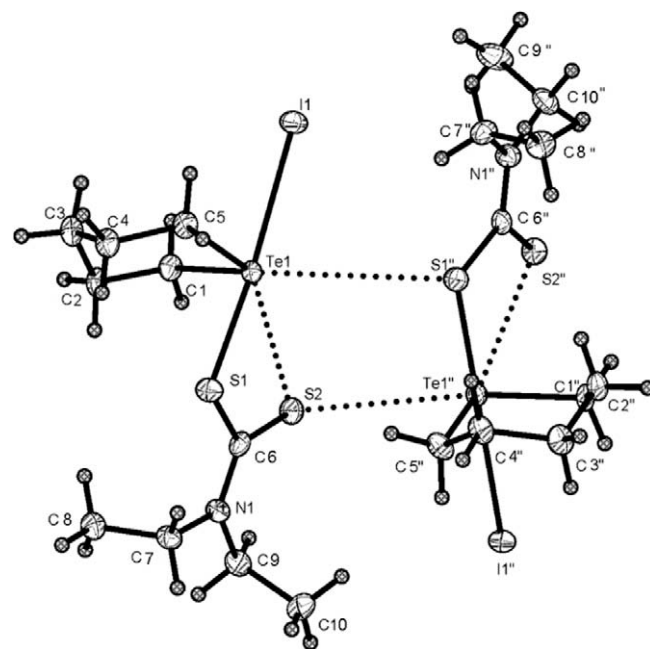


Fig. 1. ORTEP plot of two molecules of C₅H₁₀Te[S₂CN(CH₂CH₃)₂] **2**, showing the dimeric supramolecules through secondary bond Te...S. The heavy atoms are drawn with thermal ellipsoids with a 50% of probability.

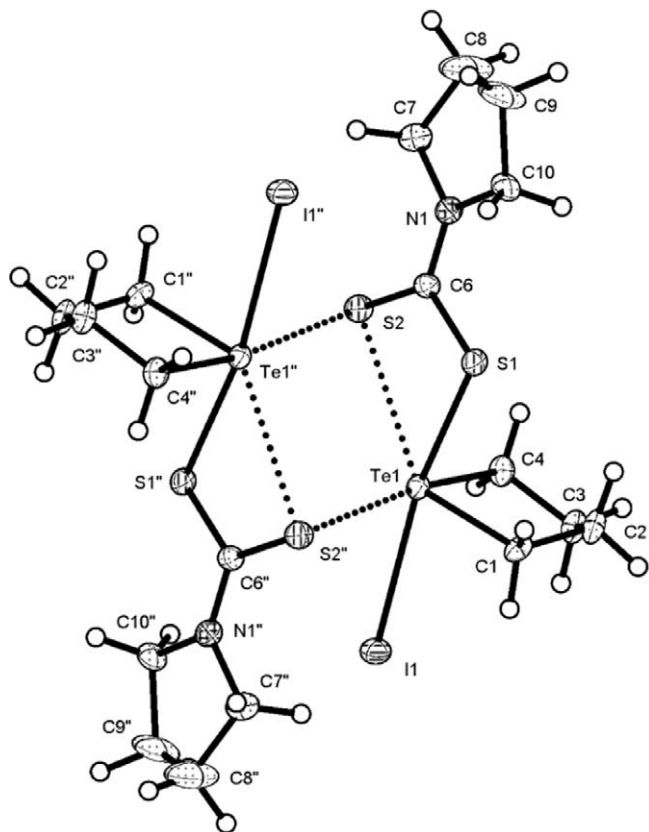


Fig. 2. ORTEP plot of two molecules of $C_4H_8Te[S_2CN(CH_2CH_2)_2]$ **3**, showing the dimeric supramolecules through secondary bond $Te \cdots S$. The heavy atoms are drawn with thermal ellipsoids with a 50% of probability.

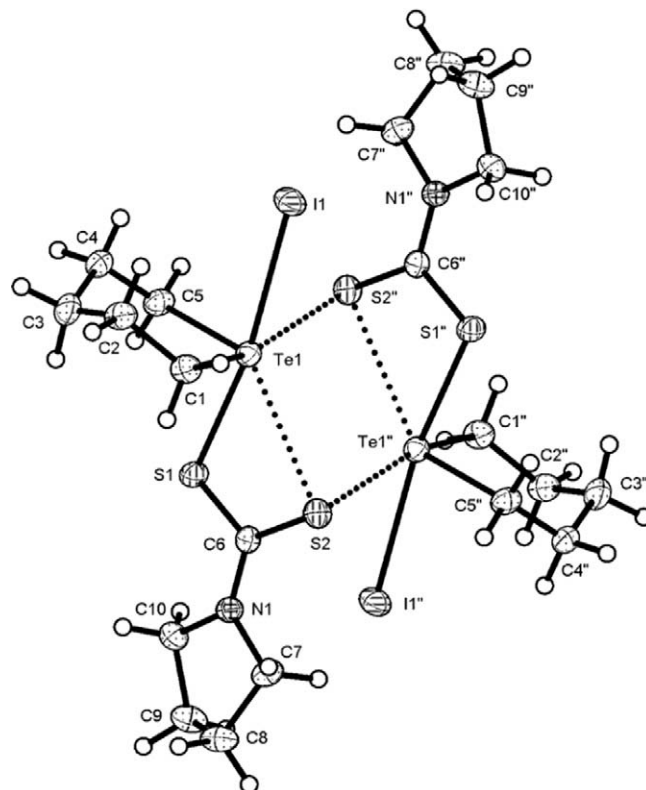


Fig. 4. ORTEP plot of two molecules of $C_5H_{10}Te[S_2CN(CH_2CH_2)_2]$ **6**, showing the dimeric supramolecules through secondary bond $Te \cdots S$. The heavy atoms are drawn with thermal ellipsoids with a 50% of probability.

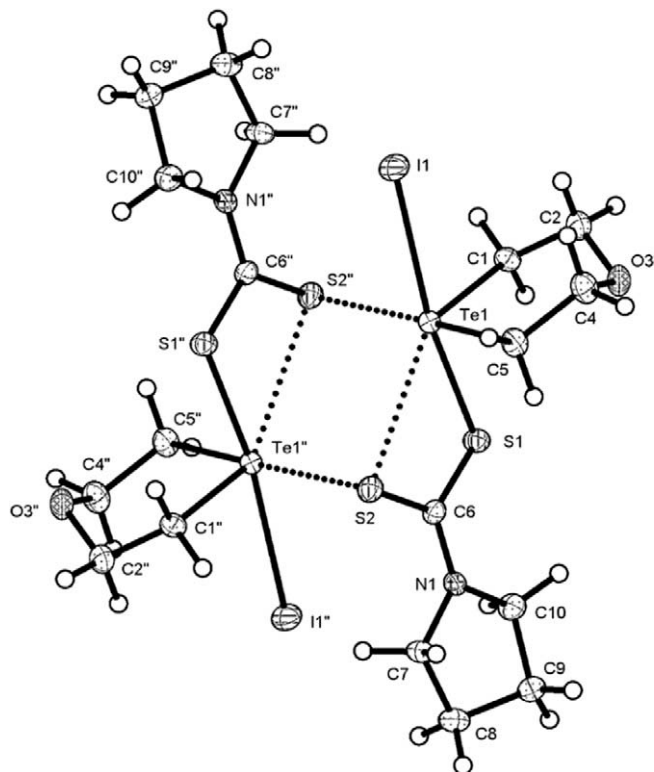


Fig. 3. ORTEP plot of two molecules of $C_4H_8OTe[S_2CN(CH_2CH_2)_2]$ **5**, showing the dimeric supramolecules through secondary bond $Te \cdots S$. The heavy atoms are drawn with thermal ellipsoids with a 50% of probability.

pounds is in average 2.155 Å, essentially the same as that found in $C_4H_8Te(S_2CNET_2)$ (2.148(7) Å) [1], $C_8H_8Te(S_2CNET_2)$ (2.143(6) Å) [2], $Me_2Te(S_2CNET_2)$ (2.12(1) Å) [13], $C_4H_8Te[S_2CN(CH_2CH_2)_2]$ (2.163(10) Å) [1], $C_4H_8Te[S_2CNET_2]$ (2.148(7) Å) [1], $C_8H_8Te[S_2CNET_2]$ (2.143(6) Å) [2] and in the disubstituted compound $Me_2Te(S_2CNMe_2)_2$ (2.13(1) Å) [14].

The C–Te–C bond angles in compounds **2**, **5** and **6** correspond to 93.0(1)°, 95.9(2)° and 96.9(1)°, respectively. These values are related to those observed for $C_5H_{10}Te_2$ 94.1(4)° [15] and $C_4H_8OTe_2$ 98.1(5)° [16] as well as those in $Me_2Te(S_2CNMe_2)_2$ 93.9(2)° [14]. On the other hand, compound **3** shows an angle of 84.9(3)°, considerably more acute than those in **2**, **5** and **6** but similar to the corresponding angle in $C_4H_8Te_2$ 84.5(4)° [16] and to the related compounds $C_4H_8Te[S_2CN(CH_2CH_2)_2]$ 84.0(5)° and $C_4H_8TeS_2CNET_2$ 84.1(3)° [1].

The axial positions in these compounds are occupied by an iodine atom and by one sulfur atom from of each ligand. The bond angles I–Te–S(1), 175.5(1)° (**2**), 170.2(1)° (**3**), 171.7(1)° (**5**) and 171.3(1)° (**6**) are similar to those reported for $C_4H_8Te(S_2CNET_2)$ (176.5(1)° [1], $C_4H_8Te[S_2CN(CH_2CH_2)_2]$ (170.9(1)° [1], $Me_2Te(S_2CNET_2)$ (171.7(1)° [13] and $Me_2Te(S_2CN(CH_2CH_2)_2)$ (174.1(1)° [13] but more obtuse than that found in the disubstituted compound $Me_2Te(S_2CNMe_2)_2$ 166.5(2)° [14]. The six-membered rings (C_4H_8OTe and $C_5H_{10}Te$) in compounds **2**, **5** and **6** show a chair conformation in which the part of the ring that includes the tellurium atom is slightly flattened.

The dithiocarbamate ligands show an anisobidentate chelating coordination mode through a secondary bond with the tellurium center. The long $Te \cdots S$ bond distances in the four compounds cover the range from 3.223(2) to 3.272(1) Å at an average of 3.238 Å and are significantly shorter than the sum of their van der Waals radii ($\Sigma_{vdW} Te, S = 3.86$ Å) [18]. These values are comparable to that

Table 1Crystallographic data for compounds $C_5H_{10}Te[S_2CN(CH_2CH_3)_2]$ **2** and $C_4H_8Te[S_2CN(CH_2CH_3)_2]$ **3**.

	2	3
Compound formula	$C_{10}H_{20}INS_2Te$	$C_9H_{16}INS_2Te$
Formula weight	472.89	456.85
Crystal size (mm)	$0.22 \times 0.21 \times 0.18$	$0.19 \times 0.21 \times 0.36$
Wave length (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$
<i>Unit cell dimensions</i>		
a (Å)	6.6157(9)	6.3258(8)
b (Å)	10.1397(13)	20.434(3)
c (Å)	22.460(3)	10.7393(13)
α (°)	90	90
β (°)	90	101.260(2)
γ (°)	90	90
V (Å ³)	1506.6(3)	1361.7(3)
Z	4	4
D_{calc} (mg m ⁻³)	2.085	2.228
Absorption coefficient (mm ⁻¹)	4.275	4.726
F(0 0 0)	896	856
T (K)	293(2)	100(2)
θ Range for data collection (°)	1.81–25.00	1.99–25.00
Index ranges of hkl	$-7 \leq h \leq 7$, $-12 \leq k \leq 11$, $-26 \leq l \leq 26$	$-7 \leq h \leq 7$, $-24 \leq k \leq 24$, $-12 \leq l \leq 12$
Reflections collected	10 891	13 018
Independent reflections (R_{int})	2648(0.0238)	2401(0.0298)
Observed reflections	2638	2397
Completeness to $\theta = 25.00^\circ$	99.9%	100%
Absorption correction		
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2648/0/138	2401/0/127
Goodness-of-fit (GOF)	1.116	1.378
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0137$, $wR_2 = 0.0327$	$R_1 = 0.0347$, $wR_2 = 0.0795$
R indices (all data)	$R_1 = 0.0139$, $wR_2 = 0.0327$	$R_1 = 0.0348$, $wR_2 = 0.0796$
Largest difference in peak and hole (e Å ⁻³)	0.322 and -0.464	0.787 and -0.772

found in $C_4H_8Te[S_2CN(C_4H_6)]$ (3.266(3) Å) [1] and relatively larger than that observed for $C_4H_8Te[S_2CN(C_2H_5)_2]$ (3.127(2) Å) [1] and $Me_2Te(S_2CN(C_2H_5)_2)$ (3.136(3) Å) [13]. The short Te–S bond lengths range from 2.505(1) to 2.546(1) Å at an average of 2.520 Å, which is shorter than that found in $Me_2Te(S_2CNMe_2)_2$ (2.654(2) and 2.629(2) Å) [14] and larger than that found in $C_8H_8Te[S_2CN(C_2H_5)_2]$ (2.490(2) Å) [2]. The Te–I bond distances range from 3.006(1) to 3.071(1) Å with an average of 3.036 Å, these values are comparable to those reported for $Me_2Te(S_2CN(C_2H_5)_2)$ (3.100(1) Å) [13], $C_4H_8Te[S_2CN(C_4H_6)]$ (3.046(1) Å) and $C_4H_8Te[S_2CN(C_2H_5)_2]$ (3.040(1) Å) [1]. However, they are longer than those present in α - Me_2TeI_2 [17] (2.885(3)–2.965(3) Å) and in the diiodo-tellurocyclic $C_4H_8TeI_2$ (2.899(1) Å), $C_8H_8TeI_2$ (2.902(7) Å) [16], and $C_4H_8OTeI_2$ (2.938(1) Å) [15]. The shortening of the Te–S bonds and the lengthening of the Te–X bonds are due to the *trans* influence operating on a main group metal and have been also observed for compounds $Me_2Te[S_2CN(CH_2)_n(CH_3)]$ [11], $Me_2Te(S_2CN(C_2H_5)_2)$ [13], $C_4H_8Te[S_2CN(C_4H_6)]$ and $C_4H_8Te[S_2CN(C_2H_5)_2]$ [1].

Additionally, compounds **3**, **5** and **6** consist of two molecules that are associated through the secondary bonds (Te...S1'' or Te...S2'') with bond distances corresponding to 3.516(2), 3.392(1) and 3.592(1) Å, respectively. These values are smaller than the sum of their van der Waals radii ($\Sigma_{vdw} Te, S = 3.86$ Å) [18] and result in the formation of dimeric supramolecules (Figs. 1–4). These

Table 2Crystallographic data for compounds $C_4H_8OTe[S_2CN(CH_2CH_2)_2]$ **5** and $C_5H_{10}Te[S_2CN(CH_2CH_2)_2]$ **6**.

	5	6
Compound formula	$C_9H_{18}INS_2Te$	$C_{10}H_{18}INS_2Te$
Formula weight	472.85	470.87
Crystal size (mm)	$0.18 \times 0.19 \times 0.21$	$0.40 \times 0.52 \times 0.51$
Wave length (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
<i>Unit cell dimensions</i>		
a (Å)	10.3587(10)	11.3722(8)
b (Å)	9.8302(9)	12.852(9)
c (Å)	14.5898(14)	10.8520(7)
α (°)	90	90
β (°)	105.140(2)	112.69(10)
γ (°)	90	90
V (Å ³)	1434.1(2)	1463.33(17)
Z	4	4
D_{calc} (mg m ⁻³)	2.190	2.137
Absorption coefficient (mm ⁻¹)	4.496	4.401
F(0 0 0)	888	888
T (K)	100(2)	293(2)
θ Range for data collection (°)	2.17–25.00	1.94–25.00
Index ranges of hkl	$-12 \leq h \leq 11$, $-11 \leq k \leq 11$, $-17 \leq l \leq 11$	$-13 \leq h \leq 13$, $-15 \leq k \leq 15$, $-12 \leq l \leq 12$
Reflections collected	6764	13 822
Independent reflections (R_{int})	2443(0.0364)	2579(0.0279)
Observed reflections	2339	2470
Completeness to $\theta = 25.00^\circ$	96.6%	100%
Absorption correction		
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2443/0/136	2579/0/136
Goodness-of-fit (GOF)	1.149	1.082
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0243$, $wR_2 = 0.0547$	$R_1 = 0.0186$, $wR_2 = 0.0445$
R indices (all data)	$R_1 = 0.0260$, $wR_2 = 0.0555$	$R_1 = 0.0197$, $wR_2 = 0.0451$
Largest difference in peak and hole (e Å ⁻³)	0.823 and -0.440	0.438 and -0.513

associations are similar to those observed for $C_4H_8Te[S_2CN(C_4H_6)]$ (3.603(3) Å) and $C_4H_8Te[S_2CN(C_2H_5)_2]$ (3.582(2) Å) [1] but differ from those in compounds $Me_2Te[S_2CN(C_2H_5)_2]$ [13], Me_2TeI_2 and Me_2-

Table 3Selected bond lengths (Å) for compounds $C_5H_{10}Te[S_2CN(CH_2CH_3)_2]$ **2**, $C_4H_8Te[S_2CN(CH_2CH_2)_2]$ **3**, $C_4H_8OTe[S_2CN(CH_2CH_2)_2]$ **5** and $C_5H_{10}Te[S_2CN(CH_2CH_2)_2]$ **6**.

	2	3	5	6
Te(1)–C(1)	2.154(3)	2.154(6)	2.164(4)	2.153(3)
Te(1)–C(5)	2.157(3)		2.152(4)	2.166(3)
Te(1)–C(4)		2.147(7)		
Te(1)–S(1)	2.5053(8)	2.5279(17)	2.5211 (10)	2.5461(7)
Te(1)–I(1)	3.0707(4)	3.0282(7)	3.0415(5)	3.0055(3)
S(2)–C(6)	1.694(3)	1.687(7)	1.696(4)	1.691(3)
S(1)–C(6)	1.776(3)	1.765(7)	1.760(4)	1.757(3)
C(6)–N(1)	1.322(4)	1.313(9)	1.314(5)	1.317(3)
C(1)–C(2)	1.516(4)	1.526(10)	1.523(5)	1.515(4)
N(1)–C(7)	1.475(4)	1.475(9)	1.472(5)	1.478(4)
N(1)–C(9)	1.476(4)			
N(1)–C(10)		1.483(9)	1.480(4)	1.476(4)
Te(1)–S(2)	3.2293(8)	3.223(2)	3.228(1)	3.272(1)
Te(1)–S(2'')	3.5442(8)	3.516(2)	3.392(1)	3.592(1)
Te(1)–S(1'')	3.8841(8)	3.903(2)	3.896(1)	4.103(1)
S(1)–S(2)	3.028(1)	3.018(3)	3.025(2)	3.020(1)

Table 4
Selected bond angles (°) for the compound $C_5H_{10}TeI[S_2CN(CH_2CH_3)_2]$ **2**, $C_4H_8TeI[S_2CN(CH_2CH_2)_2]$ **3**, $C_4H_8OTeI[S_2CN(CH_2CH_2)_2]$ **5** and $C_5H_{10}TeI[S_2CN(CH_2CH_2)_2]$ **6**.

	2	3	5	6
C(1)–Te(1)–C(5)	92.97(11)		95.95(15)	96.89(12)
C(1)–Te(1)–C(4)		84.9(3)		
C(1)–Te(1)–S(1)	92.00(8)	83.6(2)	84.81(11)	90.60(9)
C(5)–Te(1)–S(1)	86.96(8)		89.91(11)	83.60(8)
C(4)–Te(1)–S(1)		91.4(2)		
C(1)–Te(1)–I(1)	86.67(7)	86.6(2)	87.45(11)	87.41(9)
C(5)–Te(1)–I(1)	88.85(4)		87.90(11)	88.20(8)
C(4)–Te(1)–I(1)		87.00(2)		
S(1)–Te(1)–I(1)	175.53(2)	170.16(4)	171.71(3)	171.28(2)
C(6)–S(1)–Te(1)	98.99(10)	98.6(2)	98.60(13)	99.65(9)
N(1)–C(6)–S(2)	124.0(2)	123.4(5)	123.1(3)	122.8(2)
N(1)–C(6)–S(1)	114.5(2)	114.7(5)	114.8(3)	114.9(2)
S(2)–C(6)–S(1)	121.5(2)	121.9(4)	122.1(2)	122.3(2)
C(2)–C(1)–Te(1)	115.2(2)	101.5(4)	113.8(3)	115.3(2)
C(6)–N(1)–C(7)	123.3(2)	123.5(6)	123.1(3)	123.7(2)
C(6)–N(1)–C(10)		125.3(6)	125.7(3)	125.2(2)
C(6)–N(1)–C(9)	121.6(3)			
C(7)–N(1)–C(9)	115.1(2)			
C(7)–N(1)–C(10)		111.1(6)	111.2(3)	110.9(2)
S(1)–Te(1)–S(2)	62.23(2)	61.92(4)	62.06(3)	61.03(2)
I(1)–Te(1)–S(2)	121.62(2)	127.25(4)	125.32(3)	126.79(2)
C(1)–Te(1)–S(2)	79.81(8)		146.55(11)	79.84(9)
C(4)–Te(1)–S(2)		81.2(2)		
C(1)–Te(1)–S(2'')		142.2(2)		168.46(9)
C(4)–Te(1)–S(2'')		172.2(2)		
C(5)–Te(1)–S(2)			80.44(11)	144.29(9)
C(5)–Te(1)–S(2'')			173.77(11)	

$TeI[S_2CN(CH_2CH_2)_2]$ [11], which also exhibit $Te\cdots I$ secondary bonding.

In compound **2** the secondary bonds $Te\cdots S1''$ (3.8841(8) Å) and $Te''\cdots S2$ (3.5442(8) Å) along with the intra-molecular interaction $Te\cdots S2$ (3.2293(8) Å), generate a similar arrangement to that observed in the previous examples. However, in this case it extends the union by means of a vertex to another neighboring molecule, $Te\cdots S2\cdots Te''\cdots S2''\cdots Te'''\cdots S2'''$, allowing the formation of self-assembled chains in a zigzag fashion (Fig. 5). Although the longer length of these interactions exceeds the sum of their van der Waals radii ($\Sigma_{vdw} Te, S$) reported by Bondi [18] (3.86 Å), they fall within the value considered [19] (4.05 Å). Similar self-assembled chains have been reported in others tellerium compounds [13,11,20].

The bond angles $Te-S1-C(6)$, 99.0 (1)°, 98.6(1)°, 99.7(1)° and 98.6(2), and $S1-Te-S2$, 62.2(1)°, 62.1(1)°, 61.0(1)° and 61.9(1)°, in compounds **2**, **5**, **6** and **3**, respectively, are similar to those reported for $Me_2TeI[S_2CNEt_2]$ [13] [98.3(3)° and 63.2(1)°], $C_4H_8TeI[S_2CN(CH_2CH_2)_2]$ [98.7(3)° and 61.6(3)°] and $C_4H_8TeI[S_2CNEt_2]$ [1] [97.3(3)° and 62.9(1)°].

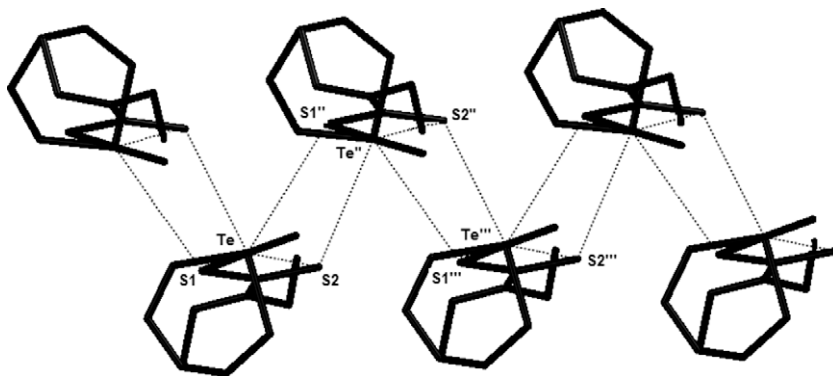


Fig. 5. Self-assembled chain in disposition zigzag of compound $C_5H_{10}TeI[S_2CN(CH_2CH_3)_2]$ **2**.

On the other hand, the bond angles $TeS1-C(6)-S2$ and $S2-C(6)-N$ with 121.5(2)° and 124.0(2)° for **2**, 121.9(4)° and 123.4(5)° for **3**, 122.1(2)° and 123.1(3)° for **5** and 122.3(2)° and 122.8(2)° for **6**, are consistent with the delocalization of the π bond within the planar S_2CN group. Furthermore, the sum of the three angles around nitrogen atom corresponds to 360° which confirms the planar environment of the nitrogen atom. The $TeS-C$ bond lengths (1.757(3)–1.776(3) Å) are shorter than the sum of their covalent radii ($\Sigma_{vdw} S, C = 1.81$ Å) and thus suggest a small degree of participation in the delocalized π -system. The terminal $C-S$ bonds (1.687(7)–1.696(4) Å) are shorter than the previous bond lengths but longer than those in CS_2 (1.56 Å). The S_2C-N bond lengths (1.313(9)–1.322(4) Å) are shorter than the sum of their covalent radii ($\Sigma_{vdw} C, N = 1.51$ Å) confirming that the delocalized π -system extends to the S_2C-N bond.

When the intra-molecular secondary bonds $Te\cdots S2$ (3.2293(8) Å for **2**, 3.223(2) Å for **3**, 3.228(1) Å for **5** and 3.272(1) Å for **6**) are included in the coordination sphere of the tellurium atoms, the geometric arrangement for this atom can be considered as a distorted square-based pyramid. In compound **2** the C5, I, S1 and S2 atoms are almost coplanar while the C1 atom is located above this plane. The sum of the bond angles in **2** ($S1-Te-S2$ (62.2(1)°), $S2-Te-I$ (121.6(1)°), $I-Te-C5$ (88.9(1)°) and $C5-Te-S1$ of 87.0(1)°) gives a value close to 360°. In compounds **3** and **5** the base of the pyramid is formed by the C1, S1, S2 and I atoms, while for **6** these correspond to the C5, S1, S2 and I atoms. The apical positions in these arrangements correspond to C4 for **3**, C5 for **5** and C1 for **6**, all of which form close to 90° angles with the atoms located in the vertices of the base, these data are included in Tables 1–4.

On the other hand, when the intermolecular secondary bonds ($Te\cdots S2''$) are also taken into account (3.516(2) Å for **3**, 3.392(1) Å for **5** and 3.592(1) Å for **6**), the geometry around the tellurium atoms can be considered as a distorted octahedron with the lone pair being stereochemically inactive. The $S2''$ atom can thus be considered as lying in a *trans* position relative the C4, C5 and C6 atoms in compounds **3**, **5** and **6**, respectively. This generates the angles $C4-Te-S2''$ (172.2(2)°), $I-Te-S1$ (170.2(1)°) and $C1-Te-S2$ (142.2(2)°) for **3**, $C5-Te-S2''$ (173.8(1)°), $S2-Te-C1$ (146.6(1)°) and $S1-Te-I$ (171.7(1)°) for **5** and $I-Te-S1$ (171.3(1)°), $C5-Te-S2$ (144.3(1)°) and $C1-Te-S2''$ (168.5(1)°) for **6**.

4. Experimental

All reagents were of commercial grade and were used as received. The 1,1-diiodotellurane $C_4H_8TeI_2$, 1,3-dihydro-2λ⁴-benzotellur-2-diodide $C_8H_8TeI_2$, 1-oxa-4,4-diiio-dotellurane $C_4H_8OTeI_2$ and 1,1-diiodotellurane $C_5H_{10}TeI_2$ were prepared according to the methods described by Ziolo and Gunther [21]. The sodium salts

of diethyl-dithiocarbamate and pyrrolidinyl-*N*-carbodithioate were prepared according to literature [22].

IR spectra were recorded in the region 4000–500 cm⁻¹ as KBr pellets using a Bruker spectrometer. The ¹H, ¹³C and ¹²⁵Te magnetic resonance spectra were obtained on a Varian Gemini 200 and Varian Inova 400 Spectrometer at room temperature in CDCl₃. The chemical shifts are relative to internal Me₄Si (¹H and ¹³C), and 1,1-diiodotellurothane, C₄H₈TeI₂ (¹²⁵Te) for the indicated nuclei. Mass spectra determinations were performed on a JEOL JMS-WSX 102A instrument by electron impact at 70 eV.

Single-crystals of **2**, **3**, **5** and **6** suitable for X-ray diffraction were obtained by diffusion using a dichloromethane-*n*-hexane mixture. Crystallographic and solution data are summarized in Tables 1–4. Data collections were carried out in a Bruker APEX CCD diffractometer at 100(2) K for **3** and **5** and at room temperature in the case of **2** and **6**.

Compounds **1–6** were prepared in a similar manner with a 1:1 molar ratio of diiodo-tellurocycle: dithiocarbamate. In each case, the diiodo-tellurocycle was dissolved in methanol (30 ml) and the corresponding dithiocarbamate ligand was added. The solution was stirred for 2 h, filtered off and evaporated to dryness, subsequently dissolved in dichloromethane and filtered in order to separate the sodium iodide. Finally the solvent was removed under vacuum and the resulting solid was recrystallized from a dichloromethane-*n*-hexane mixture.

4.1. Synthesis of C₄H₈OTeI[S₂CN(CH₂CH₃)₂] **1**

Compound **1** was prepared by the reaction of C₄H₈OTeI₂ (0.500 g, 1.1026 mmol) with (CH₂CH₃)₂NCS₂Na (0.1886 g, 1.1026 mmol) in methanol (30 ml). The resulting product is a pale yellow solid, m.p. 123–125 °C. Yield (0.3487 g, 67%). EI-MS (70 eV) *m/z* 405 (C₅H₈OS₂TeI⁺, <5%), 329 (C₄H₈OTeI⁺, <5%), 296 (C₁₀H₂₀N₂S₄⁺, 15%), 278 (C₅H₈OS₂Te⁺, <5%), 254 (I₂⁺, 55%), 202 (C₄H₈OTe⁺, 25%), 148 (C₅H₁₀NS₂⁺, 100%), 116 (C₅H₁₀NS⁺, 100%). IR (cm⁻¹) 2970 w, 2926 w, 2865 w (νC–H), 1488 m, 1381 w (δC–H), 1426 m (νNC=S), 1267 m (νC–O), 1267 m, 1194 m (νC–N), 1145 m, 1087 m (νC=S), 1087 m, 1003 m, 967 m, 903 w (νC–S). δ ¹H NMR (200 MHz) 1.29 (t, 6H) NCH₂CH₃, 3.03 (bs, 2H) CH_{ec}CH_{ec}Te, 3.22 (bs, 2H) CH_{ax}CH_{ax}Te, 3.86 (q, 4H) NCH₂CH₃, 4.42 (bs, 4H) OCH₂CH₂Te. δ ¹³C NMR (50.28 MHz) 12.54 (NCH₂CH₃), 26.82 (OCH₂CH₂Te), 49.49 (NCH₂CH₃), 65.68 (OCH₂CH₂), 193.80 (S₂CN). δ ¹²⁵Te NMR (94 MHz) 496.79.

4.2. Synthesis of C₅H₁₀TeI[S₂CN(CH₂CH₃)₂] **2**

Compound **2** was prepared by the reaction of C₅H₁₀TeI₂ (0.2500 g, 0.5537 mmol) with (CH₂CH₃)₂NCS₂Na (0.0947 g, 0.5537 mmol) in methanol (30 ml). The resulting product is a pale yellow solid, m.p. 117–120 °C. Yield (0.1085 g, 42%). EI-MS (70 eV) *m/z* 403 (C₆H₁₀S₂TeI⁺, <5%), 327 (C₅H₁₀TeI⁺, <10%), 296 (C₁₀H₂₀N₂S₄⁺, 15%), 278 (C₅H₁₀NS₂Te⁺, <5%), 254 (I₂⁺, 30%), 200 (C₅H₁₀Te⁺, 20%), 148 (C₅H₁₀NS₂⁺, <25%), 116 (C₅H₁₀NS⁺, 100%). IR (cm⁻¹) 2970 m, 2923 m, 2854 w (νC–H), 1491 s, 1425 s (νNC=S), 1379 w (δC–H), 1266 w, 1229 m (νC–N), 1193 m, 1142 w, 1067 w (νC=S), 970 m, 904 m (νC–S). δ ¹H NMR, (200 MHz) 1.29 (t, 6H) NCH₂CH₃, 1.81 (bs, 2H) CH₂CH₂CH₂Te, 2.13 (bs, 2H) CH_{ec}CH₂Te, 2.36 (bs, 2H) CH_{ax}CH₂Te, 3.31 (bs, 2H) CH_{ec}Te, 3.53 (bs, 2H) CH_{ax}Te, 3.88 (q, 4H) NCH₂CH₃. δ ¹³C NMR (50.28 MHz) 12.57 (NCH₂CH₃), 22.51 (CH₂CH₂CH₂Te), 26.51 (CH₂CH₂Te), 30.97 (CH₂Te), 49.58 (NCH₂CH₃), 193.47 (S₂CN). δ ¹²⁵Te NMR (94 MHz) 572.98.

4.3. Synthesis of C₄H₈TeI[S₂CN(CH₂CH₂)₂] **3**

Compound **3** was prepared by the reaction of C₄H₈TeI₂ (0.6000 g, 1.3716 mmol) with (CH₂CH₂)₂NCS₂Na (0.2320 g,

1.3716 mmol) in methanol (30 ml). The resulting product is a pale yellow solid, m.p. 163–165 °C. Yield (0.4705 g, 75%). EI-MS (70 eV) *m/z* 357 (C₅H₈STeI⁺, 25%), 313 (C₄H₈TeI⁺, <5%), 292 (C₁₀H₁₆N₂S₄⁺, <5%), 276 (C₅H₈NS₂Te⁺, <10%), 254 (I₂⁺, <10%), 186 (C₄H₈Te⁺, 5%), 147 (C₅H₈NS₂⁺, >15%), 114 (C₅H₈NS⁺, 100%). IR (cm⁻¹) 2950 w, 2858 w (νC–H), 1435 s, 1330 m (δC–H), 1435 s (νNC=S), 1241 w, 1152 m (νC–N), 1152 m, 1033 w (νC=S), 994 m, 940 m (νC–S). δ ¹H NMR (400 MHz) 2.07 (m, 4H) N(CH₂CH₂)₂, 2.73 (bs, 2H) CH_{ec}CH₂Te, 2.98 (bs, 2H) CH_{ax}CH₂Te, 3.35 (bs, 2H) CH₂CH_{ec}Te, 3.64 (bs, 2H) CH₂CH_{ax}Te, 3.74 (m, 4H) N(CH₂CH₂)₂. δ ¹³C NMR (100.51 MHz) 26.09 (N(CH₂CH₂)₂), 33.52 (CH₂CH₂Te), 42.34 (CH₂CH₂Te), 54.28 (N(CH₂CH₂)₂), 191.07 (S₂CN). δ ¹²⁵Te NMR (126.18 MHz) 792.61.

4.4. Synthesis of C₈H₈TeI[S₂CN(CH₂CH₂)₂] **4**

Compound **4** was prepared by the reaction of C₈H₈TeI₂ (0.8000 g, 1.6478 mmol) with (CH₂CH₂)₂NCS₂Na (0.2787 g, 1.6478 mmol) in methanol (30 ml). The resulting product is a pale yellow solid, m.p. 135 °C. Yield (0.6821 g, 82%). EI-MS (70 eV) *m/z* 384 (TeI₂⁺, <5%), 254 (I₂⁺, 25%), 234 (C₈H₈Te⁺, 40%), 147 (C₅H₈NS₂⁺, <5%), 114 (C₅H₈NS⁺, <50%), 104 (C₈H₈⁺, 100%). IR (cm⁻¹) 2962 w, 2895 w, 2854 w (νC–H), 1471 m, 1326 w (δC–H), 1435 s 1422 m (νNC=S), 1154 w (νC–N), 990 w, 940 w (νC=S), 990 w (νC–S). δ ¹H NMR (400 MHz) 2.04 (q, 4H) N(CH₂CH₂)₂, 3.71 (m, 4H) N(CH₂CH₂)₂, 4.68 (d, 2H) CH_{ec}Te, *J* = 14.00 Hz, 5.01 (d, 2H) CH_{ax}Te, *J* = 14.40 Hz, 7.21 (s, 4H) aromatics. δ ¹³C NMR (100.51 MHz) 26.22 (N(CH₂CH₂)₂), 46.91 (CH₂CH₂Te), 54.51 (N(CH₂CH₂)₂), 127.93–139.47 (ArCH₂Te), 191.85 (S₂CN). δ ¹²⁵Te NMR (126.18 MHz) 695.13.

4.5. Synthesis of C₄H₈OTeI[S₂CN(CH₂CH₂)₂] **5**

Compound **5** was prepared by the reaction of C₄H₈OTeI₂ (0.7000 g, 1.5437 mmol) with (CH₂CH₂)₂NCS₂Na (0.2611 g, 1.5437 mmol) in methanol (30 ml). The resulting product is a pale yellow solid, m.p. 137–140 °C. Yield (0.5836 g, 80%). EI-MS (70 eV) *m/z* 384 (TeI₂⁺, <5%), 348 (C₉H₁₆NOS₂Te⁺, <5%), 276 (C₅H₈NS₂Te⁺, <5%), 254 (I₂⁺, <5%), 202 (C₄H₈OTe⁺, <5%), 148 (C₅H₈NS₂⁺, <60%), 114 (C₅H₈NS⁺, 100%). IR (cm⁻¹) 2971 w, 2927 w, 2860 w (νC–H), 1474 s, 1434 s (δC–H), 1434 w (νNC=S), 1275 w, 1216 w (νC–O), 1275 w, 1216 w, 1156 w (νC–N), 1087 w, 1001 w, 946 w (νC=S), 1001 w, 946 w (νC–S). δ ¹H NMR (200 MHz) 2.08 (m, 4H) N(CH₂CH₂)₂, *J* = 14.00, *J* = 3.00 Hz, 3.06 (bs, 2H) CH_{ec}CH_{ec}Te, 3.18 (bs, 2H) CH_{ax}CH_{ax}Te, 3.75 (m, 4H) N(CH₂CH₂)₂, *J* = 14.80, *J* = 3.00, 4.38 (bs, 4H) OCH₂CH₂Te. δ ¹³C NMR (100.51 MHz) 26.20 (N(CH₂CH₂)₂), 26.63 (OCH₂CH₂Te), 54.41 (N(CH₂CH₂)₂), 65.63 (OCH₂CH₂), 191.24 (S₂CN). δ ¹²⁵Te NMR (126.18 MHz) 498.78.

4.6. Synthesis of C₅H₁₀TeI[S₂CN(CH₂CH₂)₂] **6**

Compound **6** was prepared by the reaction of C₅H₁₀TeI₂ (0.7000 g, 1.5505 mmol) with (CH₂CH₂)₂NCS₂Na (0.2622 g, 1.5505 mmol) in methanol (30 ml). The resulting product is a pale yellow solid, m.p. 142–145 °C. Yield (0.5829 g, 80%). EI-MS (70 eV) *m/z* 384 (TeI₂⁺, <5%), 254 (I₂⁺, <10%), 200 (C₅H₁₀Te⁺, <5%), 147 (C₅H₈NS₂⁺, 50%), 114 (C₅H₈NS⁺, 100%). IR (cm⁻¹) 2937 w, 2856 w (νC–H), 1462 m, 1435 s, 1331 w (δC–H), 1435 s (νNC=S), 1245 w, 1155 w (νC–N), 997 w, 940 w (νC=S), 997 w, 940 w (νC–S). δ ¹H NMR (400 MHz) 1.82 (bs, 2H) CH₂CH₂CH₂Te, 2.15 (q, 4H) N(CH₂CH₂)₂, 2.15 (bs, 2H) CH_{ec}CH₂Te, 2.38 (bs, 2H) CH_{ax}CH₂Te, 3.26 (bs, 2H) CH_{ec}Te, 3.60 (bs, 2H) CH_{ax}Te, 3.78 (t, 4H) N(CH₂CH₂)₂. δ ¹³C NMR (100.51 MHz) 22.27 (CH₂CH₂CH₂Te), 26.23 (NCH₂CH₂)₂), 26.29 (CH₂CH₂Te), 30.80 (CH₂Te), 54.44 (N(CH₂CH₂)₂), 191.24 (S₂CN). δ ¹²⁵Te NMR (126.18 MHz) 573.95.

Appendix A. Supplementary material

CCDC 673669, 673668, 673670 and 673671 contain the supplementary crystallographic data for compounds **2**, **3**, **5** and **6** respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2010.01.036](https://doi.org/10.1016/j.jorganchem.2010.01.036).

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