

Synthesis, characterization and structural studies of dithiocarbamate derivatives of 2,2,6,6-tetramethyl-1-oxa-4,4-diiodo-4-tellura-2,6-disilacyclohexane, $O[Si(CH_3)_2CH_2]_2Te(dtc)$

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ABSTRACT

Five new hetero-organotellurium (IV) dithiocarbamates $O[Si(CH_3)_2CH_2]_2TeS_2CN(CH_2CH_2)_2$ (**1**), $O[Si(CH_3)_2CH_2]_2TeS_2CN(CH_2CH_2)_2$ (**2**), $O[Si(CH_3)_2CH_2]_2TeS_2CN(CH_2CH_2)_2O$ (**3**), $O[Si(CH_3)_2CH_2]_2TeS_2CN(CH_2CH_2)_2S$ (**4**) and $O[Si(CH_3)_2CH_2]_2TeS_2CN(CH_2CH_2)_2CH_2$ (**5**) were prepared from the 2,2,6,6-tetramethyl-1-oxa-4,4-diiodo-4-tellura-2,6-disilacyclohexane and the corresponding dithiocarbamate (dtc) sodium salts in ethanol. The compounds were characterized by means of Elemental Analyses, FAB MS, IR, ¹H, ¹³C, ¹²⁵Te NMR spectroscopy. The crystal structures of **1**, **3** and **4** were determined. Dithiocarbamate ligands display an anisobidentate chelating coordination mode on interacting with the tellurium center in all compounds. The Te(IV) immediate environment 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 methylene groups occupy the other equatorial positions with a sulfur atom of the dithiocarbamate group and the iodine atom occupying the axial positions. The solid state structures of **3** and **4** exhibit important intermolecular interaction $Te \cdots S(2B)$. This interaction results in the formation of a dimer, which is better described as a distorted octahedron with an apparently inactive lone pair.

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1. Introduction

The great structural diversity of organotellurium (IV) derivatives with 1,1-dithio ligands [1], such as dithiocarbamates [1–16], dithiophosphates [4,14–17], dithiophosphinates [11,12] and xanthates [13,14,18] are greatly influenced by the nature of the ligands, and little changes in aspects, such as the size of the ligand's bite, the strong tendency to form inter- and intra-molecular interactions, and the presence of the apparently stereochemically active lone pair of electrons could influence the coordination geometry. As an extension, of our previous studies on organotellurium (IV) derivatives of dithiocarbamate ligands, we present herein the results of the preparation and spectroscopic characterization of five new monosubstituted bicyclic complexes $O[Si(CH_3)_2CH_2]_2TeS_2CN(CH_2CH_2)_2$ (**1**), $O[Si(CH_3)_2CH_2]_2TeS_2CN(CH_2CH_2)_2$ (**2**), $O[Si(CH_3)_2CH_2]_2TeS_2CN(CH_2CH_2)_2O$ (**3**), $O[Si(CH_3)_2CH_2]_2TeS_2CN(CH_2CH_2)_2S$ (**4**) and $O[Si(CH_3)_2CH_2]_2TeS_2CN(CH_2CH_2)_2CH_2$ (**5**), such compounds contain, in addition to a cyclic dithiocarbamate ligand an interesting silicon containing organometallic tellurium six-

membered heterocycle ring. These tellurium compounds were obtained, in order to know if the presence of the bulky silicon-containing heterocycle prevents the substitution of the two iodine atoms, with the corresponding synthesis of monosubstituted complexes and if the dithiocarbamate coordination is totally monodentate or at least anisobidentate.

The obtained compounds were characterized by means of elemental analysis, mass spectrometry, IR and multinuclear NMR (¹H, ¹³C and ¹²⁵Te). In addition, the molecular structures of three compounds **1**, **3** and **4**, determined by single-crystal X-ray diffraction, are also reported.

2. Results and discussion

Compounds **1–5** were prepared from the 2,2,6,6-tetramethyl-1-oxa-4,4-diiodo-4-tellura-2,6-disilacyclohexane [19] with five different heterocyclic dithiocarbamate ligands (pyrrolidine-, 3-pyrrolone-, morpholine-, thiomorpholine- and piperidine-carbodithioate of sodium, RCS_2Na) in ethanol (Fig. 1). All compounds are yellow crystalline solids, soluble in common organic solvents such as $CHCl_3$ or CH_2Cl_2 . Their elemental analyses and spectroscopic properties are in agreement with the proposed compounds.

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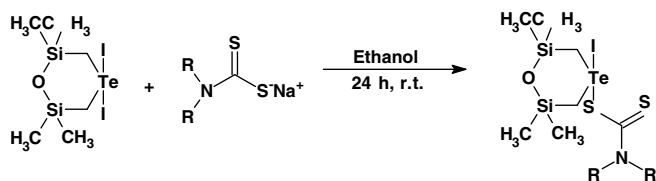


Fig. 1. Reaction scheme.

In spite of the presence of two possible replaceable iodines in the dithiocarbamate ligands, only one was substituted, due to steric considerations of the bulky heterocyclic rings. The coordination of the dithiocarbamate ligand in all obtained complexes was anisobidentate.

The IR spectra exhibit absorption bands characteristic of both the heterocyclic O[Si(CH₃)₂CH₂]₂Te moiety and the dithiocarbamate ligand. These bands were assigned by comparison with the spectra of the starting materials and literature data [19,20]. The strong bands present in the regions 1438–1419 and 1260–1250 cm⁻¹ are assigned to asymmetric and symmetric deformations of the methyl group (Si–CH₃), respectively. The three strong bands at 871–803 cm⁻¹ are due to the ν (Si–CH₃). The Si–O stretching vibration is assigned to the bands in 1065–1023 cm⁻¹ the region. The two weak to medium bands observed in the region 572–507 cm⁻¹ are attributed to asymmetric and symmetric stretching vibrations of the C–Te, respectively. In general, these bands are significantly at higher wavenumber than those observed in the heterocyclic O[Si(CH₃)₂CH₂]₂TeI₂ [19]. In all compounds there is a strong band at 1460–1480 cm⁻¹, found also in many other dithiocarbamates [2–4]. This band is due to the stretching vibration of the C–N bond with partial double bond, this is consistent with the shorter C–N bond being found in structures **1**, **3** and **4**. The presence of two strong-medium absorption bands in the region 1024–950 cm⁻¹ are characteristic of ν (CS₂) vibrations and suggests an anisobidentate behavior of the dithiocarbamate ligand [20].

The positive ion FAB mass spectra show low-intensity signals for the corresponding molecular ion, but rather intense fragments containing tellurium atom, i.e. C₆H₁₆OSi₂STedtc⁺, C₆H₁₆OSi₂STe⁺, C₆H₁₆OSi₂Te⁺. These signals exhibit the expected characteristic isotopic distribution patterns. In addition, the spectra shows the characteristic signal due to the fragment R₂NCS⁺ of the dithiocarbamate ligand.

The ¹H NMR spectra of compounds **1–5** in CDCl₃, show two doublet signals between 2.56–2.54 and 2.42–2.35 ppm that reveal the non-equivalence of the protons of the methylene groups CH₂–Te. In addition, the methyl attached to the silicon atoms are non equivalent as well, showing two singlet signals in the ranges 0.43–0.40 and 0.32–0.30 ppm. The signal corresponding to CH₂–Te and CH₃–Si shows an up field shift relative to that of the starting material O[Si(CH₃)₂CH₂]₂TeI₂ [19]. The ¹³C NMR spectra of these compounds exhibit two signals in the ranges 4.35–4.08 and 7.72–3.49 ppm assigned to the resonances of the methyl carbon CH₃–Si, these signals confirm the non equivalence of such groups. The signals of the methylene carbons CH₂–Te appear in the range 12.60–12.07 ppm, these carbon atoms experience an up field shift relative to the O[Si(CH₃)₂CH₂]₂TeI₂, (14.7 ppm) [19]. The signals assigned to all the carbon atoms of the cyclic dithiocarbamate groups are consistent with their structures. The ¹²⁵Te spectral data show the presence of a single peak in the compounds **1–5**, indicating the presence of only one species containing tellurium. The signals are shifted downfield if compared to that of O[Si(CH₃)₂CH₂]₂TeI₂ (601 ppm) in the region 648–638 ppm. These data are in contrast to the up field shift observed for (CH₃)₂TeI[S₂CN(CH₂CH₂)₂ (507 ppm) and (CH₃)₂TeI[S₂CN(CH₂CH₂)₂CH₂ (501 ppm) [2].

3. Description of the structures

The structure of the complexes O[Si(CH₃)₂CH₂]₂TeI[S₂CN(CH₂CH₂)₂ (**1**), O[Si(CH₃)₂CH₂]₂TeI[S₂CN(CH₂CH₂)₂O (**3**) and O[Si(CH₃)₂CH₂]₂TeI[S₂CN(CH₂CH₂)₂S (**4**) was determined by single crystal X-ray diffraction methods. The molecular structures are shown in Figs. 2–4, respectively. The crystallographic and structural solution data are summarized in the Table 1. Selected bond distances and angles are given in Tables 2 and 3. The coordination geometry of the tellurium center in the three compounds can be described as the sawhorse structure typical of Te(IV) compounds in which the lone-pair of electrons is apparently stereochemically active and occupies an equatorial position in a distorted trigonal bipyramid [1–12]. The two carbon atoms of

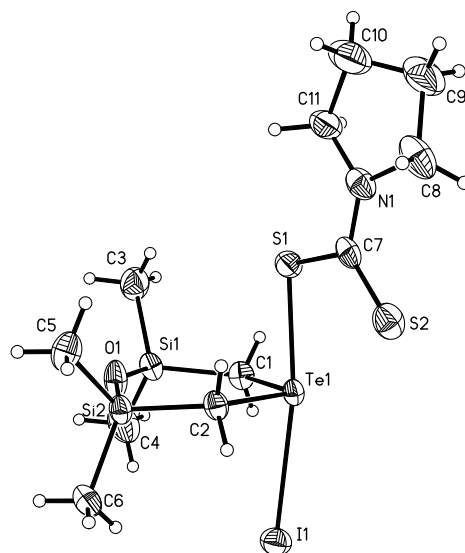


Fig. 2. ORTEP plot of the structure of O[Si(CH₃)₂CH₂]₂TeI[S₂CN(CH₂CH₂)₂ (**1**).

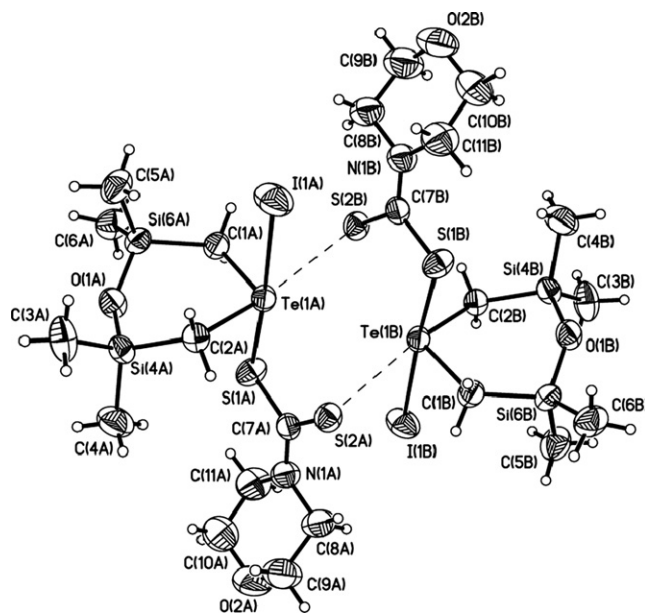


Fig. 3. ORTEP plot of the structure of O[Si(CH₃)₂CH₂]₂TeI[S₂CN(CH₂CH₂)₂O (**3**) showing the intermolecular interactions involving the sulfur atoms leading to a dimer.

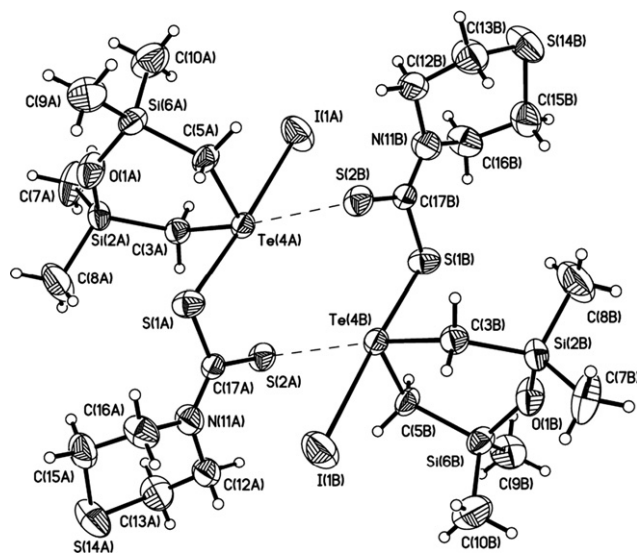


Fig. 4. ORTEP plot of the structure of $O[Si(CH_3)_2CH_2]_2TeIS_2CN(CH_2CH_2)_2S$ (**4**) showing the intermolecular interactions involving the sulfur atoms leading to a dimer.

methylene groups occupy the other equatorial positions with a C–Te–C angle of 106.95° for **1** and an average 101.67° for **3** and **4**. A sulfur atom from the dithiocarbamate group and the iodine atom

Table 1
Crystallographic data for compounds **1**, **3** and **4**

	1	3	4 ^a
Formula	$C_{11}H_{24}INOS_2Si_2Te$	$C_{11}H_{24}INO_2S_2Si_2Te$	$C_{11}H_{24}INOS_3Si_2Te$
Formula weight	561.11	577.11	593.20
Crystal size (mm)	$0.305 \times 0.171 \times 0.092$	$0.13 \times 0.27 \times 0.31$	$0.68 \times 0.16 \times 0.16$
Temperature (K)	293(2)	293(2)	293(2)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$	$C2/c$
<i>a</i> (Å)	8.865(1)	30.493(2)	30.676(3)
<i>b</i> (Å)	10.748(2)	8.459(1)	8.496(2)
<i>c</i> (Å)	12.001(2)	21.656(1)	22.008(2)
α (°)	103.243(2)	90	90
β (°)	110.367(2)	132.45(1)	132.07(1)
γ (°)	98.962(2)	90	90
<i>V</i> (Å ³)	1008.1(3)	4121.7(9)	4257.8(13)
<i>Z</i>	2	8	8
<i>D</i> _{calc} (mg m ⁻³)	1.849	1.860	1.851
<i>F</i> (000)	540	2224	2288
<i>U</i> (mm ⁻¹)	3.326	3.261	3.250
θ range (°)	1.9–25.4	2.5–25.00	1.80–25.00
Reflections collected	7443	17629	4352
Independent reflections	3651[0.020]	3635[0.030]	3733[0.03]
<i>R</i> _(int)			
Absorption correction	Multi-scan	Multi-scan	Psi-scan
Max/min transmission	0.6699 and 0.8673	0.3757 and 0.6564	0.955 and 0.769
Parameters refined	213	185	182
<i>R</i> (<i>F</i> _o)	0.0317	0.0310	0.0498
<i>R</i> _w (<i>F</i> _o)	0.0752	0.0775	0.1333
Largest difference peca/hole (e Å ⁻³)	0.94 and –0.75	0.80 and –1.34	1.612 and –0.958
Goodness-of-fit (GOF)	0.968	1.167	1.092

^a The high residual electron density in difference Fourier syntheses (up to $+1.61 \text{ e} \text{ \AA}^{-3}$), is in the close environment of iodine atom (0.894 Å) and can be ascribed to absorption corrections inaccuracies.

Table 2

Selected bond lengths (Å) and bond angles for $O[Si(CH_3)_2CH_2]_2TeIS_2CN(CH_2CH_2)_2$ (**1**)

Te(1)–I(1)	3.0379(7)	S(1)–Te(1)–I(1)	169.74(3)
Te(1)–S(1)	2.5164(14)	C(1)–Te(1)–I(1)	86.10(13)
Te(1)–C(1)	2.141(4)	C(2)–Te(1)–I(1)	86.99(12)
Te(1)–C(2)	2.140(3)	C(1)–Te(1)–S(1)	84.90(13)
S(1)–C(7)	1.765(5)	C(2)–Te(1)–S(1)	90.91(12)
S(2)–C(7)	1.669(5)	C(1)–Te(1)–C(2)	106.95(16)
N(1)–C(7)	1.322(7)	S(1)–C(7)–S(2)	122.8(3)
N(1)–C(8)	1.469(10)	C(7)–N(1)–C(11)	124.1(6)
N(1)–C(11)	1.477(13)	C(7)–N(1)–C(8)	124.9(6)
Si(1)–O(1)	1.619(3)	C(8)–N(1)–C(11)	111.0(7)
Si(1)–C(1)	1.877(5)	N(1)–C(7)–S(1)	113.7(4)
Si(1)–C(3)	1.839(7)	N(1)–C(7)–S(2)	123.5(4)
Si(1)–C(4)	1.838(5)	C(7)–S(1)–Te(1)	97.4(2)
Si(2)–O(1)	1.620(4)	Si(1)–O(1)–Si(2)	148.1(2)
Si(2)–C(2)	1.882(4)	O(1)–Si(1)–C(1)	109.76(19)
Si(2)–C(5)	1.843(6)	O(1)–Si(2)–C(2)	109.16(17)
Si(2)–C(6)	1.831(4)	Si(1)–C(1)–Te(1)	121.5(2)
		Si(2)–C(2)–Te(1)	120.8(2)

occupy the axial positions with angles I–Te–S of $169.74(3)^\circ$, 176.73° and 176.57° for **1**, **3** and **4**, respectively. The angle for complexes **3** and **4** are considerably higher to those observed in related compounds, Table 4.

The Te–I bonds in the range 3.008–3.038 Å are longer than in $O[Si(CH_3)_2CH_2]_2TeI_2$ [19] (2.90(1) and 2.91(1) Å), with a shortening of the Te–S bond; this behavior has been observed in $Me_2TeX[S_2CN(CH_2)_nCH_2]$ [2].

The dithiocarbamate ligands show an anisobidentate chelating coordination mode when interacting with the tellurium center. The short Te–S(1) bond distances in the three compounds cover the range 2.516(3)–2.554(2) Å at an average of 2.532 Å, comparable with the range 2.484–2.58 Å reported for R_2TeXL structures [2–7]. The long Te···S lengths range from 3.173 Å to 3.195 Å are significantly shorter than the sum of the van der Waals radii of 3.86 Å [21], with bite angles which average of 62.1° , characteristic of anisobidentate tellurium dithiocarbamates, Table 4. The carbon–sulfur bond lengths C–S(1) (average 1.762 Å), and C–S(2) (average 1.679 Å), are indicative of single and double bonds, respectively. Two different sets of nitrogen–carbon bonds are observed, the single N–C (average 1.467 Å), in the heterocycles of the dithiocarbamate ligands, are significantly longer than the exocyclic N–C (average 1.33 Å) suggesting a partial double bond character. These data are consistent with the IR data. The approximately sp^2 hybridization of the nitrogen atom is also supported by the angles surrounding the nitrogen atom, that is $\sum(C-N-C) \approx 360^\circ$.

The torsion angles of the three compounds are indicative of the boat conformation of the six-member rings, as happens in $O[Si(CH_3)_2CH_2]_2TeI_2$ [19]. The Si–O–Si angle of $148.1(2)^\circ$ for **1** is considerably higher than that observed for $O[Si(CH_3)_2CH_2]_2TeI_2$ (144.3°); however, for **3** and **4** this angle is considerably smaller (average 136.3°).

Complexes **3** and **4** consist of two molecules that are associated through intermolecular Te···S(2B) interactions 3.518(11) Å and 3.55(3) Å in **3** and **4**, respectively. Such interactions result in the formation of a dimer, then the coordination around tellurium is better described as a distorted octahedral with the lone pair apparently inactive. The S(1), S(2), I(1), C(1) and Te(1) for **3** and S(1), S(2), I(1), C(15) and Te(1) for **4** form a plane (mean deviation from plane from 0.033 and 0.026 Å for **3** and **4**, respectively). The carbon atom of the other methylene group and the sulfur atom of a neighboring molecule occupy the axial position with C–Te–S angle of 155.92° and 174.85° for **3** and **4**, respectively. A similar behavior was observed for $Me_2TeIS_2CN(CH_2CH_2)_2$ [2].

Table 3Selected bond lengths (Å) and bond angles for O[Si(CH₃)₂CH₂]₂TeI₂SCN(CH₂CH₂)₂O (**3**) and O[Si(CH₃)₂CH₂]₂TeI₂SCN(CH₂CH₂)₂S (**4**)

3		4	
Te(1)–I(1)	3.0077(5)	Te(4)–I(1)	3.0128(11)
Te(1)–S(1)	2.5531(10)	Te(4)–S(1)	2.554(2)
Te(1)–C(1)	2.137(6)	Te(4)–C(3)	2.131(9)
Te(1)–C(2)	2.139(3)	Te(4)–C(5)	2.161(15)
S(1)–C(7)	1.754(5)	S(1)–C(17)	1.769(12)
S(2)–C(7)	1.688(4)	S(2)–C(17)	1.682(10)
N(1)–C(7)	1.328(5)	N(11)–C(17)	1.341(12)
N(1)–C(8)	1.469(9)	N(11)–C(12)	1.464(9)
N(1)–C(11)	1.469(7)	N(11)–C(16)	1.475(7)
Si(1)–O(1)	1.628(4)	Si(2)–O(1)	1.624(11)
Si(1)–C(2)	1.877(5)	Si(2)–C(3)	1.886(12)
Si(1)–C(3)	1.856(5)	Si(2)–C(7)	1.856(11)
Si(1)–C(4)	1.849(5)	Si(2)–C(8)	1.853(13)
Si(2)–O(1)	1.641(3)	Si(6)–O(1)	1.642(9)
Si(2)–C(1)	1.876(5)	Si(6)–C(5)	1.870(13)
Si(2)–C(5)	1.844(5)	Si(6)–C(9)	1.874(16)
Si(2)–C(6)	1.848(7)	Si(6)–C(10)	1.844(14)
Te(1)···S(2)	3.5196(11)	Te(4)···S(2)	3.550(3)
S(1)–Te(1)–I(1)	176.73(4)	S(1)–Te(4)–I(1)	176.57(9)
C(1)–Te(1)–I(1)	90.84(9)	C(3)–Te(4)–I(1)	88.9(2)
C(2)–Te(1)–I(1)	89.04(9)	C(5)–Te(4)–I(1)	91.0(3)
C(1)–Te(1)–S(1)	86.15(9)	C(3)–Te(4)–S(1)	90.4(2)
C(2)–Te(1)–S(1)	90.31(9)	C(5)–Te(4)–S(1)	85.9(3)
C(1)–Te(1)–C(2)	101.34(18)	C(3)–Te(4)–C(5)	102.0(5)
S(1)–C(7)–S(2)	120.9(2)	S(1)–C(17)–S(2)	120.7(5)
C(7)–N(1)–C(11)	125.4(5)	C(16)–N(11)–C(17)	125.2(11)
C(7)–N(1)–C(8)	122.5(4)	C(12)–N(11)–C(17)	121.5(10)
C(8)–N(1)–C(11)	111.9(4)	C(12)–N(11)–C(16)	113.3(8)
N(1)–C(7)–S(1)	116.6(4)	N(11)–C(17)–S(1)	115.9(8)
N(1)–C(7)–S(2)	122.5(4)	N(11)–C(17)–S(2)	123.5(9)
C(7)–S(1)–Te(1)	97.8(12)	C(17)–S(1)–Te(4)	98.1(3)
Si(1)–O(1)–Si(2)	135.2(2)	Si(2)–O(1)–Si(6)	137.4(7)
O(1)–Si(2)–C(1)	108.4(2)	O(1)–Si(2)–C(3)	109.5(5)
O(1)–Si(1)–C(2)	109.36(18)	O(1)–Si(6)–C(5)	108.9(6)
Si(1)–C(2)–Te(1)	121.8(2)	Si(2)–C(3)–Te(4)	121.8(6)
Si(2)–C(1)–Te(1)	119.78(18)	Si(6)–C(5)–Te(4)	119.6(5)

4. Experimental

All reagents were of commercial grade and were used as received. The 2,2,6,6-tetramethyl-1-oxa-4-tellura-2,6-disilacyclohexane was prepared according to the method described by Al-Rubaie and coworkers [13]. Sodium salts of dithiocarbamates were prepared by methods reported in the literature [6]. IR spectra were recorded in the region 4000–500 cm⁻¹ as KBr pellets using Bruker spectrometer. The ¹H, ¹³C and ¹²⁵Te magnetic resonance spectra were obtained on a Varian Inova 400 and Varian Gemini 200 spectrometer operating at (399.99, 199.99 and 126.184, 63.118 MHz),

respectively, using CDCl₃ as solvent. The chemical shifts are relative to internal Me₄Si (¹H, ¹³C) and external 1,1-diiodotellurolane (¹²⁵Te). The FAB mass spectra were measured on a 3-nitrobenzyl alcohol support in the positive ion mode on a JEOL MStation JMS-700 instrument. Elemental analyses were obtained in an Elemental Vario El, TCD instruments.

Single crystals of **1**, **3** and **4** suitable for X-ray diffraction were obtained by diffusion using a dichloromethane-*n*-hexane mixture. Crystallographic and structure solution data are summarized in Table 1. Data collections were carried out in a Bruker APEX **1**, **3** or Siemens P4/PC **4** diffractometer at room temperature, with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$). The structures were solved by direct methods using SHELXTL program PLUS (PC version).

4.1. Preparation of dithiocarbamate derivatives of 2,2,6,6-tetramethyl-1-oxa-4,4-diiodo-4-tellura-2,6-disilacyclohexane

4.1.1. O[Si(CH₃)₂CH₂]₂TeI₂SCN(CH₂CH₂)₂ (**1**)

(CH₂CH₂)₂NCS₂Na (0.093 g, 0.553 mmol) was added to a solution of O[Si(CH₃)₂CH₂]₂TeI₂ (0.3 g, 0.553 mmol) in dried ethanol. The mixture was stirred for 24 h and then the product was filtered. The solid was dissolved in CH₂Cl₂ to remove NaI and unreacted materials. The solvent was reduced and the product was recrystallized in CH₂Cl₂/hexane. The solid was washed with *n*-hexane and dried under vacuum to yield a yellow solid (0.204, 66%), m.p. 110 °C. Anal. Calc. for C₁₁H₂₄INOS₂Si₂Te: C, 23.55; H, 4.31. Found: C, 23.63; H, 4.28%. MS (FAB+, CHCl₃, for ¹³⁰Te) *m/z*: 562 [M⁺]; 436 [M⁺–I], C₁₁H₂₄NOS₂Si₂Te⁺; 417 C₆H₁₆O₂Si₂Te⁺; 322 C₆H₁₆O₂Si₂Te⁺; 290 C₆H₁₆O₂Si₂Te⁺; 114 C₄H₈NCS⁺. IR (KBr) 2976m, 2945m, 2898m ν (C–H); 1437s δ_{as} (Si–CH₃); 1253s δ_a (Si–CH₃); 1345m δ_a (Si–CH₂); 1099m, 870m, 837s, 800s $\nu_{as/s}$ (Si–CH₃); 1064s ν (Si–O); 1460s ν (C–N); 1010m, 998m (C–S) cm⁻¹. ¹H NMR (CDCl₃): δ 0.30 (6H, s) SiCH₃; 0.41 (6H, s) SiCH₃; 2.35 (2H, d, ¹J_{HH} = 13.2 Hz); TeCH₂; 2.54 (2H, d, ¹J_{HH} = 13.6 Hz) TeCH₂; 3.78 (4H, t) NCH₂; 2.08 (4H, t) NCH₂CH₂. ¹³C NMR (CDCl₃): δ 4.08, 3.5 (Si–CH₃); 12.07 (Si–CH₂–Te); 54.40 (N–CH₂CH₂); 31.13 (N–CH₂CH₂). ¹²⁵Te NMR (CDCl₃): δ 641.5.

4.1.2. O[Si(CH₃)₂CH₂]₂TeI₂SCN(CH₂CH₂)₂ (**2**)

Following the procedure for the **1** compound (CHCH₂)₂NCS₂Na (0.092 g, 0.553 mmol) was reacted with O[Si(CH₃)₂CH₂]₂TeI₂ (0.3 g, 0.553 mmol) to yield a yellow solid (0.215 g, 70%), m.p. 127 °C. Anal. Calc. for C₁₁H₂₂INOS₂Si₂Te: C, 23.63; H, 3.97. Found C, 23.45; H, 3.70%. MS (FAB+, CHCl₃, for ¹³⁰Te) *m/z*: 560 [M⁺], 434 [M⁺–I], C₁₁H₂₂NOS₂Si₂Te⁺; 417 C₆H₁₆O₂Si₂Te⁺; 322 C₆H₁₆O₂Si₂Te⁺; 290 C₆H₁₆O₂Si₂Te⁺; 112 C₄H₆NCS⁺. IR (KBr) 2947m, 2899m, 2853w

Table 4

Bond distances (Å) and angles in some tellurium (IV) compounds

Compounds	Te–S	Te···S _a	Te···S _b	Te–X _b	X–Te–S	S–Te–S	C–Te–C	Reference
Me ₂ TeClS ₂ CNEt ₂	2.485(3)	3.151(3)		3.521(4)	170.80(1)	62.98(9)	93.7(4)	[4]
Me ₂ TeBrS ₂ CNEt ₂	2.484(2)	3.143(3)		3.597(1)	171.43(7)	63.18(8)	94.3(4)	[4]
Me ₂ TeI ₂ S ₂ CNEt ₂	2.501(3)	3.136(3)		3.746(1)	171.70(7)	63.16(8)	95.7(4)	[4]
C ₈ H ₈ TeI ₂ S ₂ CNEt ₂	2.490(2)	3.084(3)		3.698(5)	159.83(15)	63.83(5)	85.3(2)	[5]
Ph ₂ TeBrS ₂ CNEt ₂ · ½CS ₂	2.518(3)	3.183(3)	3.678(3)		169.2(1)	62.2(3)	98.7(3)	[3]
C ₄ H ₈ TeI ₂ SCN(CH ₂ CH ₂) ₂	2.550(3)	3.266(3)	3.603(3)		170.89(7)	61.6(3)	84.6(5)	[11]
Me ₂ TeClS ₂ CN(CH ₂ CH ₂) ₂	2.501(3)	3.281(3)	3.562(3)		168.05(9)	61.01(7)	96.8(4)	[2]
Me ₂ TeBrS ₂ CN(CH ₂ CH ₂) ₂	2.519(6)	3.232(7)	3.562(7)		169.0(2)	61.6(2)	98.6(9)	[2]
Me ₂ TeI ₂ SCN(CH ₂ CH ₂) ₂	2.527(4)	3.143(4)	3.497(5)		174.1(1)	63.1(1)	95.4(6)	[2]
Me ₂ TeClS ₂ CN(CH ₂ CH ₂) ₂ CH ₂	2.489(5)	3.171(5)		3.601(6)	171.2(2)	62.5(1)	94.3(8)	[2]
Me ₂ TeI ₂ SCN(CH ₂ CH ₂) ₂ CH ₂	2.514(5)	3.139(5)		3.872(4)	175.3(1)	62.5(1)	93.2(7)	[2]
O[Si(CH ₃) ₂ CH ₂] ₂ TeI ₂ SCN(CH ₂ CH ₂) ₂	2.516(14)	3.194			169.74(3)	62.44	106.9(16)	This work
O[Si(CH ₃) ₂ CH ₂] ₂ TeI ₂ SCN(CH ₂ CH ₂) ₂ O	2.553(10)	3.173	3.519(11)		176.73(4)	61.95	101.3(18)	This work
O[Si(CH ₃) ₂ CH ₂] ₂ TeI ₂ SCN(CH ₂ CH ₂) ₂ S	2.554(2)	3.182	3.55(3)		176.57(9)	61.91	102.0(5)	This work

S_a intramolecular distance S_b, X_b intermolecular distance.

ν (C–H); 1433s δ_{as} (Si–CH₃); 1252s δ_{a} (Si–CH₃); 1356m δ_{a} (Si–CH₂); 1097m, 870m, 834s, 805s $\nu_{\text{as,s}}$ (Si–CH₃); 1064s ν (Si–O); 1464s ν (C–N); 1018m, 998m (C–S) cm^{-1} . ¹H NMR (CDCl₃): δ 0.31 (6H, s) SiCH₃; 0.43 (6H, s) SiCH₃; 2.41 (2H, d, ¹J_{HH} = 12.8 Hz); TeCH₂; 2.57 (2H, d, ¹J_{HH} = 13.6 Hz) TeCH₂; 4.50 (4H, sb) NCH₂; 5.92 (2H, s) NCH₂CH. ¹³C NMR (CDCl₃): δ 4.12, 3.55 (Si–CH₃); 12.13 (Si–CH₂–Te); 60.22 (N–CH₂CH₂); 125.78 (N–CH₂CH). ¹²⁵Te NMR (CDCl₃): δ 645.

4.1.3. O[Si(CH₃)₂CH₂]₂TeI₂SCN(CH₂CH₂)₂O (3)

Following the procedure for the **1** compound O(CH₂CH₂)₂NCS₂Na (0.102 g, 0.553 mmol) was reacted with O[Si(CH₃)₂CH₂]₂TeI₂ (0.3 g, 0.553 mmol) to yield a yellow solid (0.200 g, 63%), m.p. 125 °C. Anal. Calc. for C₁₁H₂₄INO₂S₂Si₂Te: C, 22.89; H, 4.19. Found C, 22.86; H, 4.10%. MS (FAB+, CHCl₃, for ¹³⁰Te) *m/z*: 579 [M⁺]; 452 [M⁺–I], C₁₁H₂₄O₂Si₂NS₂Te⁺; 417 C₆H₁₆O₂Si₂TeI⁺; 322 C₆H₁₆O₂Si₂Te⁺; 290 C₆H₁₆O₂Si₂Te⁺; 131 C₄H₈ONCS⁺. IR (KBr) 2958m, 2922m, 2901m ν (C–H); 1425s δ_{as} (Si–CH₃); 1263s δ_{a} (Si–CH₃); 1389m δ_{a} (Si–CH₂); 1086s, 872s, 838s, 805s $\nu_{\text{as,s}}$ (Si–CH₃); 1065m ν (Si–O); 1111s ν (C–O); 1467s ν (C–N); 1008s, 998s (C–S) cm^{-1} . ¹H NMR (CDCl₃): δ 0.31 (6H, s) SiCH₃; 0.43 (6H, s) SiCH₃; 2.41 (2H, d, ¹J_{HH} = 13.2 Hz); TeCH₂; 2.58 (2H, d, ¹J_{HH} = 13.8 Hz) TeCH₂; 3.77 (4H, t) NCH₂; 4.18 (4H, t) NCH₂CH₂O. ¹³C NMR (CDCl₃): δ 4.08, 3.49 (Si–CH₃); 12.3 (Si–CH₂–Te); 51.72 (N–CH₂CH₂O); 66.45 (N–CH₂CH₂O). ¹²⁵Te NMR (CDCl₃): δ 647.

4.1.4. O[Si(CH₃)₂CH₂]₂TeI₂SCN(CH₂CH₂)₂S (4)

Following the procedure for the **1** compound S(CH₂CH₂)₂NCS₂Na (0.111 g, 0.553 mmol) was reacted with O[Si(CH₃)₂CH₂]₂TeI₂ (0.3 g, 0.553 mmol) to yield a yellow solid (0.208 g, 63%), m.p. 115 °C. Anal. Calc. for C₁₁H₂₄INOS₃Si₂Te: C, 22.27; H, 4.08. Found: C, 22.46; H, 4.11%. MS (FAB+, CHCl₃, for ¹³⁰Te) *m/z*: 594 [M⁺]; 468 [M⁺–I], C₁₁H₂₄NOS₃Si₂Te⁺; 417 C₆H₁₆O₂Si₂TeI⁺; 322 C₆H₁₆O₂Si₂Te⁺; 290 C₆H₁₆O₂Si₂Te⁺; 147 C₄H₈SNCS⁺. IR (KBr) 2949m, 2912m, 2890m ν (C–H); 1419s δ_{as} (Si–CH₃); 1252s δ_{a} (Si–CH₃); 1354w δ_{a} (Si–CH₂); 1086s, 872s, 838s, 805s $\nu_{\text{as,s}}$ (Si–CH₃); 1046m ν (Si–O); 1470s ν (C–N); 1023s, 950m (C–S) cm^{-1} . ¹H NMR (CDCl₃): δ 0.31 (6H, s) SiCH₃; 0.49 (6H, s) SiCH₃; 2.40 (2H, d, ¹J_{HH} = 14 Hz); TeCH₂; 2.58 (2H, d, ¹J_{HH} = 13.8 Hz) TeCH₂; 4.45 (4H, t) NCH₂; 2.77 (4H, t) NCH₂CH₂S. ¹³C NMR (CDCl₃): δ 4.12, 3.53 (Si–CH₃); 12.23 (Si–CH₂–Te); 54.50 (N–CH₂CH₂S); 27.84 (N–CH₂CH₂S). ¹²⁵Te NMR (CDCl₃): δ 647.8.

4.1.5. O[Si(CH₃)₂CH₂]₂TeI₂SCN(CH₂CH₂)₂CH₂ (5)

Following the procedure for the **1** compound CH₂(CH₂CH₂)₂NCS₂Na (0.100 g, 0.553 mmol) was reacted with O[Si(CH₃)₂CH₂]₂TeI₂ (0.3 g, 0.553 mmol) to yield a yellow solid (0.266 g, 83.8%), m.p. 120 °C. Anal. Calc. for C₁₂H₂₆INOS₂Si₂Te: C, 25.06; H, 4.56. Found: C, 25.43; H, 4.49. MS (FAB+, CHCl₃, for ¹³⁰Te) *m/z*: 574 [M⁺]; 450 [M⁺–I], C₁₂H₂₆NOS₂Si₂Te⁺; 417 C₆H₁₆O₂Si₂TeI⁺; 322 C₆H₁₆O₂Si₂Te⁺; 290 C₆H₁₆O₂Si₂Te⁺; 128 C₅H₁₀NCS⁺. IR (KBr) 2937s, 2890m, 2854m ν (C–H); 1438s δ_{as} (Si–CH₃); 1254s δ_{a} (Si–CH₃); 1349m δ_{a} (Si–CH₂); 1086s, 871s, 840s, 804s $\nu_{\text{as,s}}$ (Si–CH₃); 1024m ν (Si–O); 1480s ν (C–N); 1012s, 972m (C–S) cm^{-1} . ¹H NMR (CDCl₃): δ 0.312 (6H, s) SiCH₃; 0.416 (6H, s) SiCH₃; 2.48 (2H, d,

¹J_{HH} = 13.2 Hz); TeCH₂; 2.55 (2H, d, ¹J_{HH} = 13.4 Hz) TeCH₂; 4.09 (4H, sb) NCH₂; 1.70 (6H, sb) N(CH₂CH₂)₂CH₂. ¹³C NMR (CDCl₃): δ 4.35, 3.72 (Si–CH₃); 12.60 (Si–CH₂–Te); 53.34 [N(CH₂CH₂)₂CH₂]; 26.30 [N(CH₂CH₂)₂CH₂]; 23.97 [N(CH₂CH₂)₂CH₂]. ¹²⁵Te NMR (CDCl₃): δ 637.8.

Appendix A. Supplementary data

CCDC 667714, 667715 and 667716 contains the supplementary crystallographic data **1**, **3** and **4**. 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.2008.07.007.

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