Inorg. Chem. **2002**, *41*, 4739–4747

Inorganic Chemistry
Article

Conformation versus Coordination: Synthesis and Structural Investigations of Tellurium(II) Dithiolates Derived from *β*-Donor-Substituted Thiols

Holger Fleischer*,† and Dieter Schollmeyer‡

Institut für Anorganische Chemie und Analytische Chemie and Institut für Organische Chemie, Universität Mainz, Duesbergweg 10-14, D-55099 Mainz, Germany

Received April 16, 2002

New methods of preparing tellurium(II) dithiolates, Te(SR)$_2$, are presented. Te(SCH$_2$CH$_2$OAc)$_2$, **1**, was made from Te(SCH$_2$CH$_2$OH)$_2$ by acetylation of the hydroxyl groups. Te(SCH$_2$CH$_2$SAc)$_2$, **2**, [Te(SCH$_2$CH$_2$NH$_3$)$_2$]Cl$_2$, **3**, and Te(SC$_6$H$_4$(*o*-NH$_2$))$_2$, **4**, were synthesized by ligand exchange reactions of Te(S^{t}Bu)$_2$ with 2 equiv of HSCH$_2$CH$_2$SAc, [HSCH$_2$CH$_2$NH$_3$]Cl, and HSC$_6$H$_4$(*o*-NH$_2$), respectively. Of all compounds, **4** exhibits the strongest thermal sensitivity toward decomposition and the largest low-field shift of the ^{125}Te NMR signal, two features that are attributed to weak Te···N interactions. The structural parameters of the CSTeSC unit exhibit very similar values for all four compounds, while the torsion angles of the side chains differ between the molecules, a feature rationalized by ab initio studies. In the solid state, different kinds of intermolecular aggregation and contacts to the Te atoms are present. **1** and **2** crystallize in the same space group (orthorhombic, *Pbcn*) and exhibit C_2 symmetric molecules, with two intermolecular Te···S contacts, leading to a trapezoidal coordination mode of the Te atoms. SCCE and C$_S$CEC (with E = O, S) torsion angles represent the major differences between **1** and **2**, which are attributed to their unlike intermolecular hydrogen bridges. In the solid state structure of **3**, [Te(SCH$_2$CH$_2$NH$_3$)$_2$]$^{2+}$ cations and Cl$^-$ anions form a three-dimensional network via N–H···Cl and C–H···Cl hydrogen bonds (triclinic, $P\bar{1}$). Two neighboring [Te(SCH$_2$CH$_2$NH$_3$)$_2$]$^{2+}$ cations are linked via two Te···S contacts, and each Te atom forms one additional Te···Cl contact, resulting in a slightly distorted trapezoidal coordination mode. In the solid state structure of **4**, adjacent molecules form Te···Te and Te···N contacts as well as hydrogen bridges. Two chemically different Te atoms are present, both of which are tetracoordinate with distorted sawhorse configurations. The absence of intramolecular Te···O, Te···S, or Te···N contacts in **1**, **2**, and **4**, respectively, is attributed to the conformational rigidity of the CSTeS unit, where conformation ruling coordination is the case.

Introduction

Tellurium(II) dithiolates, Te(SR)$_2$ (R = alkyl, aryl) are of both chemical[1−5] and biochemical[6] interest, especially with R containing functional groups.[7] So far, tellurium(II) dithiolates have been prepared by means of reductive elimination starting from TeO$_2$ (or a tellurium(IV) tetraalkoxide) and the corresponding thiol according to eq 1.[1,2,4,7] This method

$$\mathrm{TeO_2 + 4HSR \rightarrow Te(SR)_2 + RSSR} \qquad (1)$$

suffers the drawbacks that at best 50% of the thiol are converted into the desired product, while the other half gives a disulfide whose separation from the tellurium(II) dithiolate might raise difficulties. We were thus interested in finding a new way of preparing Te(SR)$_2$, in order to get around those

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* Author to whom correspondence should be addressed. E-mail: fleische@mail.uni-mainz.de. Fax: (+)49 6131 3923351.

† Institut für Anorganische Chemie und Analytische Chemie.

‡ Institut für Organische Chemie.

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10.1021/ic020277v CCC: $22.00

disadvantages. Investigations of the molecular structures of compounds containing a $\mathrm{R{-}EE^1E^2{-}R}$ unit (E, $\mathrm{E^1}$, $\mathrm{E^2}$ = S, Se, or Te) reveal helical conformations with torsion angles $\tau(\mathrm{REE^1E^2})$ and $\tau(\mathrm{EE^1E^2R})$ close to 90° or −90°.[4,5,7,8] Recent ab initio quantum chemical studies for $\mathrm{Te(SCH_3)_2}$ showed $\mathrm{n_p(S^1){-}\sigma^*(Te{-}S^2)}$ orbital interactions to play a major role regarding the conformation.[4] Tellurium(II) dithiolates derived from β-donor-substituted thiols represent an interesting class of compounds. Intramolecular Te···X (with X = N, O, S) donor−acceptor interactions with the formation of five-membered chelating rings and hypervalent Te atoms should be feasible, a feature already found in some Se(II) and Te(II) derivatives.[9,10] We were interested in seeing whether such an interaction would occur and what impact it would have on the molecular conformation and especially on the STeSC torsion. With the present study, we report on the synthesis and the molecular and crystal structures of tellurium(II) dithiolates derived from β-donor-substituted thiols.

Results and Discussion

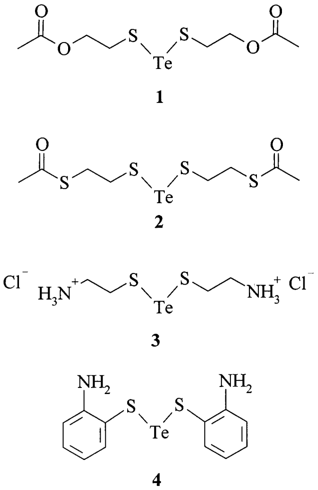

Figure 1. Structural formulas of compounds **1**−**4**.

Synthesis and Spectroscopy. The exchange of thiolate ligands between a given tellurium(II) dithiolate, $\mathrm{Te(SR^1)_2}$, and a thiol ($\mathrm{HSR^2}$) according to eq 2 offers a novel and highly efficient route to new tellurium(II) thiolates. The reactions

$$\mathrm{Te(SR^1)_2 + 2HSR^2 \rightleftharpoons Te(SR^2)_2 + 2HSR^1} \tag{2}$$

were carried out in either methanol or benzene. With $\mathrm{R^1}$ = $\mathrm{^tBu}$, the volatile *tert*-butylthiol, $\mathrm{HS^tBu}$, is formed in the course of the exchange reaction, which can easily be removed from the reaction mixture by distillation. The equilibrium (eq 2) is subsequently shifted toward the right side. After the solvent had been distilled, the product was obtained in high yields. Tellurium bis[2-(acetylthio)ethylthiolate], $\mathrm{Te[SCH_2CH_2SC(O)CH_3]_2}$, **2**, tellurium bis[(2-ammonium)-ethylthiolate] dichloride, $\mathrm{[Te(SCH_2CH_2NH_3)_2]Cl_2}$, **3**, and tellurium bis[(2-amino)phenylthiolate], $\mathrm{Te(SC_6H_4(\mathit{o}\text{-}NH_2))_2}$, **4**, could be prepared in this way (Figure 1). For tellurium bis[2-(acetoxy)ethylthiolate], $\mathrm{Te[SCH_2CH_2OC(O)CH_3]_2}$, **1**, another synthetic approach was applied. It was prepared from tellurium bis[(2-hydroxy)ethylthiolate], $\mathrm{Te(SCH_2CH_2OH)_2}$,[7] by acetylation of the hydroxyl groups. Despite being similar to **1**, **2** could not, however, be prepared in such a way since the analogous precursor, $\mathrm{Te(SCH_2CH_2SH)_2}$, is elusive,[11] and the exchange of thiolate groups with $\mathrm{Te(S^tBu)_2}$ according to reaction 2 has to be preceded by monoacetylation of the ethanedithiol. On the other hand, the preparation of **1** by reaction of $\mathrm{Te(S^tBu)_2}$ with $\mathrm{HSCH_2CH_2OAc}$, in analogy to the synthesis of **2**−**4**, is not the method of choice. This is due to the fact that preparation of $\mathrm{HSCH_2CH_2OAc}$ requires the selective O-acetylation of 2-mercaptoethanol, $\mathrm{HSCH_2CH_2OH}$, which represents a difficult task since S-acetylation is the kinetically favored reaction.[12] In the actual preparation of **1**, the acetylation of the OH group takes place after the linkage of the thiolate ligand with the Te atom. In this respect, tellurium can be regarded as a kind of “protective group” for mercaptans. At room temperature, **1**−**3** are yellow, crystalline solids, while **4** forms orange red crystals. **1** and **2** exhibit good solubility in nonpolar solvents such as petroleum ether and diethyl ether, **3** dissolves in methanol and water, as can be expected of an ionic compound, and **4** easily dissolves in benzene, methanol, and acetone. All four compounds are thermally unstable, especially in solution, with **3** being more and **4** less stable than **1** and **2**. Like $\mathrm{Te(S^iPr)_2}$, $\mathrm{Te(S^tBu)_2}$, $\mathrm{Te(SPh)_2}$, and $\mathrm{Te(SCH_2CH_2OH)_2}$, **1**−**4** are sensitive to light. As soon as their solutions are exposed to daylight, deposition of elemental tellurium on the glass surface occurs within 1 h. So as to avoid decomposition as mentioned above, the compounds were stored in a freezer at −45 °C. An attempt to prepare $\mathrm{Te(SCH_2CH_2NH_2)_2}$ from **3** by dehydrochlorination failed, since, on addition of stoichiometric amounts of aqueous NaOH to a solution of **3** in $\mathrm{H_2O}$ kept at 0 °C, elemental tellurium precipitated immediately and quantitatively. This result, as well as the increased instability of **4** compared to **1**−**3**, indicates a vital role of the N atom in view of the decomposition reaction. The higher the basicity of the N atom is, the more unstable is the tellurium(II) dithiolate, as can be anticipated by comparison of the $\mathrm{p}K_\mathrm{b}$ values of aniline, 9.38,[13] and ethyl-

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Table 1. Selected Structural Data of **1** from Single-Crystal XRD and ab Initio Geometry Optimization[a]

	XRD	ab initio		XRD	ab initio
Te1−S2	2.398(1)	239.6	S2−C3−C4	114.5(3)	114.5
Te1⋯S2a	3.388(1)		C3−C4−O5	106.5(4)	107.0
S2−C3	1.807(6)	183.7	C4−O5−C6	116.0(4)	114.7
C3−C4	1.505(7)	151.8	O5−C6−O8	122.5(4)	123.3
C4−O5	1.456(6)	144.5	O5−C6−C7	111.1(4)	110.5
O5−C6	1.340(6)	136.3	O8−C6−C7	126.4(4)	126.2
C6−O8	1.200(7)	122.4	S2#−Te1−S2−C3	77.1(2)	72.5
C6−C7	1.484(8)	150.9	Te1−S2−C3−C4	71.8(4)	73.4
S2−Te1−S2a	102.47(4)	99.1	S2−C3−C4−O5	70.8(4)	64.1
S2−Te1⋯S2#	164.69(3)		C3−C4−O5−C6	−174.0(5)	−176.2
S2#⋯Te1⋯S2#a	72.42(3)		O8−C6−O5−C4	3.5(5)	−0.8
Te1−S2−C3	102.5(2)	101.9	C7−C6−O5−C4	−177.1(5)	179.2

[a] Distances are given in angstroms, angles in degrees.

Table 2. Selected Structural Data of **2** from Single-Crystal XRD and ab Initio Geometry Optimization[a]

	XRD	ab initio		XRD	ab initio
Te1−S2	2.405(1)	239.8	S2−C3−C4	112.9(3)	112.5
Te1⋯S2#	3.402(1)		C3−C4−S5	111.7(3)	111.6
S2−C3	1.822(5)	183.8	C4−S5−C6	100.5(2)	99.0
C3−C4	1.514(6)	152.8	S5−C6−O8	122.3(4)	122.9
C4−S5	1.810(5)	182.5	S5−C6−C7	113.7(4)	113.9
S5−C6	1.778(5)	178.8	O8−C6−C7	124.0(5)	123.1
C6−O8	1.205(6)	122.9	S2a−Te1−S2−C3	74.3(2)	72.3
C6−C7	1.487(6)	151.6	Te1−S2−C3−C4	67.5(4)	73.4
S2−Te1−S2a	102.9(1)	98.8	S2−C3−C4−S5	−173.9(2)	180.0
S2−Te1⋯S2#	161.8(1)		C3−C4−S5−C6	−84.4(4)	−79.8
S2#⋯Te1⋯S2#a	66.5(3)		O8−C6−S5−C4	−1.3(6)	1.0
Te1−S2−C3	103.4(2)	102.0	C7−C6−S5−C4	179.0(4)	−177.5

[a] Distances are given in angstroms, angles in degrees.

Table 3. Selected Structural Data of **3** from Single-Crystal XRD and of the $[Te(SCH_2CH_2NH_3)_2]^{2+}$ Dication from ab Initio Geometry Optimization[a]

	XRD	ab initio		XRD	ab initio
Te1−S2	2.389(1)	240.0	Te1−S2−C3	102.3(1)	103.2
Te1−S6	2.388(1)		Te1−S6−C7	106.9(1)	
Te1⋯S2b	3.476(1)		S2−C3−C4	107.0(2)	106.4
Te1⋯Cl2	3.498(1)		S6−C7−C8	117.1(3)	
S2−C3	1.823(4)	184.6	C3−C4−N5	110.6(3)	110.4
S6−C7	1.830(4)		C7−C8−N9	112.1(3)	
C3−C4	1.505(5)	153.1	S6−Te1−S2−C3	82.7(1)	89.8
C7−C8	1.493(5)		S2−Te1−S6−C7	83.3(1)	
C4−N5	1.490(5)	152.5	Te1−S2−C3−C4	176.8(3)	152.2
C8−N9	1.490(5)		Te1−S6−C7−C8	45.3(3)	
S2−Te1−S6	98.99(3)	102.4	S2−C3−C4−N5	−180.0(2)	177.6
S6−Te1⋯S2#	174.8(1)		S6−C7−C8−N9	55.3(4)	
S2−Te1⋯Cl2	173.2(1)				

[a] Distances are given in angstroms, angles in degrees. The six different N⋯Cl distances range from 3.082(3) to 3.216(3) Å and the corresponding angles N−H⋯Cl from 152.3° to 170.5°, but they are not specified explicitly here.

amine, 3.0,[14] as a rough measure for the basicities of 2-aminophenylthiol and 2-aminoethylthiol, respectively.

The ^1H NMR signal of the $TeSCH_2$ group in **1** (3.07 ppm) is significantly low-field shifted compared to the signal of the $HSCH_2$ protons in $HOCH_2CH_2SH$ (2.52 ppm). The same trend occurs for the signal of the $TeSCH_2$ group in **2** (3.1 ppm) compared to the signal of the $HSCH_2$ protons in $HSCH_2CH_2SAc$ (2.31 ppm) or in $HSCH_2CH_2SH$ (2.13 ppm). Hence, the Te atom has a strong deshielding influence on the α-protons. The ^{125}Te NMR signals of **1**−**3** have a shift similar to $Te(SCH_2CH_2OH)_2$,[7] but are low-field shifted by approximately 200 and 350 ppm relative to the signals of $Te(S^iPr)_2$ and $Te(S^tBu)_2$, respectively.[1] The ^{125}Te NMR signal of **4** (1699.7) is significantly downfield shifted compared to that of $Te(SPh)_2$ (1582.6),[1] a fact that is presumably due to Te⋯N interactions.

Symmetric and antisymmetric Te−S vibrational stretching frequencies of **1**−**3** are slightly lower than those reported for $Te(S^iPr)_2$, $Te(S^tBu)_2$, and $Te(SPh)_2$.[4]

Molecular and Solid State Structures. **1** and **2** crystallize in the same space group, *Pbcn*, with similar cell parameters; their molecules exhibit C_2 symmetry with a trans conformation of the side chains relative to the STeS plane. The structural parameters of the CSTeSC units are similar to those found for other tellurium(II) thiolates (see Table 5). Intermolecular Te⋯S contacts are significantly shorter in **1** and **2** than in $Te(S^iPr)_2$, $Te(S^tBu)_2$, and $Te(SPh)_2$ (see Table 5), differing in their respective mode of aggregation.[4] While in $Te(S^iPr)_2$, $Te(S^tBu)_2$, and $Te(SPh)_2$ adjacent molecules are linked by centrosymmetric Te_2S_2 units leading to "zigzag" chains, each molecule of **1** and **2** forms contacts with four different neighbors, one to each S atom and two to each Te atom (see Figures 2b and 3b). Coordination of Te in **1** and **2** can be described best as trapezoidal, with $CN_{Te} = 4$ and nearly planar TeS_4 units. Nevertheless, there are considerable dissimilarities in the crystal structures of **1** and **2**, which are due to differences in the conformations of the SCH_2CH_2-OAc and SCH_2CH_2SAc chains. **1** exhibits a S2−C3−C4−O5 torsion angle of 70.8(4)°, and a C3−C4−O5−C6 torsion angle of −174.0(5)° (Table 1) ("gauche−anti conformation"). In contrast to this, **2** has got a S2−C3−C4−S5 torsion angle of −173.9(2)°, and a C3−C4−S5−C6 torsion angle of −84.4(4)° (Table 2) ("anti−gauche conformation"; see also Figures 2a and 3a).

On the other hand, there is a very good correspondence between all structural parameters of **2** and of $AcSCH_2CH_2$-SAc,[15] including the SCCS and the CCSC torsion angles.

Short C⋯O distances and C−H⋯O angles larger than 150° indicate the presence of intermolecular hydrogen bridges in the solid state structure of **1** and **2** (see Figures 2b and 3b). In both structures, hydrogen bonds from the methyl groups to the acetylic O atom are formed between two molecules, which both coordinate by one of their S atoms to the same Te atom of a third molecule. In **1**, the acetylic O atoms of this third molecule additionally act as hydrogen bridge acceptors toward one OCH_2 group of each of the other two molecules. Thus, in the case of **1** and **2**, intermolecular coordination via hydrogen bridges dominates the SCCE (with E = O, S) conformation and leads to different shapes of these similar molecules.

Compound **3** is the first ionic tellurium(II) thiolate, and the molecular structure of its cations as well as its crystal structure exhibit some interesting features. The structural parameters of the CSTeSC unit are similar to those of **1**, **2**,

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Table 4. Selected Structural Data of **4** from Single-Crystal XRD[a]

Te1−S10	2.413(1)	S2−Te1−S10	99.2(1)	S10−Te1−S2−C3	−91.1(1)
Te1−S2	2.416(1)	S22−Te2−S30	98.8(1)	S2−Te1−S10−C11	−90.6(1)
Te2−S30	2.407(1)	Te1−S2−C3	103.6(1)	S30−Te2−S22−C23	−86.4(1)
Te2−S22	2.430(1)	Te1−S10−C11	106.0(1)	S22−Te2−S30−C31	−96.4(1)
S2−C3	1.785(3)	Te2−S22−C23	102.1(1)	Te1−S2−C3−C4	−99.1(2)
S10−C11	1.774(3)	Te2−S30−C31	104.0(1)	Te1−S10−C11−C12	81.2(2)
S22−C23	1.774(3)	S10−Te1···Te2	164.3(1)	Te2−S22−C23−C24	−95.7(2)
S30−C31	1.774(3)	S22−Te2···Te1	94.1(1)	Te2−S30−C31−C32	78.2(2)
C4−N9	1.386(3)	S30−Te2···Te1	81.9(1)	S2−C3−C4−N9	4.4(3)
C12−N17	1.372(3)	S22−Te2···N9	172.5(1)	S10−C11−C12−N17	−2.1(3)
C24−N29	1.370(4)	N29#−H···Te1	173(1)	S22−C23−C24−N29	5.1(4)
C32−N37	1.359(3)			S30−C31−C32−N37	−6.4(3)
Te1···Te2	3.685(1)				
Te2···N9	3.027(2)				
Te1···N29b	4.029(3)				

[a] Distances are given in angstroms, angles in degrees. Structural parameters of the phenyl rings are not explicitly given here. C−C bond lengths range from 1.368(4) to 1.414(4) Å and C−C−C angles from 117.9(2)° to 121.3(3)°. The sum of the C−C−C angles amounts to 719.9° at least, showing the planarity of the phenyl rings; N and S atoms are virtually placed in the planes of the rings they are bound to.

Table 5. Comparison of Selected Structural Parameters of $\mathrm{Te(SR)_2}$ Compounds[a]

	$\mathrm{Te{-}S_{av}}$	$\mathrm{Te\cdots S_{av}}$	$\mathrm{Te\cdots X_{av}}$	$\mathrm{S{-}Te{-}S_{av}}$	$\mathrm{Te{-}S{-}C_{av}}$	τ(C−S−Te−S)
1	2.398(1)	3.388(1)		102.5(1)	102.5(2)	77.1(2)
2	2.405(1)	3.402(1)		102.9(1)	103.4(2)	74.3(2)
3	2.389(1)	3.476(1)	3.498(1)[b]	99.0(1)	104.6(1)	82.7(1)/83.3(1)
4[c]	2.414(1)		3.685(1)[d]	99.3(1)	104.8(1)	−90.6(1)/−91.1(1)
4[c]	2.419(1)		3.027(2)[e]	98.8(1)	103.1(1)	−86.4(1)/−96.4(1)
$\mathrm{Te(S^{\mathit{i}}Pr)_2}$[f]	2.394(1)	3.473(1)		99.6(1)	105.8(3)	77.0(2)/90.3(2)
$\mathrm{Te(S^{\mathit{t}}Bu)_2}$[f]	2.391(1)	3.680(1)		103.9(1)	107.6(1)	78.0(1)
$\mathrm{Te(SPh)_2}$[f]	2.406(2)	3.631(2)		100.1(1)	103.2(2)	69.0(3)
$\mathrm{Te(SCH_2CH_2OH)_2{\cdot}H_2O}$[g]	2.398(3)		2.495(10)[h]	101.3(1)	104.2(4)	75.4(4)/88.8(4)
$\mathrm{Te(SCPh_3)_2}$[i]	2.379(2)			110.8(1)	113.7(2)	80.2
$\mathrm{Te[SC(O)Ph]_2}$[j]	2.372			103.1		89.1

[a] Atomic distances are given in angstroms, bond and torsion angles in degrees. [b] X = Cl. [c] Structural parameters for each of the two independent molecules in the solid state are given. [d] X = Te. [e] X = N. [f] Values taken from ref 4. [g] Values taken from ref 7. [h] X = O. [i] Values taken from ref 5. [j] Values taken from ref 8c.

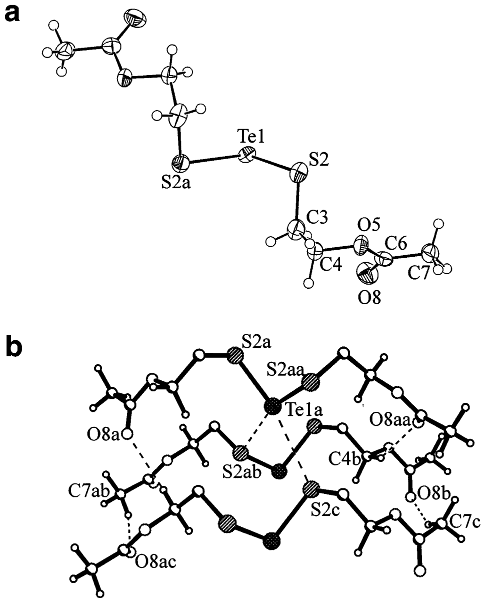

Figure 2. (a) ORTEP diagram of **1**. Displacement ellipsoids are at the 50% probability level. (b) Packing diagram of **1**.

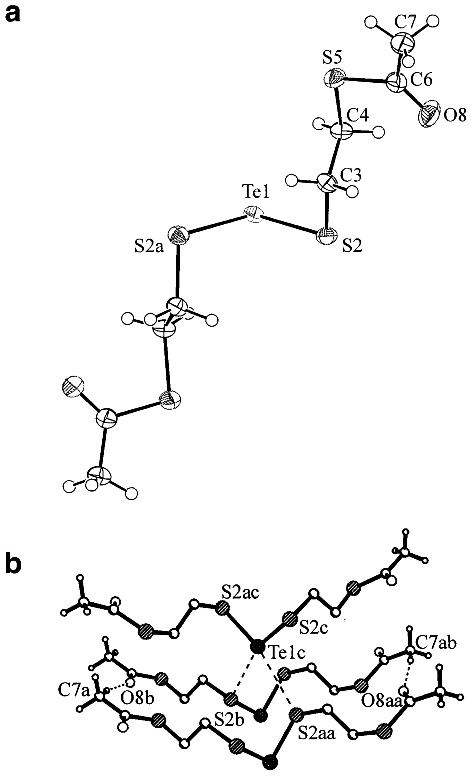

Figure 3. (a) ORTEP diagram of **2**. Displacement ellipsoids are at the 50% probability level. (b) Packing diagram of **2**.

and other tellurium(II) dithiolates (see Table 5). The TeSCC and the SCCN torsion angles in the two side chains are entirely different. While one ammoniumethylthio group exhibits anti TeSCC and anti SCCN conformations, the other one adopts gauche conformations. According to MP2/LANL2DZP geometry optimization and vibrational frequen-

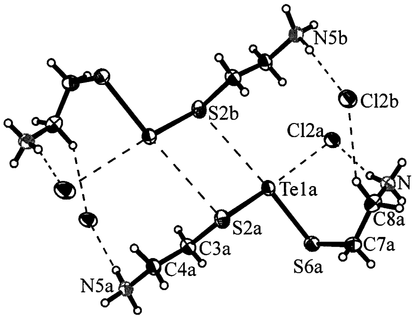

Figure 4. ORTEP diagram of two formula units of **3**. Displacement ellipsoids are at the 50% probability level.

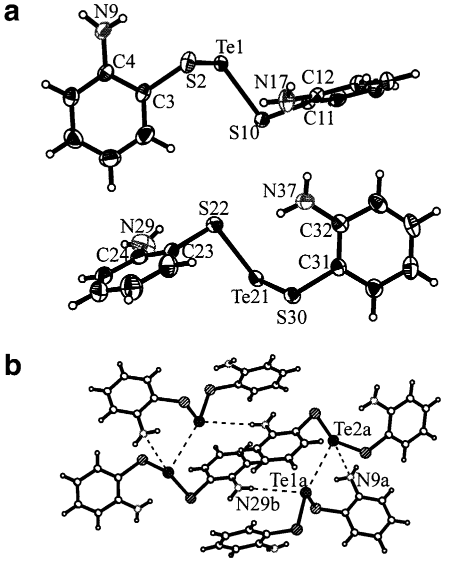

Figure 5. (a) ORTEP diagram of two formula units of **4**. Displacement ellipsoids are at the 50% probability level. (b) Packing diagram of **4**.

cies, the latter does not represent a minimum for the isolated cation. The "intramolecular" Cl^- bridge between NH_3^+ and Te is supposed to enable the gauche–gauche conformation in the solid state (see Figure 4). N–H···Cl and C–H···Cl contacts in the solid state form a three-dimensional network between the cations and the Cl^- anions. The Te atoms are tetracoordinate, by three S atoms and a Cl^- ion, and exhibit a distorted trapezoidal coordination geometry. Apart from chlorotris(*N*,*N'*-dicyclohexylthiourea-S)tellurium(II) chloride,[16] this is the only example known for a $Te(S_3Cl)$ coordination mode. It is noteworthy that two Te···S contacts link two like-charged $[Te(SCH_2CH_2NH_3)_2]^{2+}$ dications together.

In contrast to **1**–**3**, there are no Te···S interactions in the solid state structure of **4**, but rather intermolecular Te···N and Te···Te contacts (see Figure 5b and Table 4). Two different Te atoms are found in the solid state structure of **4**, Te1 and Te2, both of which are tetracoordinate with slightly distorted sawhorse structures. Te1 exhibits a $Te(S_2HTe)$ and Te2 a $Te(S_2NTe)$ coordination mode, both of which have been unknown so far. The molecules of **4** lack any symmetry (see Figure 5a), a fact that is due to the different coordination modes of the two N atoms. One acts as an electron pair donor toward a Te atom whereas the other one is involved in a hydrogen bridge (see Figure 5b). Secondary bonds, where the Te atoms act as electron pair acceptors, are trans to one of the primary Te–S bonds (Te1···Te2 and Te2···N9). Secondary bonds, where the Te atoms act as electron pair donors, are orthogonal to the TeS_2 planes of the donating Te atom (Te1···H(N29b) and Te2···Te1). The Te···N distance in **4** is comparable to the intermolecular Te···N contacts in solid $Te(NMe)_2$ (2.959(2)–2.960(2) Å),[5] but it is still significantly longer than the intramolecular Te···N bond in 8-(dimethylamino)-1-naphthyltellurium diethyldithiocarbamate (2.505(3) Å).[10] The Te···Te distance remains significantly below the sum of the van der Waals radii.[17]

Ab Initio Studies on Conformation and Intramolecular Coordination. Experimental and ab initio optimized structural parameters correspond in a reasonably good, though not excellent, way, given the fact that r_e structures of isolated molecules are compared to r_α solid state structures (see Tables 1–3). Hence, it is no surprise that the overall deviation between experiment and theory is largest for the ionic compound **3**, where the "naked" $[Te(SCH_2CH_2NH_3)_2]^{2+}$ ion was structurally optimized.

It is interesting to note that the molecular structures of **1**, **2**, and **4** in the solid state as well as the ab initio optimized molecular structures of **1** and **2** lack any intramolecular donor acceptor interactions of the Lewis-basic O, S, and N atoms with the Te atom, although such Te···E bonds (with E = O, S, N) would form favorable five-membered rings. This lack cannot be due to the absence of acceptor power of the Te atoms, since intermolecular contacts are found in the solid state of all compounds (see above). This contradicts recent findings for organochalcogen (Se(II), Te(II)) compounds derived from 1-(*N*,*N*-dimethylamino)naphthalene and *N*,*N*-dimethylbenzylamine, which represent molecules forming intramolecular Se···N and Te···N interactions.[10]

Ab initio geometry optimizations, single-point energy and thermochemical calculations, and natural bond orbital (NBO) analyses were performed to find out what might have caused the absence of these interactions. For each of the model compounds $Te(SCH_2CH_2EH_n)_2$ [with E = N ($n = 2$), O ($n = 1$), S ($n = 1$); C_2 symmetry] two different conformations were optimized (see Figure 6), one with two short Te···E-distances and nearly planar, five-membered TeSCCE rings [$\tau(STeSC) = 180.0°$], such that each Te···E bond occupies the position trans to a Te–S bond (trapezoidal $Te(S_2E_2)$ coordination). In the second conformation, starting structures with torsion angles S6–Te1–S2–C3, Te1–S2–C3–C4, and S2–C3–C4-E of 90.0°, 180.0°, and 180.0°, respectively, were applied, such that no Te···E interactions were present (see Figure 6 for the numbering of the atoms). Whereas the torsion angles in the second conformation remained close to their starting values, the optimized structures with short Te···E distances differed depending on E more or less from the starting structures (see Figure 6). Differences between conformations with and without Te···E bonds must be due

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(16) Husebye, S.; Törnroos, K. W.; Zhu, H. *Acta Crystallogr.* **2001**, *C57*, 854–856.

(17) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441–451.

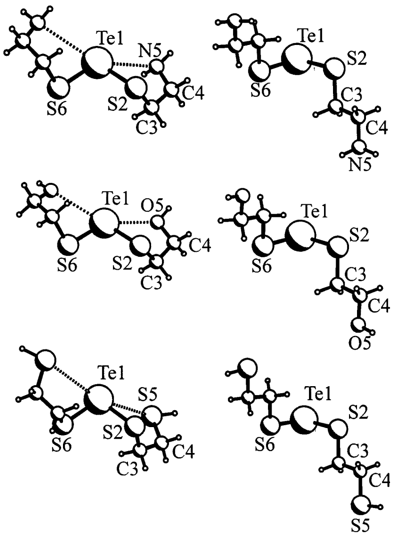

Figure 6. Ab initio molecular structures of $Te(SCH_2CH_2NH_2)_2$ (top), $Te(SCH_2CH_2OH)_2$ (middle), and $Te(SCH_2CH_2SH)_2$ (bottom), with (left) and without (right) intramolecular Te···E bonds.

Table 6. Selected ab Initio Structural Parameters (Internuclear Distances in Å, Bond and Torsion Angles in deg), $n_p(S)-\sigma^*(Te-S)$ and $n(X)-\sigma^*(Te-S)$ Energies of Interaction and Thermochemical Data (in $kJ \cdot mol^{-1}$) of the Model Compounds $Te(SCH_2CH_2EH_n)_2$ [with E = N (n = 2), O (n = 1), S (n = 1); C_2 symmetry] with and without an Intramolecular Te···E Bond (See Figure 6)[a]

	$Te(SCH_2CH_2NH_2)_2$ with Te···N bond	$Te(SCH_2CH_2OH)_2$ with Te···O bond	$Te(SCH_2CH_2SH)_2$ with Te···S bond
Te1−S2	2.444	2.415	2.397
Te1···E	2.959	3.152	3.723
S2−Te1−S6	93.0	97.6	100.7
S6−Te1···E	161.3	153.6	136.5
S6−Te1−S2−C3	135.7	119.4	94.0
Te1−S2−C3−C4	71.2	79.6	92.1
S2−C3−C4−X	−63.1	−63.4	−71.2
$n_p(S)-\sigma^*(Te-S)$[b]	31	52	80
$n(E)-\sigma^*(Te-S)$[b]	91	31	14
ΔH^{298} [c]	−14	−3	+14

	$Te(SCH_2CH_2NH_2)_2$ without Te···N bond	$Te(SCH_2CH_2OH)_2$ without Te···O bond	$Te(SCH_2CH_2SH)_2$ without Te···S bond
Te1−S2	2.393	2.392	2.417
S2−Te1−S6	99.9	100.1	103.5
S6−Te1−S2−C3	76.2	76.1	81.2
Te1−S2−C3−C4	−178.4	−178.9	176.9
S2−C3−C4−X	−179.3	179.9	179.6
$n_p(S)-\sigma^*(Te-S)$[b]	76	77	76

[a] E = N5, O5, and S5 for $Te(SCH_2CH_2NH_2)_2$, $Te(SCH_2CH_2OH)_2$, and $Te(SCH_2CH_2SH)_2$. [b] Sum of both interactions per molecule. [c] $\Delta H^{298} = H^{298}$(with Te···E bond) − H^{298}(without Te···E bond).

to these interactions, i.e., the more distinct the two with the same E are, the stronger is the Te···E bond. The order E = N > O > S for the strength of the Te···E bond follows from the data given in Table 6. Especially the S−Te−S−C torsion angle decreases in the same sequence. Tellurium(II) dithiolates, which are thermodynamically unstable, receive part of their kinetic stability from the $n_p(S^1)-\sigma^*(Te-S^2)$ orbital interaction, which reaches a maximum for S−Te−S−C torsion angles of +90° or −90°.[4,7] The increase of the S−Te−S−C torsion angles beyond 90°, enforced by the Te···E interaction, thus leads to a decrease of the kinetic stability of the tellurium(II) dithiolates. With E = N, the conformation with Te···E interaction is *thermodynamically* significantly more stable than the conformation without such an interaction, but it is *kinetically* destabilized. This result explains why $Te(SCH_2CH_2NH_2)_2$, formed by dehydrochlorination from **3**, is decomposed immediately after its formation (vide infra). With E = O, both conformations exhibit nearly the same thermodynamic stability, and with E = S, the conformation with Te···E interaction is less stable than the one that lacks such an interaction. Thus, **1** and **2** are kinetically more stable than $Te(SCH_2CH_2NH_2)_2$ and, in the solid state, two inter- rather than intramolecular Te···E bonds (with E = O, S) are formed to each Te atom.

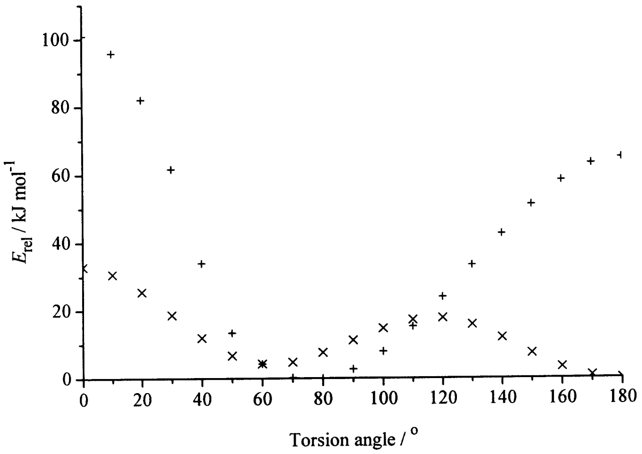

Figure 7. MP2/LANL2DZP potential energy as a function of the STeSC torsion of $Te(SCH_3)_2$ (+) and of the SCCS torsion of $HSCH_2CH_2SH$ (×).

In order to investigate the molecular rigidity of the tellurium(II) dithiolates in terms of STeSC and SCCE torsion angles, MP2/LANL2DZP potential energy surface scans for these torsion angles of the model compounds $Te(SCH_3)_2$ and $HSCH_2CH_2SH$ were performed. Plots of the relative energies vs the torsion angles are shown in Figure 7. Ranging from 0° to 180°, there is only a single energy minimum for the STeSC torsion at $\tau = 80°$, but there are two energy minima for the SCCS torsion, the anti conformation ($\tau = 180°$) being about 5 kJ mol^{-1} lower in energy than the gauche conformation ($\tau = 60°$). Data in Figure 7 clearly shows that a planar TeSCCE five-membered ring and a STeSC torsion angle of 180°, i.e., the starting values for the above-discussed model compounds $Te(SCH_2CH_2EH_n)_2$, are far from the minima of the potenial energy surface (PES). The energy for a conformation of $HSCH_2CH_2SH$ with τ(SCCS) = 0° exceeds the one with τ(SCCS) = 60° by approximately 30 kJ mol^{-1}, and the energy for a conformation of $Te(SCH_3)_2$ with τ(STeSC) = 180° surpasses the one with τ(STeSC) = 80° by nearly 65 kJ mol^{-1}.

The SCCS torsion angle is much floppier than the STeSC torsion angle, with only a small difference between anti and gauche conformations (see above). In the solid state, slight differences in packing might suffice to get the gauche conformation in one case and the anti conformation in the other. Hence, the molecular structures of **1** and **2**, in which SCCO and SCCS units, respectively, are present, were investigated in detail by means of ab initio geometry optimizations. Their molecular structures as found in the solid, i.e., the gauche−anti conformation of **1** and the anti−

gauche conformation of **2** (see above) represent minima on the PES of the respective isolated molecules. Subsequently, two further geometry optimizations were performed, with **1** having the anti−gauche conformation and **2** the gauche−anti conformation as initial structures. **1** retained the anti−gauche conformation, with a S2−C3−C4−O5 torsion angle of 175.1° and a C3−C4−O5−C6 torsion angle of 81.3°. The energy of the anti−gauche conformation is 6.0 kJ mol^{-1} below that of the gauche−anti conformation. Thus, the gauche−anti conformation found in the solid state must be stabilized by the hydrogen bridges. **2** adopted a gauche−gauche conformation with a S2−C3−C4−S5 torsion angle of −69.5° and a C3−C4−S5−C6 torsion angle of −78.1°. The energy of the gauche−gauche conformation exceeds that of the anti−gauche conformation by 8.5 kJ mol^{-1}, corresponding to the energy difference of the gauche and anti conformations of $HSCH_2CH_2SH$. Hence, different from what is found for **1**, the gauche−anti conformation does not represent a minimum on the PES of **2**, and the conformation found in the solid state represents the more stable one.

Conclusion

The preparation of tellurium(II) thiolates, $Te(SR)_2$, from $Te(SR')_2$ and HSR by exchange of thiolate ligands offers a new and straightforward approach. In some respects, it is superior to the reductive elimination method using a Te^{IV} compound and HSR.

The tellurium atom acts strongly deshielding on the α-protons in $Te(SR)_2$, as can be seen in the ^1H NMR, while the substitution pattern of the α-C atom has a great impact on the chemical shift of the ^{125}Te NMR signal.

Among different tellurium(II) thiolates, the structural parameters of the CSTeSC unit are very similar while the way in which $Te(SR)_2$ associate in the solid state largely depends on R. The absence of intramolecular Te···E contacts in **1**, **2**, and **4** is due to the rigidity of the STeSC conformation, and only intermolecular coordination of the Te atoms is found. Thus, tellurium(II) dithiolates derived from β-donor substituted thiols represent a case of conformation dominating coordination. On the other hand, the SCCE conformation is floppier than the STeSC conformation. Hence, the conformational flexibility around the S−C and C−C bonds enables intermolecular hydrogen bridges as well as the intramolecular N−H···Cl···Te connection in **3**.

Experimental Section

General Procedures. All procedures were carried out under an inert gas atmosphere or in a vacuum. Solvents were purified according to standard procedures. As far as it was possible, exposure of the tellurium dithiolates to daylight was avoided. $Te(S^tBu)_2$[4] and $HSCH_2CH_2SC(O)CH_3$[18] were prepared according to literature procedure. Due to their thermal instability, the tellurium(II) thiolates were stored at −40 °C.

NMR: Bruker DRX 400, $B_1(^1H) = 400.0$, $B_1(^{13}C) = 100.577$, $B_1(^{125}Te) = 126.387$ MHz. Standard: TMS (^1H, ^{13}C) and $Te(CH_3)_2$ (^{125}Te). IR: Mattson Galaxy 2030 FTIR, resolution 4 cm^{-1}, CsI pellets, range 4000−200 cm^{-1}. MS: Finnigan MAT 8230, EI, 70 eV. CHNS analysis was performed with an Elemental Vario EL2.

Preparation of Tellurium Bis(2-hydroxyethylthiolate), $Te(SCH_2CH_2OH)_2$. $Te(SCH_2CH_2OH)_2$ was prepared differently from the recently reported procedure.[7] Tellurium bis(*tert*-butylthiolate), $Te(S^tBu)_2$ (4.19 g, 13.7 mmol), and 2-mercaptoethanol, $HSCH_2CH_2OH$ (2.23 g, 28.5 mmol), were dissolved in 20 mL of THF. The orange-yellow solution was stirred and heated to reflux for 30 min; then THF and *tert*-butylmercaptan were distilled at normal pressure. The residue was dissolved in methanol and the solution filtered from small amounts of elemental tellurium that had been formed during the reaction. On addition of petroleum ether and by means of cooling to −45 °C, $Te(SCH_2CH_2OH)_2$ precipitated as a yellow solid and was separated by filtration and dried in vacuo. Yield: 3.34 (86.5%). The product was identified by its melting point and its purity checked by ^1H NMR spectroscopy.

Preparation of Tellurium Bis(2-acetoxyethylthiolate), $Te[SCH_2CH_2OC(O)CH_3]_2$, 1. First acetyl chloride (0.50 g, 6.3 mmol) and then pyridine (0.50 g, 6.3 mmol) were added to a stirred solution of tellurium bis[(2-hydroxy)ethylthiolate], $Te(SCH_2CH_2OH)_2$ (0.60 g, 2.1 mmol), in 30 mL of diethyl ether kept at −78 °C and protected against light. The orange-yellow solution was slowly warmed to room temperature and filtered from small amounts of tellurium. The solution was concentrated in vacuo, and 5 mL of ethyl acetate was added. From this solution, **1** precipitated at −45 °C and was dried in vacuo. Yield: 0.35 g (46%). Single crystals of **1** suitable for X-ray diffraction were obtained from the precipitate. Mp 55−56 °C. Anal. Calcd for $C_8H_{14}O_4S_2Te$ (fw = 365.92 g mol^{-1}): C, 26.26; H, 3.86; S, 17.52. Found: C, 26.71; H, 4.14; S, 16.80. MS: 368 [M^+, 8.8%], 238 [$(SCH_2CH_2OC(O)CH_3)_2^+$, 9.3%], 87 [$CH_2CH_2OC(O)CH_3^+$, 100%]. ^1H NMR (C_6D_6): 4.15 (t, $^3J = 6.6$ Hz, 2H, $-OCH_2-$); 3.07 (t, $^3J = 6.6$ Hz, 2H, $-SCH_2-$); 1.69 (s, 3H, CH_3). ^{13}C NMR (C_6D_6): 64.4 ($-OCH_2-$), 36.8($-SCH_2-$), 19.9 (CH_3).[19] ^{125}Te NMR (C_6D_6): 1282.8. IR: 2949 (m, $\nu_{as}(CH_3)$), 2925 (s, $\nu_s(CH_3)$), 2855 (m, $\nu(CH_2)$), 1732 (vs, $\nu(C{=}O)$), 1459 (m, $\delta_{as}(CH_3)$), 1432 (m, $\delta_{as}(CH_3)$), 1404 (m, $\delta_{wag}(CH_2)$), 1386 (s, $\delta_s(CH_3)$), 1364 (m), 1279 (s), 1251 (vs, $\nu_{as}(C(O)-O)$), 1071 (s, $\nu_{as}(H_2C-O)$), 986 (m, $\nu(H_3C-C)$, 934 (m), 800 (m), 634 (m, $\nu_{as}(S-C)$), 610 (m, $\nu_s(S-C)$), 467 (w), 420 (w), 327 (m, $\nu_s(Te-S)$), 305 (w, $\nu_{as}(Te-S)$), 221 (w, $\delta(TeS_2)$).

Preparation of Tellurium Bis(2-acetylthioethylthiolate), $Te[SCH_2CH_2SC(O)CH_3]_2$, 2. **2** was prepared in a procedure similar to the one applied for $Te(SCH_2CH_2OH)_2$, using tellurium bis(*tert*-butylthiolate), $Te(S^tBu)_2$ (3.50 g, 11.4 mmol), 1,2-dithioglycol monoacetate, $HSCH_2CH_2SC(O)CH_3$ (3.19 g, 23.4 mmol), 25 mL of benzene as solvent, and THF to extract the residue. Yield: 3.84 g (84.6%). Single crystals of **2** suitable for X-ray diffraction were obtained by slowly cooling a solution of **2** in toluene from room temperature to −45 °C. Mp 69−70 °C. Anal. Calcd for $C_8H_{14}O_2S_4Te$ (fw = 398.04 g mol^{-1}): C, 24.14; H, 3.54; S, 32.22. Found: C, 24.04; H, 3.59; S, 31.94. MS: 400 [M^+, 50.9%], 357 [$(M - C(O)CH_3)^+$, 14.6%], 222 [$(TeSCH_2CH_2S-)^+$, 13.5%], 103 [$CH_2CH_2SC(O)CH_3$, 100%]. ^1H NMR (C_6D_6): 3.1 (m, 4H, $-TeSCH_2CH_2S-$); 1.86 (s, 3H, CH_3). ^{13}C NMR (C_6D_6): 193.4 ($-C(O)CH_3$), 37.9 [$-C(O)SCH_2-$], 31.6 ($TeSCH_2-$), 29.6 (CH_3). ^{125}Te NMR (C_6D_6): 1246.5. IR: 2971 (w, $\nu_{as}(CH_3)$), 2926 (m, $\nu_s(CH_3)$), 2854 (vw, $\nu(CH_2)$), 1687 (vs, $\nu(C{=}O)$), 1428 (s, $\delta_{as}(CH_3)$), 1417 (s, $\delta_{as}(CH_3)$) 1396 (sh, $\delta_{wag}(CH_2)$), 1355 (s), 1270 (w), 1202 (s), 1140 (vs), 1105 (s), 1000 (sh), 974 (s, $\nu(H_3C-C)$, 930 (m), 801 (w, broad), 747 (w, $\nu(C(O)-S)$), 725 (m, $\nu(C(O)-S)$), 686 (m,

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[18] Wiesler, W. T.; Caruthers, M. H.; Marvin, H. *J. Org. Chem.* **1996**, *61*, 4272−4281.

[19] ^{13}C NMR signal for $-C(O)CH_3$ in **1** was not observed.

Table 7. Crystal Data for Compounds **1**−**3**[a]

	1	**2**	**3**	**4**
empirical formula	$C_8H_{14}O_4S_2Te$	$C_8H_{14}O_2S_4Te$	$C_4H_{14}Cl_2N_2S_2Te$	$C_{12}H_{12}N_2S_2Te$
fw/g mol^{-1}	365.92	398.03	352.79	375.96
cryst syst	orthorhombic	orthorhombic	triclinic	monoclinic
space group	*Pbcn*	*Pbcn*	$P\bar{1}$	$P2_1/n$
Z	4	4	2	8
temp/K	183	183	183	186
ρ_{calcd}/g cm^{-3}	1.871	1.859	1.909	1.816
μ/cm^{-1} [b]	26.0	26.6	31.5	24.5
F(000)	712	776	340	1456
cryst size/mm^3	0.05 × 0.13 × 0.24	0.025 × 0.2 × 0.49	0.035 × 0.08 × 0.305	0.166 × 0.226 × 0.235
θ range/deg	$2.0 < \theta < 28.3$	$2.0 < \theta < 28.2$	$2.0 < \theta < 28.3$	$2.0 < \theta < 28.3$
limiting indices	$6 \geq h \geq -6$, $11 \geq k \geq -11$, $39 \geq l \geq -39$	$6 \geq h \geq -6$, $11 \geq k \geq -11$, $42 \geq l \geq -42$	$6 \geq h \geq -6$, $14 \geq k \geq -14$, $16 \geq l \geq -16$	$13 \geq h \geq -13$, $25 \geq k \geq -25$, $18 \geq l \geq -18$
a/Å	5.2006(6)	5.1470(5)	4.8378(5)	10.2853(2)
b/Å	8.4710(10)	8.6904(5)	11.0918(12)	19.0645(3)
c/Å	29.479(3)	31.7950(18)	12.7061(14)	14.0781(3)
α/deg	90.0	90.0	114.478(2)	90.0
β/deg	90.0	90.0	96.877(2)	94.839(1)
γ/deg	90.0	90.0	91.624(2)	90.0
V/Å^3	1298.7(4)	1422.2(3)	613.8(2)	2750.6(2)
reflns measd	10945	13044	5647	20388
unique reflns	1607	1768	2963	6802
reflns $\|F\| > 4\sigma(F)$	1075	1372	2495	5742
$R\ [\|F\| > 4\sigma(F)]$[c]	0.036	0.040	0.030	0.0263
GOF on F^2	1.059	1.163	1.034	1.008
largest diff peak and hole/e Å^{-3}	−1.81/0.96	−2.65/0.85	−1.20/1.15	−1.94/0.84

[a] Mo Kα radiation with $\lambda = 0.71069$ Å was used. [b] Absorption correction with MULABS.[22] [c] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

ν_{as}(S−CH$_2$)), 630 (s, ν_s(S−CH$_2$)), 531 (w), 331 (m, ν_s(Te−S)), 284 (s, ν_{as}(Te−S)), 234 (m, δ(TeS$_2$)).

Preparation of Tellurium Bis(2-ammoniumethylthiolate) Dichloride, [Te(SCH$_2$CH$_2$NH$_3$)$_2$]Cl$_2$, 3. Tellurium bis(*tert*-butylthiolate), Te(S^{t}Bu)$_2$, (0.69 g, 2.3 mmol) and 2-mercaptoethylammonium chloride, HSCH$_2$CH$_2$NH$_3$Cl, (0.53 g, 4.7 mmol) were dissolved in 30 mL of methanol. The yellow solution was stirred and heated to reflux for 30 min, and then the solvent and *tert*-butylmercaptan were distilled under a slight vacuum. The remaining yellow solid was extracted three times with 5 mL of methanol. From the extract, the product precipitated at −20 °C and was filtered off and dried in vacuo. Yield: 0.72 g (88%). Single crystals of **3** suitable for X-ray diffraction were obtained by slowly condensing petroleum ether at room temperature into a saturated solution of **3** in methanol. Dec 80−85 °C. Anal. Calcd for $C_4H_{14}Cl_2N_2S_2Te$ (fw = 352.79 g mol^{-1}): C, 13.62; H, 4.00; N, 7.94; S, 18.17. Found: C, 13.63; H, 4.15; N, 8.14; S, 18.25. ^{1}H NMR (DMSO-*d*$_6$): 8.17 (broad s, 3H, N*H*$_3$), 3.23 (m, 2H, NC*H*$_2$), 3.01 (m, 2H, SC*H*$_2$). ^{13}C NMR (CD$_3$OD): 40.6 (N*C*H$_2$), 33.9 (−S*C*H$_2$−). ^{125}Te NMR (CD$_3$OD): 1274.2. IR: 3000 (vs, broad ν(NH$_3^+$)), 2961 (sh, ν(CH$_2$)), 2950 (sh, ν(CH$_2$)), 2915 (vs, ν(CH$_2$)), 2836 (sh, ν(CH$_2$)), 1599 (s, δ(NH$_3^+$)), 1507 (s, δ(NH$_3^+$)), 1462 (m, δ(CH$_2$)), 1439 (m, δ(CH$_2$)), 1413 (m, δ(CH$_2$)), 1381 (w, δ(CH$_2$)), 1334 (w, δ(CH$_2$)), 1257 (m, δ(CH$_2$)), 1233 (m, δ(CH$_2$)), 1142 (m, ν(N−C)), 1096 (m), 941 (m), 805 (m, ν(S−C)), 776 (w, ν(S−C)), 404 (s), 342 (s, ν_s(Te−S)), 288 (m, ν_{as}(Te−S)), 248 (m, δ(Te−S)).

Preparation of Tellurium Bis[(2-amino)phenylthiolate], Te(SC$_6$H$_4$(*o*-NH$_2$))$_2$, 4. Tellurium bis(*tert*butylthiolate), Te(S^{t}Bu)$_2$ (2.19 g, 7.2 mmol), and 2-aminothiophenol, HSC$_6$H$_4$(*o*-NH$_2$) (1.92 g, 15.3 mmol), were dissolved in 20 mL of benzene. The red solution was protected against light and stirred and heated under reduced pressure in order to distill the solvent and *tert*-butylmercaptan. During the reaction, the solution turned black and substantial amounts of elemental tellurium were formed. The residue was several times extracted with small amounts of toluene. From these combined solutions, red crystals precipitated at −45 °C, which were dried in vacuo. Yield: 1.34 g (49.9%). Dec 70−73 °C. Anal. Calcd for $C_{12}H_{12}N_2S_2Te$ (fw = 375.96 g mol^{-1}): C, 38.34; H, 3.22; N, 7.45; S, 17.05. Found: C, 38.93; H, 2.25; N, 7.54; S, 17.00. ^{1}H NMR (C$_6$D$_6$) 7.55 (d, ^3J = 8.0 Hz, 1H, *H*^{6}), 6.92 (t, ^3J = 7.6 Hz, 1H, *H*^{5}), 6.59 (t, ^3J = 8.0 Hz, 1H, *H*^{4}), 6.31 (d, ^3J = 8.2 Hz, 1H, *H*^{3}), 3.85 (broad s, 2H, N*H*$_2$). ^{13}C NMR (C$_6$D$_6$): 148.7, 136.0, 130.4, 118.4, 118.1, 114.8. ^{125}Te NMR (C$_6$D$_6$): 1699.7.

Crystal Structure Determination. Diffraction experiments were performed on a BRUKER Nonius CCD diffractometer. The crystal structures were solved by direct methods and difference Fourier techniques (SIR-92);[20] structural refinement was against F^2 (SHELXL-97).[21] Details of the crystal structure determination of compounds **1**−**4**, and their crystal data are given in Table 7.

Theoretical Methods. The ab initio calculations were performed on various servers of the Zentrum für Datenverarbeitung, Universität Mainz, using the GAUSSIAN94 software package.[23] Geometry optimization, calculation of vibrational frequencies, and an analysis of the electronic structure in terms of natural orbitals[24] were performed at the Hartree−Fock level (HF), followed by second-order Møller Plesset perturbation theory (MP2), with an effective

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core double-ζ valence basis set according to Hay and Wadt [25] augmented by appropriate polarization functions for Te, S (with exponents according to Höllwarth et al. [26]), N (exponent 0.80), and C (exponent 0.75), the basis set being designated as LANL2DZP. For all molecules $Te(SR)_2$ investigated, C_2 symmetry was enforced. Only MP2/LANL2DZP structures, energies, and enthalpies are presented.

Acknowledgment. We would like to thank Mrs. Sandra Hennig for performing the diffraction experiments and the Emil und Paul Müller-Gedächtnisstiftung for financial support.

Supporting Information Available: X-ray crystallographic files in CIF format for all structures presented. This material is available free of charge via the Internet at http://pubs.acs.org.

IC020277V

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