2786 *Inorg. Chem.* **1998,** *37,* 2786−2791

Plasticity of Cl−Te−Cl Fragments. Synthesis, Single-Crystal X-ray, and NBO Study of (1-Thia-2-tellura-1-phenyl-4-chloro)cyclopentane 2,2,2-Trichloride

Markku R. Sundberg,[†] **Tarja Laitalainen,**[‡] **Jan Bergman,***[,§] **Rolf Uggla,**[†]
Jorma Matikainen,[‡] **and Seppo Kaltia**[‡]

Department of Chemistry, Laboratories of Inorganic Chemistry and Organic Chemistry, P.O. Box 55, FIN-00014 University of Helsinki, Finland, and Department of Organic Chemistry, CNT, NOVUM, S-14157 Huddinge, Sweden

Received April 9, 1997

Tellurium tetrachloride and allylphenyl sulfide react to form (1-thia-2-tellura-1-phenyl-4-chloro)cyclopentane 2,2,2-trichloride. The crystal and molecular structure were determined by single-crystal X-ray techniques. The crystals belong to the monoclinic system, space group $P2_1/c$ (No. 14) with $a = 6.020(3)$ Å, $b = 11.46(1)$ Å, $c = 20.156(2)$ Å, $\beta = 97.53(2)°$, $V = 1379(1)$ Å^3, and $Z = 4$. The structure was refined to the final R value of 0.036. The coordination around Te^{IV} is distorted ψ octahedral with three Cl atoms in the equatorial positions. The axial Te(1)−C(1) bond opposite to the lone pair of electrons at the Te^{IV} atom completes the coordination polyhedron. The intramolecular Te−S distance is 2.903(3) Å. Symmetric and asymmetric deformation modes were established to describe the plasticity of the Cl−Te−Cl fragments extracted from the Cambridge Structural Database. The hypervalency of Te^{IV} manifests itself as plasticity in the equatorial plane of the coordination sphere. The NBO calculations show that all of the equatorial Te−Cl bonds are highly polarized and the electrons reside mainly on the Cl atoms.

Introduction

Plasticity of coordination sphere is a well-established concept in transition metal chemistry.[1] It is also well-known that many of the nontransition elements may form hypervalent compounds. The usual approach to hypervalent bonding utilizes 3c−4e bonding in terms of the VSEPR model.[2] In a recent article Barton et al. discussed qualitatively the unusual attractive interactions between Se and O atoms in selenoiminoquinones in terms of the VSEPR model.[3] More recently, the sensitivity of equatorial bonds in intermolecular interactions in ammonium trichloro(ethane-1,2-diolato-*O*,*O′*)tellurate(IV) (**2**, Figure 1) was elucidated by ab initio methods.[4] The variation in the equatorial Te−O and opposite Te−Cl bond lengths showed significant variation between **2** and the corresponding tetraphenylphosphonium salt,[5] where the intermolecular distance was longer. In general, strong closed-shell interactions have been reviewed in detail by Pyykkö.[6]

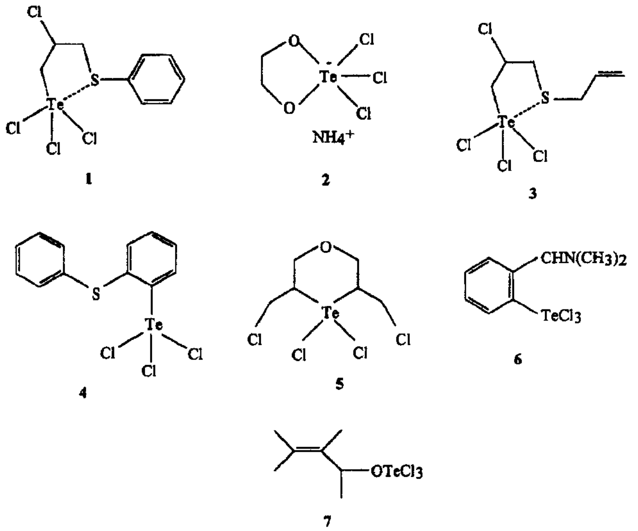

Figure 1. Relevant tellurium compounds **1**−**7** discussed in the article.

To study further the plasticity of the equatorial bonding in Te(IV) compounds, we synthesized a new compound (**3**) where sulfur replaces the equatorial oxygen.[7] NBO analyses were also carried out for **3**, but the calculations were made at the HF/LANL1DZ level of theory with no polarization for the d orbitals. The Te−S bond in **3** was designated as a coordination bond on the basis of the NBO analyses. The structure of **3** was previously assigned by Migalina et al. as an S-analogue of **5**.[8,9] The authors have claimed the preparation of the S-analogue of **3** from *in situ*-generated TeCl$_4$ and diallyl sulfide. We repeated

---

[†] Laboratory of Inorganic Chemistry, University of Helsinki.
[‡] Laboratory of Organic Chemistry, University of Helsinki.
[§] NOVUM.

(1) (a) Gazo, J.; Bersuker, I. B.; Garaj, J.; Kabesova, M.; Kohout, J.; Langfelderova, H.; Melnik, M.; Serator, M.; Valach, F. *Coord. Chem. Rev.* **1976**, *19*, 253. (b) Valach, F.; Ondracek, J.; Melnik, M. *Crystallographic Statistics in Chemical Physics*; Inorganic Chemistry Concepts; Springer-Verlag: Berlin, 1988.
(2) Gillespie, R. J.; Hargittai, I. *The VSEPR Model of Molecular Geometry*; Allyn and Bacon: Boston, MA, 1991.
(3) Barton, D. H. R.; Hall, M. B.; Lin, Z.; Parekh I.; Reibenspies, J. *J. Am. Chem. Soc.* **1993**, *115*, 5056.
(4) Sundberg, M. R.; Uggla, R.; Laitalainen, T.; Bergman, J. *J. Chem. Soc., Dalton Trans.* **1994**, 3279.
(5) Buscher, K.; Heuer, S.; Krebs, B. *Z. Naturforsch.* **1981**, *36B*, 307.
(6) Pyykkö, P. *Chem. Rev.* **1997**, *97*, 597.
(7) Bergman, J.; Laitalainen, T.; Sundberg, M. R.; Uggla, R.; Kivekäs, R., *Polyhedron*, in print.
(8) Migalina, Yu. V.; Balog, I. M.; Lendel, V. G.; Koz'min, A. S.; Zefirov, N. S. *Khim. Geterotsikl. Soedin.* **1978**, 1212.
(9) Migalina, Yu, V.; Staninets, V. G.; Lendel, V. G.; Balog, I. M.; Palyulin, V. A.; Koz'min, A. S.; Zefirov, N. S. *Khim. Geterotsikl. Soedin.* **1977**, 58.

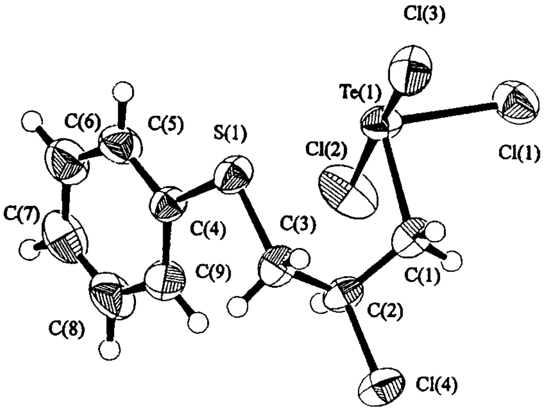

Figure 2. ORTEP drawing of (1-thia-2-tellura-1-phenyl-4-chloro)-cyclopentane 2,2,2-trichloride showing the numbering scheme (**1**). The thermal ellipsoids are drawn at the 50% probability level.

the experiment with $TeCl_4$ in acetonitrile, and instead of the S-analogue of **2**, a monoalkylation reaction by Markovnikov regiochemistry had taken place to give **3**. Derivatives of the same heterocyclic system were reported earlier by Bergman et al.[10] Our interpretation about the regiochemical outcome of the reactions of diallyl ether and diallyl sulfide with $TeCl_4$ relies on the strength of Te−O and Te−S interactions. We assumed that the initial Te−S interaction would be responsible for the regiochemistry and that the 1,4-oxatellurane had formed via a kind of concerted pathway. The Te−S bond in **3** was designated as a coordination bond on the basis of the NBO analysis.

As far as the present authors know, there is only one similar structure studied before, namely, trichloro(2-phenylthiophenyl)-tellurium (**4**, Figure 2).[11] Other types of tellurium complexes with sulfur ligands have been reviewed recently.[12]

The structure of **1** was determined by single-crystal diffraction methods, and the electronic properties of **1** and **3** were studied by ab initio methods at the MP2/LANL1DZ* level of theory (including relativistic effect) with the help of NBO analyses.

Results and Discussion

Synthesis. The formation of the heterocycles **1**, **3**, and **5** in the reactions of tellurium tetrachloride with allylic O and S ethers are shown in Scheme 1. The reaction between allylphenyl sulfide and $TeCl_4$ has only one conceivable route, to attack the two nucleophilic centers, the double bond and the S atom, since the reaction of the aromatic system is slower due to its lower nucleophilicity. The formation of a chiral center at C(2) (Figure 2) is obvious, but if there is a chiral center at the S atom, it depends on the Te−S bond and the direction of the d orbital of the S atom. If it is not directed toward Te atom, there is no chiral center at the S atom. Due to the centrosymmetric crystal system there is only a molecule of **1** in the asymmetric unit unlike in the case of **3** where a racemate occupies the asymmetric unit with an inversion center between the enantiomers.

Description of the Structure. Selected bond angles are given in Table 1. The molecular structure of **1** is shown in Figure 2. Selected bond lengths are shown in Tables 2 and 3. The coordination around Te(IV) is distorted ψ octahedral with three Cl atoms in the equatorial positions. The Te atom is

Scheme 1

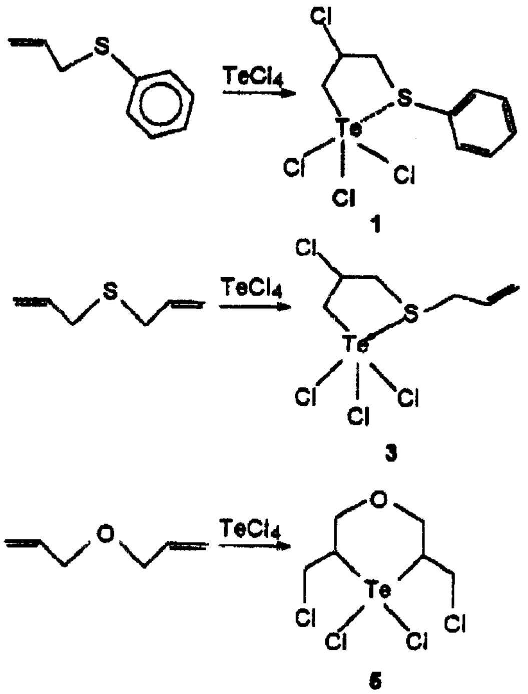

Table 1. Selected Bond Angles (deg) for the Non-Hydrogen Atoms of (1-Thia-2-tellura-1-phenyl-4-chloro)cyclopentane 2,2,2-Trichloride (**1**)[a]

C(1)−Te(1)−Cl(1)	89.9(2)	Cl(3)−Te(1)−S(1)	83.71(7)
C(1)−Te(1)−Cl(2)	87.1(2)	C(2)−C(1)−Te(1)	114.4(4)
C(1)−Te(1)−Cl(3)	86.6(2)	C(1)−C(2)−C(3)	114.1(6)
C(1)−Te(1)−S(1)	77.9(2)	C(1)−C(2)−Cl(4)	107.3(5)
Cl(1)−Te(1)−Cl(2)	92.56(8)	C(3)−C(2)−Cl(4)	108.9(5)
Cl(1)−Te(1)−Cl(3)	90.59(7)	C(4)−S(1)−C(3)	104.9(3)
Cl(1)−Te(1)−S(1)	166.73(7)	C(5)−C(4)−S(1)	114.7(5)
Cl(2)−Te(1)−S(1)	91.88(7)	C(9)−C(4)−S(1)	124.1(6)
Cl(3)−Te(1)−Cl(2)	172.94(8)		

[a] The estimated standard deviations in the least significant figure are given in parentheses.

Table 2. Summary of Natural Population Analysis for the Non-Hydrogen Atoms in (1-Thia-2-tellura-1-phenyl-4-chloro)-cyclopentane 2,2,2-Trichloride(**1**) and (1-Thia-2-tellura-1-allyl-4-chloro)cyclopentane 2,2,2-Trichloride (**3**) as Well as the Te(1)−X Bond Lengths (Where X is a Coordinated Atom)

	natural charge		Te(1)−X/Å	
atom	**1**	**3**	**4**	**5**
Te(1)	1.729	1.711		
Cl(1)	−0.464	−0.513	2.382(2)	2.424(1)
Cl(2)	−0.602	−0.642	2.497(2)	2.5549(9)
Cl(3)	−0.598	−0.572	2.486(2)	2.4527(8)
Cl(4)	−0.116	−0.133		
S(1)	0.300	0.248	2.903(3)	2.763(1)
C(1)	−0.682	−0.044	2.131(7)	2.139(4)
C(2)	−0.066	−0.402		
C(3)	−0.468	−0.447		
C(4)	−0.189	−0.155		
C(5)	−0.183	−0.349		
C(6)	−0.141			
C(7)	−0.173			
C(8)	−0.135			
C(9)	−0.189			

situated 0.215(2) Å out of the least-squares plane, defined by the Cl(1), Cl(2), Cl(3), and S(1) atoms. The C(1) atom opposite the lone pair of electrons of Te(IV) in the axial position completes the coordination polyhedron. The intramolecular Te(1)−S(1) distance is rather long, 2.903(3) Å. The value is

---

(10) Laitalainen, T.; Sundberg, M. R.; Uggla, R.; Bergman, J. *Polyhedron* **1997**, *16*, 2441.

(11) Chakraworty, R.; Irgolic, K. J.; Meyers, E. A. *Acta Crystallogr., Sect. C* **1985**, *41*, 1545.

(12) Haiduc, I.; King, R. B.; Newton, M. G. *Chem. Rev.* **1994**, *94*, 301.

Table 3. Selected Natural Bond Orbitals for (1-Thia-2-tellura-1-phenyl-4-chloro)cyclopentane 2,2,2-Trichloride (**1**) and (1-Thia-2-tellura-1-allyl-4-chloro)cyclopentane 2,2,2-Trichloride (**3**) (Energy in kcal/mol (1 cal = 4.184 J))

1				**3**			
NBO	occupancy	energy	bond length/Å	NBO	occupancy	energy	bond length/Å
BD (1) Te(1)−Cl(1)	1.985	−428.6	2.382(2)	BD (1) Te(1)−Cl(1)	1.990	−421.2	2.424(1)
BD (1) Te(1)−Cl(2)	1.871	−332.2	2.497(2)	BD (1) Te(1)−Cl(2)	1.883	−332.8	2.5549(9)
BD (1) Te(1)−Cl(3)	1.868	−332.3	2.486(2)	BD (1) Te(1)−Cl(3)	1.857	−339.4	2.4527(8)
BD (1) Te(1)−C(1)	1.921	−393.2	2.131(7)	BD (1) Te(1)−C(1)	1.918	−383.2	2.139(4)
BD (1) S(1)−C(3)	1.978	−490.3	1.799(7)	BD (1) S(1)−C(3)	1.977	−474.9	1.810(5)
BD (1) S(1)−C(4)	1.974	−504.8	1.799(7)	BD (1) S(1)−C(4)	1.971	−465.5	1.828(2)
BD (1) Cl(4)−C(2)	1.975	−510.1	1.801(7)	BD (1) Cl(4)−C(2)	1.973	−500.0	1.808(4)
LP (1) Te(1)	1.994	−426.8		LP (1) Te(1)	1.992	−430.3	
LP (1) S(1)	1.969	−389.2		LP (1) S(1)	1.976	−388.3	
LP (2) S(1)	1.770	−267.9		LP (2) S(1)	1.724	−281.1	
LP (1) Cl(1)	1.996	−566.1		LP (1) Cl(1)	1.995	−554.8	
LP (2) Cl(1)	1.980	−295.6		LP (2) Cl(1)	1.980	−291.0	
LP (3) Cl(1)	1.972	−285.4		LP (3) Cl(1)	1.967	−279.5	
LP (1) Cl(2)	1.996	−543.4		LP (1) Cl(2)	1.996	−524.0	
LP (2) Cl(2)	1.983	−279.6		LP (2) Cl(2)	1.976	−290.6	
LP (3) Cl(2)	1.966	−268.7		LP (3) Cl(2)	1.969	−287.0	
LP (1) Cl(3)	1.997	−539.3		LP (1) Cl(3)	1.995	−546.5	
LP (2) Cl(3)	1.985	−286.0		LP (2) Cl(3)	1.983	−289.5	
LP (3) Cl(3)	1.970	−269.7		LP (3) Cl(3)	1.965	−278.1	
LP (1) Cl(4)	1.994	−560.4		LP (1) Cl(4)	1.995	−549.8	
LP (2) Cl(4)	1.980	−303.0		LP (2) Cl(4)	1.984	−311.7	
LP (3) Cl(4)	1.974	−296.6		LP (3) Cl(4)	1.975	−293.7	

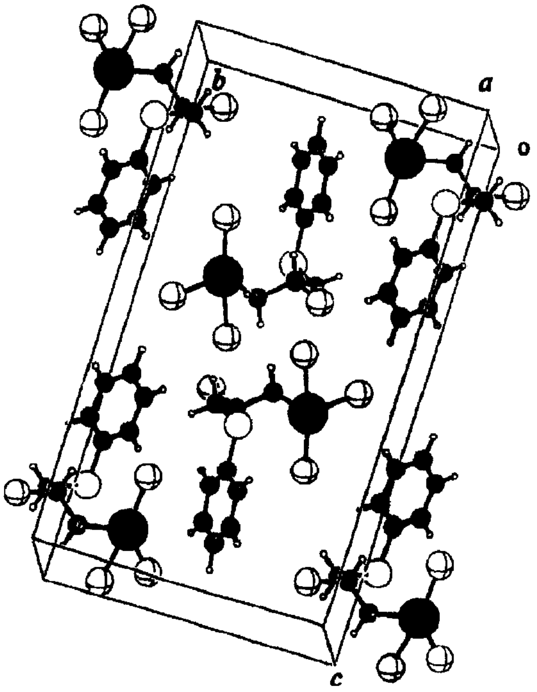

Figure 3. Packing of the molecules in (1-thia-2-tellura-1-phenyl-4-chloro)cyclopentane 2,2,2-trichloride showing the numbering scheme (**1**).

clearly longer than the sum of the corresponding covalent radii (2.65 Å) but is shorter than the sum of the corresponding van der Waals radii (3.90 Å).[13] The NBO analysis was also carried out for **3**, for which the NBO results are discussed in our earlier paper.[7]

The packing in **1** is shown in Figure 3. Discrete molecules of **1** have only a few short intermolecular distances in the crystal lattice. The shortest distances are found between the chlorine and hydrogen atoms (Supporting Information). This is in contrast with the crystal structure of 1-thia-2-tellura-1-(1-allyl-4-chloro)cyclopentane 2,2,2-trichloride (**3**, Figure 1) where intermolecular interactions dominate the structure.[7] The structure of **3** consists of (*R*,*R*)−(*S*,*S*) racemate units with a center of symmetry. The shortest distances within the units are between Te and the S and Cl atoms of a neighboring molecule. The Te(1)−S(1) bond length in **3** is shorter [2.763(1) Å] than the equivalent bond in **1** [(2.903(3) Å].

In the title compound **1**, the Te−Cl(1) bond length [2.382(2) Å] is significantly shorter than the Te−Cl(2) and Te−Cl(3) bonds. In **3** the Te−Cl(1) bond length is 2.424(1) Å, and the Te−Cl(2) and Te−Cl(3) bond lengths are 2.5549(9) and 2.4527(8) Å, respectively. It is noteworthy that the Te−Cl(1) bond length decreases simultaneously with the elongation of the Te(1)−S(1) distance on going from **3** to **1**. It is also shorter than the corresponding Te−Cl(1) bond of 2.424(1) Å in trichloro(ethane-1,2-diolato-*O*,*O*′)tellurate(IV) (**2**).[4] In trichloro(2-phenylthiophenyl)tellurium (**4**, Figure 1) the Te(1)−S(1) and Te(1)−Cl(1) distances are 2.972(1) and 2.324(1) Å, respectively.[11] These values suggest that there is a correlation for the opposite bond lengths.

The Te−C(1) bond length of 2.131(7) Å is comparable to the values of 2.078(10), 2.108(4), and 2.135(5) Å found in {2-[(*S*)-1-(dimethylamino)ethyl]phenyl}tellurium trichloride[14] (**6**), trichloro(2-phenylthiophenyl)tellurium[11] (**4**), and (4-oxo-2-methylpent-2-en-1-yl)tellurium trichloride[15] (**7**), respectively.

The angles C(5)−C(4)−S(1) and C(9)−C(4)−S(1) are 114.7(5) and 124.1(6)°, respectively. They are significantly different and deviate from the expected value of 120°. The same anomaly can be seen in **4**, where the values are 115.4(4) and 123.4(4)°, respectively.[11]

Comparison for the five-membered ring conformations between the structures **1** and **3** reveals that the conformations of **1** and **3** are near to an ideal envelope. The Q and ϕ values are 0.492 and 106.7 for **1** and 0.485 Å and 82.6° for **3**, respectively.[16] The two monomeric units of **1** and **3** were then superposed by least-squares methods so that the positions of the atoms Te(1), C(1), Cl(1), Cl(2), and Cl(3) were as close as

---

(13) Huheey, J. E. *Inorganic Chemistry*, 4th ed.; Harper Collins College Publishers: New York, 1993; p 292.

(14) Singh, H. B.; Sudha N.; Butcher, R. T. *Inorg. Chem.* **1992**, *31*, 1431.

(15) Huang, C.-K.; O'Brien, D. H.; Irgolic K. J.; Meyers, E. A. *Cryst. Struct. Commun.* **1982**, *11*, 1593.

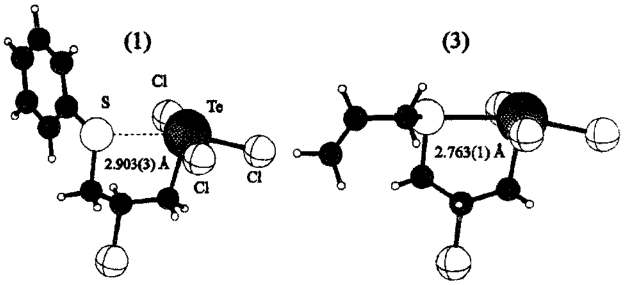

Figure 4. Comparison of the orientations of (1-thia-2-tellura-1-phenyl-4-chloro)cyclopentane 2,2,2-trichloride (**1**) and (1-thia-2-tellura-1-allyl-4-chloro)cyclopentane 2,2,2-trichloride (**3**). In **1** the phenyl ring is pointing away from the viewer, whereas in **3** it is oriented upward from the paper.

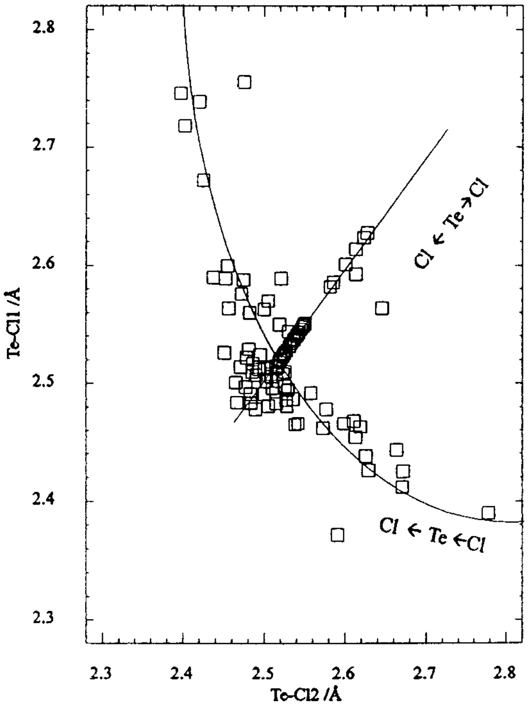

Figure 5. Scatter graphs of the opposite Te−Cl bond lengths.

possible. The result is depicted in Figure 4. There are marked differences: the substituents of the atom S(1) point to different directions, as do the flaps of the envelope points of the five-membered rings. The chlorine atom Cl(4) is situated at the equatorial position in both rings.

Statistical Evidence for Plasticity. A survey was carried out in CSD to find all the structures containing a linear (or angularly disordered) Cl−Te−Cl fragment. Only discrete molecules were accepted. Thus, e.g., the structures with Te−Cl−Te fragments were rejected. In total, there were 115 accepted fragments. The average value for a Te−Cl bond for the fragments is 2.53(6) Å, and their range is 2.372−2.778 Å. The mutual dependence of the Te−Cl bond lengths is shown in Figure 5. There are obviously both direct and indirect correlations between the bond lengths. The former may be described as trans effect, where elongation of one bond leads to shortening of the other one. In the latter, the changes are concomitant so that there are simultanaeous elongations (or compressions) in both bond lengths. These are depicted in Figure 5. The symmetric stretching does not require the Cl−Te−Cl angle to be linear, however. To summarize, the Te−Cl bond lengths display a wide range, and there are two correlations, which are the manifestations of the plasticity of the coordination sphere.

***Ab Initio* Calculations.** The natural charges were calculated for **1** and **3** at the MP2/LANL1DZ* level of theory. The inclusion of the electronic correlation was considered necessary, because the MP2 calculations reproduced the O···Se distance clearly better than the HF calculations for selenoiminoquinones.[3] The results are listed in Table 2. There are many differences in the charges between **1** and **3**. Although the charge at Te(1) is almost equal in both compounds, there are remarkable differences in the other atoms. The atom S(1) becomes more positive upon elongation of the Te(1)−S(1) distance; the Te(1)−S(1) bond lengths are 2.903(3) and 2.763 Å for **1** and **3**, respectively. The opposite behavior can be seen for the chlorine atoms coordinated to Te(1). However, the atoms C(1) and C(2) show enigmatic behavior: although the bond lengths and angles are similar in both compounds, there is significant variation in the charges. Neither variation in the conformation of the five-membered chelate ring can explain the difference, however, because both rings display envelope conformation.

The results obtained by natural bond orbital (NBO) analyses for **1** and **3** are listed in Table 3. It is of special interest to observe the changes due to differences in Te−S distances. In both compounds Te(1) has a nonbonding pair of electrons. The respective energies differ only 3.5 kcal/mol. In **1** the HOMO is the second lone pair of S(1), whereas in **3** there are lone pairs of electrons in both Cl(1) and Cl(3), respectively, which are higher in energy than the lone pair of S(1) (although the differences are about 1−3 kcal/mol). The elongation of a Te−S distance also lowers the energy of the second electron lone pair orbital of sulfur. In **1** the bonds S(1)−C(3) and S(1)−C(4) are lower in energy than in **3**. This is in accord with the differences in the respective bond lengths, since in **1** the bonds are very significantly shorter than in **3**. The Te(1)−C(1) bonding orbital is 10.0 kcal/mol higher in energy in **1**, although the bond lengths in **1** and **3** are similar, 2.131(7) and 2.139(4) Å, respectively.

Second-order perturbation theory analysis of Fock matrix in NBO basis was carried out to evaluate the donor−acceptor interactions in the NBO basis. The interactions result in a loss of occupancy from the a localized NBO of the idealized Lewis structure into an empty non-Lewis orbital. For each donor NBO (*i*) and acceptor NBO (*j*), the stabilization energy *E*(2) associated with delocalization *i* → *j* is estimated as

$$E(2) = \Delta E_{ij} = q_i \frac{F(i,j)^2}{\epsilon_j - \epsilon_i}$$

where q_i is the donor orbital occupancy, ϵ_i and ϵ_j are diagonal elements (orbital energies), and $F(i,j)$ is the off-diagonal NBO Fock matrix element.

Selected results for the relevant interactions to tellurium are given as Supporting Information. In **3** there are interactions between the lone pairs of Cl(1) and the antibonding orbitals BD* S(1)−C(4), BD* Te(1)−Cl(1), and BD* Te(1)−C(1) of the enantiomeric pair. These kinds of interactions are usually defined as secondary bonding.[17] There is no such secondary bonding in **1**. Therefore, we suggest that the donor−acceptor interaction between the lone pair LP(3) Cl(1) and the antibonding orbital BD* Te(1)−C(1) in **3** may well be a reason to the

---

(16) The *Q* value describes the total puckering of a ring, and the *ϕ* parameter desribes the amount of twisting of the ring. For the precise definition, see: Cremer, D.; Pople, J. A. *J. Am. Chem. Soc.* **1976**, *97*, 1354.

(17) Alcock, N. W. *Adv. Inorg. Chem. Radiochem.* **1972**, *15*, 1.

Table 4. Crystallographic Data for (1-Thia-2-tellura-1-phenyl-4-chloro)cyclopentane 2,2,2-Trichloride (**1**)

empirical formula $C_9H_{10}Cl_4STe$	fw 419.65
$a = 6.020(3)$ Å	space group $P2_1/c$ (No. 14)
$b = 11.46(1)$ Å	$T = 23(1)$ °C
$c = 20.156(2)$ Å	$\lambda = 0.710\ 69$ Å
$\beta = 97.53(2)°$	$\rho_{calcd} = 2.02$ g cm^{-3}
$V = 1379(1)$ Å^3	$R(F_o)^a = 0.036$
$Z = 4$	$Rw(F_o)^b = 0.041$

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

anomaly in the charge densities at C(1) and the energies in the bond Te(1)−C(1) discussed earlier.

It should be noted here that the antibonding BD* MOs do not correspond strictly to the virtual MOs in the SCF-MO theory. The virtual MOs are strictly unoccupied, whereas the BD* MOs do exhibit nonzero occupancies. However, the NBO methods are known to provide a useful tool to characterize the donor−acceptor interactions.[18]

Conclusions

The comparison of the structures of **1** and **3** reveals clearly that a tellurium − sulfur interaction is dependent on a substituent on sulfur. Moreover, the change of a substituent affects also the opposite Te−Cl bond and dimer formation. The bonds to sulfur become more stable as the distance between Te and S increases. On a more general level, statistical inspection of the bond lengths in $TeCl_3$ fragments shows that there is considerable plasticity in the coordination sphere around the tellurium atom with two possible distortion mechanisms taking place.

Experimental Section

Spectra. The IR spectra were run on a Perkin-Elmer 1600 FTIR spectrometer. Mass spectra were recorded with a JEOL JMS−SX102 mass spectrometer. The NMR spectra were recorded on a Bruker AM 400 instrument.

Synthesis of (1-Thia-2-tellura-1-phenyl-4-chloro)cyclopentane 2,2,2-Trichloride (1). A solution of allylphenyl sulfide[19] (3.00 g, 20 mmol) and tellurium tetrachloride (5.44 g, 20 mmol) in acetonitrile (35 mL) was refluxed for 10 s and filtered. Upon cooling, crystals were formed: 5.65 g (66%), mp 120 °C (dec). IR (KBr): 3010, 2960, 2960, 1479, 1439, 1398, 769, 742, 723, 687, 586, 468 cm^{-1}. MS: A low-intensity molecular ion was detected in normal EI-mode mass spectrum. The isotopic pattern for $M^{\bullet+}$ is very close to theoretical one for the elemental composition of $C_9H_{10}STeCl_4$. ^1H NMR (CD_3CN): δ 3.72 (t, $J = 13$ Hz, 1 H), 3.97 (t, $J = 13$ Hz, 1 H), 4.28 (brd, $J = 13$ Hz, 1 H), 4.49 (dm, $J = 13$ Hz, 1 H), 4.88 (tt, $J = 13$ Hz, 4 Hz, 1H, H-1), (7.38−7.58, aromatic protons). ^{13}C NMR (CD_3CN): δ 41.7 (CH_2), 55.2 (CH), 67.7 (CH_2), [129.3, 130.2, 130.9 (aromatic carbons)].

Single-Crystal X-ray Study. A pale orange needle-shaped crystal of **1** was mounted on a glass fiber. All measurements were made on a Rigaku AFC7S diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 15 carefully centered reflections in the range $20.25 < 2\theta < 24.66°$, were determined. The crystallographic data are shown in Table 4. The data were collected using the $\omega/2\theta$ scan technique to a maximum 2θ value of 53.0°. Scans of $(1.00 + 0.35 \tan \theta)°$ were made at a speed of 16°/min (in ω). The weak reflections [$I < 15\sigma(I)$] were rescanned (maximum of six scans), and the counts were accumulated to ensure good counting statistics. Of the 3308 reflections that were collected, 3020 were unique. The intensities of three representative reflections were measured after every 200 reflections. No decay correction was applied. The linear absorption coefficient, μ, for Mo $K\alpha$ radiation is 28.6 cm^{-1}. An empirical absorption correction based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.86 to 1.00. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods[20] and expanded using Fourier techniques.[21] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 1778 observed reflections [$I > 3.00\sigma(I)$] and 136 variable parameters. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.45 and −0.85 e/Å^3, respectively. All calculations were performed using the TeXsan crystallographic software package.[22]

***Ab initio* Calculations.** The calculations were carried out at the MP2/LANL1DZ* level of theory by making use of the Gaussian92 program package[23] installed on a Cray-XMP supercomputer. The basis set LANL1DZ was augmented by polarization functions and includes D95 (Dunning/Huzinaga valence double ζ)[24] on the first row as well as Los Alamos Effective Core Potential (ECP) and double ζ on Na−Bi.[25] This pseudopotential basis set was chosen because it includes the relativistic effect. No larger basis sets for the lighter atoms were considered, since the calculations could have been too time-consuming even on a supercomputer. The electronic charges and the bonding properties were analyzed with the help of the NBO program,[26] which is a subprogram in Gaussian92. Because compound **3** forms an enantiomeric racemate pair, the atomic coordinates of the two enantiomers were used as input data, whereas only the atomic coordinates of the asymmetric unit of **1** were used as input data.

The application of the NBO analyses has been described elsewhere.[27] This technique involves the construction of a Fock matrix in the basis of localized core, lone pairs, Rydberg type, and two-center σ, σ^*, π, and π^* NBOs. A particularly useful aspect of the NBO method is that it provides information about interactions involving both filled and virtual orbital spaces, thus allowing e.g. intra- and intermolecular interactions.[18]

Geometrical Parameters. Related structures were extracted from Cambridge Structural Database.[28] The listing for the compounds is available as Supporting Information.

Acknowledgment. Financial support of the University of Helsinki is gratefully acknowledged. The Center of Scientific Computing, Espoo, Finland, has provided the necessary comput-

---

(18) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(19) Hurd C. D.; Greengard, H. *J. Am. Chem. Soc.* **1930**, *52*, 3356.

(20) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, M.; Giacovazzo, C.; Guagliardi A.; Polidori, G. SIR92. *J. Appl. Crystallogr.*, in preparation.

(21) Beurskens, P. T.; Admiraal, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. DIRDIF92. *The DIRDIF Program System*; Technical Report of the Crystallography Laboratory, University of Nijmegen: The Netherlands, 1992.

(22) *TeXsan; Crystal Structure Analysis Package*; Molecular Structure Corporation: The Woodlands, TX, 1985 and 1992.

(23) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian92*, Revision B, Gaussian, Inc.: Pittsburgh, PA, 1992.

(24) Dunning, T. H.; Hay, P. J. *Modern Theoretical Chemistry*; Plenum: New York, 1976; p 1.

(25) (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270. (b) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284. (c) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(26) Glendening, E. D.; Reed, A. E., Carpenter, J. E.; Weinhold, F., *NBO*, Version 3.1 (link 607 in Gaussian92).

(27) (a) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211. (b) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1983**, *78*, 4066. (c) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 1736.

(28) Allen, F. H.; Kennard, O. *Chem. Design Autom. News* **1993**, *8*, 1 and 31.

ing resources. Ilpo Mutikainen, Ph.D., helped kindly in the single-crystal measurements.

Supporting Information Available: Listings of details for single-crystal X-ray measurements, atomic positional coordinates, geometrical parameters, thermal displacements, NBO analyses, and the CSD structure search (37 pages). Ordering information is given on any current masthead page.

IC970406L