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Stereoselective synthesis, molecular structure and NBO analyses of *cis*-3,5-di(chloromethyl)-1,4-oxatellurane(IV) 4,4-dichloride

Tarja Laitalainen,[a] Markku R. Sundberg,[b] Rolf Uggla[b] and Jan Bergman[c]*

[a]Department of Chemistry, Laboratory of Organic Chemistry, PO Box 55, FIN-00014, University of Helsinki, Finland

[b]Department of Chemistry, Laboratory of Inorganic Chemistry, PO Box 55, FIN-00014, University of Helsinki, Finland

[c]Department of Organic Chemistry, CNT, NOVUM, S-14157 Huddinge, Sweden

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Abstract—Tellurium tetrachloride and diallyl ether give stereoselectively *cis*-3,5-di(chloromethyl)-1,4-oxatellurane(IV) 4,4-dichloride. The structure was determined by single crystal X-ray diffraction. The coordination around the Te^{IV} ion is a distorted ψ trigonal bipyramid with two chlorine atoms in the axial positions. Two of the equatorial sites are occupied by carbon atoms, with the lone electron pair located at the third position. The six-membered heterocycle displays a chair conformation. The crystal structure consists of ribbons with Te···Cl contacts. The NBO (Natural Bond Order) analyses carried out by both HF/STO-3G* and HF/LANL1DZ level of theory gave different results. No intermolecular interaction (>1 kcal mol^{-1}) was found by HF/STO-3G*, whereas the main interaction can be seen between a lone pair of Cl(2) and the antibonding orbital between Te(1) and C(1) by RHF/LANL1DZ (1.1 kcal mol^{-1}). © 1997 Elsevier Science Ltd

Keywords: 1,4-oxatellurane; NBO analysis; stereoselective synthesis.

Tellurium tetrachloride is a versatile reagent for telluration reactions and manipulation of functionalities [1]. Reactions of tellurium tetrachloride with the C═C bonds of acyclic hydrocarbons give chlorotelluration products of variable regiochemistry [1,2]. Accordingly the addition of $TeCl_3$-Cl across the double bond is sensitive to subtle changes in the reaction conditions. Depending on the temperature, reactions with cyclohydrocarbons give aromatization or halogenotelluration [3]. Since $TeCl_4$ itself exists in the solid state as a cubane-like tetramer, it might either undergo self-association or coordination with suitable solvents and these can cause the variation in selectivity. Halogenated Te^{IV} derivatives can be reduced to Te^{II} and manipulated to undergo ligand transfers, elimination and Te-catenation reactions. The potential hypervalency of tellurium containing molecules is highly interesting [2]. We have previously shown [4] that $TeCl_4$ reacts with diallyl sulfide to give a five-membered heterocycle analogous to **3** rather than the *S* analog of **2** as claimed by Migalina [5].

In this paper we report the reaction of diallyl ether with $TeCl_4$, and structure determination by single-crystal X-ray diffraction analysis. To gain more information of the electronic properties, natural bond orbital (NBO) analyses were performed at the HF/STO-3G* and HF/LANL1DZ levels of theory.

RESULTS AND DISCUSSION

Synthesis

The molecular structure obtained by X-ray analysis established that tellurium tetrachloride in acetonitrile reacts stereoselectively with diallyl ether **1** to give the *meso*-stereoisomer **2** (Scheme 1 and Fig. 1) with two chiral centres. The origin of stereoselectivity may arise from a concerted reaction involving both C═C bonds

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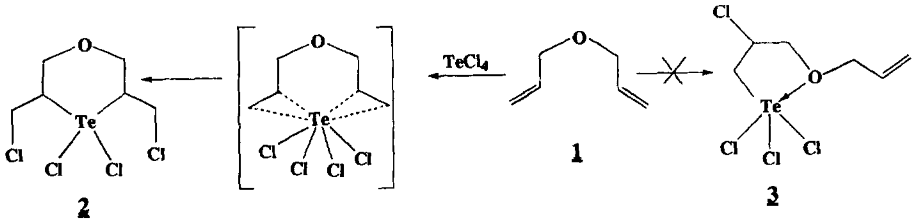
*Author to whom correspondence should be addressed.



Scheme 1. A stereoselective reaction of TeCl$_4$ with diallyl ether to give the *cis*-1,4-oxatellurane derivative **2**.

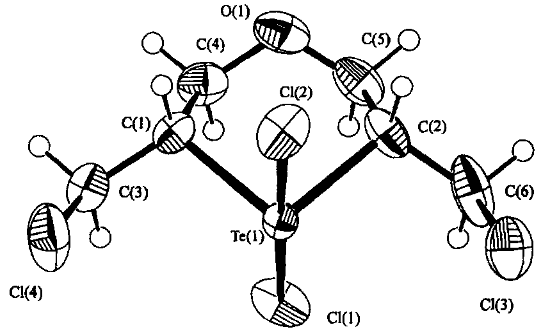


Fig. 1. ORTEP drawing of *cis*-3,5-di(chloromethyl)-1,4-oxatellurane(IV) 4,4-dichloride molecule. The thermal ellipsoids for the nonhydrogen atoms are drawn at 50% level of probability.

simultaneously coordinated to a Te atom shown in Scheme 1. Since the orientation of addition of TeCl$_3$-Cl is anti-Markovnikov electrophilic initiation of addition is ruled out and the Te···O interaction will not participate in the regiochemical outcome of the reaction. When tellurium tetrabromide was reacted with diallyl ether, Migalina claims that a separable mixture of the *cis*- and *trans*-isomers analogous to **2** was obtained, although the experimental details were scant [5]. Reactions of 1,5-hexadiene also reportedly give a mixture of *cis* and *trans* isomers with selenium tetrabromide [6] or bis(2-bromoethyl) selenium dibromide [7].

1,4-Oxatellurane is a known ring system [8] and a previous structure determination by X-ray analysis has been reported for 1,4-oxatellurane(IV) 4,4-diiodide [9].

Description of the structure

Selected bond lengths and angles of the *cis*-3,5-di(chloromethyl)-1,4-oxatellurane(IV) 4,4-dichloride (**2**) are given in Table 1. The asymmetric unit with the labelling scheme for the non-hydrogen atoms is depicted in Fig. 1. The neutral molecule of **2** displays a pseudo mirror plane through the Cl(1), Cl(2), Te(1) and O(1) atoms. The intermolecular distances are listed in Table 2 and a view of the crystal structure in Fig. 2 shows short Te···Cl contacts which further form zigzag chains. Comparison of the intramolecular bond lengths and angles between **2** and 1,4-dioxatellurane(IV) 4,4-diiodide [9] reveals no significant differences within experimental errors.

The coordination polyhedron around the central Te atom is a ψ trigonal bipyramid with two C atoms of the ligand and the unshared electron pair of Te in the equatorial positions as well as two Cl atoms in the axial positions.

The range for Te—Cl bond lengths in 22 compounds varies between 2.34 and 2.60 Å with the average value of 2.52(3) Å [10]. The Te—Cl bonds in **2** meet well the values observed earlier. The same conclusion applies to the Te—C bonds, for which the average value of 13 compounds was 2.16(3) Å [10].

The six-membered ring exists in chair confor-

Table 1. The bond lengths (Å) and angles (°) of the non-hydrogen atoms with their standard deviations for *cis*-3,5-di(chloromethyl)-1,4-oxatellurane(IV) 4,4-dichloride (**2**)

Te(1)—Cl(1)	2.505(3)
Te(1)—Cl(2)	2.487(3)
Te(1)—C(1)	2.166(9)
Te(1)—C(2)	2.163(8)
Cl(3)—C(6)	1.79(1)
Cl(4)—C(3)	1.758(9)
O(1)—C(4)	1.41(1)
O(1)—C(5)	1.36(1)
C(1)—C(3)	1.50(1)
C(1)—C(4)	1.53(1)
C(2)—C(5)	1.52(1)
C(2)—C(6)	1.52(1)
Cl(1)—Te(1)—Cl(2)	176.89(8)
Cl(1)—Te(1)—C(1)	89.1(2)
Cl(1)—Te(1)—C(2)	88.7(2)
Cl(2)—Te(1)—C(1)	89.7(2)
Cl(2)—Te(1)—C(2)	88.6(3)
C(1)—Te(1)—C(2)	94.0(3)
C(4)—O(1)—C(5)	113.3(8)
Te(1)—C(1)—C(3)	110.2(6)
Te(1)—C(1)—C(4)	111.1(6)
C(3)—C(1)—C(4)	112.0(7)
Te(1)—C(2)—C(5)	112.1(5)
Te(1)—C(2)—C(6)	109.1(6)
C(5)—C(2)—C(6)	111.1(7)
Cl(4)—C(3)—C(1)	112.3(6)
O(1)—C(4)—C(1)	112.5(7)
O(1)—C(5)—C(2)	114.2(8)
Cl(3)—C(6)—C(2)	110.9(6)

Table 2. The shortest intermolecular distances. The roman superscripts refer to the symmetry operations given

Contact	Distance (Å)	Symmetry operation	Description
Te(1)···Cl(1)^{i}	3.808(2)	$^{i}1/2-x,1/2+y,1/2-z$	Intrachain
Te(1)···Cl(3)^{ii}	4.014(3)	$^{ii}1/2-x,-1/2+y,1/2-z$	Intrachain
Cl(1)···Cl(3)^{iii}	3.733(3)	$^{iii}x,y-1,z$	Intrachain
Cl(2)···Cl(3)^{iv}	3.519(12)	$^{iv}-x+1,-y,-z$	Intrachain
Cl(3)···Cl(4)^{v}	3.624(4)	$^{v}1/2+x,1/2-y,1/2+z$	Intrachain
Cl(3)···Cl(3)^{vi}	3.756(4)	$^{vi}-x+1,-y+1,-z+1$	Interchain
Cl(3)···Cl(4)^{ii}	3.661(5)	$^{ii}1/2-x,-1/2+y,1/2-z$	Intrachain

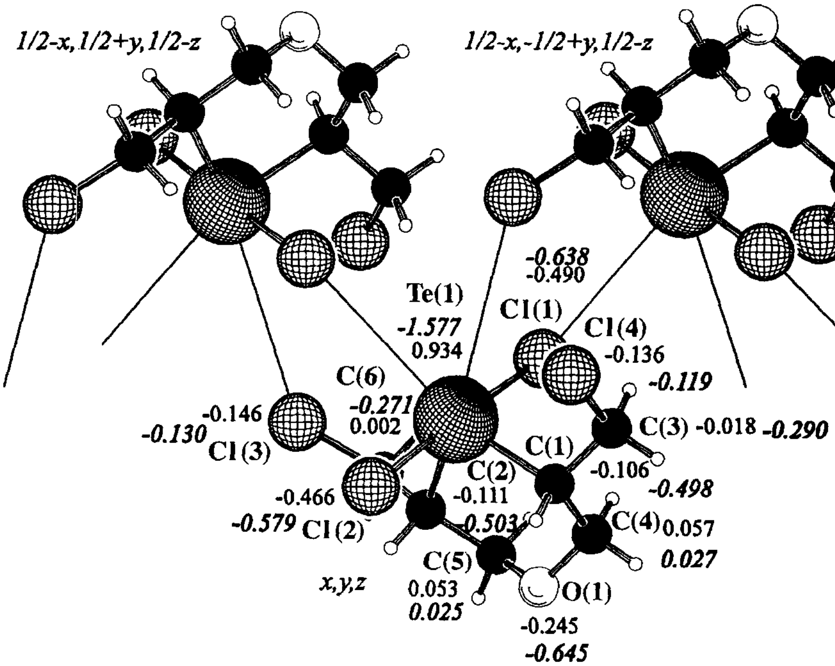


Fig. 2. View in the direction of the *b* axis. The Te···Cl intermolecular contacts are shown by thin solid lines. The numerical values refer to Natural Charges calculated at the RHF/STO-3G* and the RHF/LANL1DZ level of theory.

mation. The puckering parameters are $\theta = 18.7$, $\phi = 8.6°$ and Q = 0.189 Å, which means that the ring is only slightly puckered and twisted [11]. Both the Te and O atoms are displaced from the [C(1), C(2), C(4), C(5)] plane by 0.73(1) Å. Dihedral angles between the planes [C(1), C(2), C(4), C(5)]-[C(1), Te(1), C(2)] and [C(1), C(2), C(4), C(5)]-[C(4), O(1), C(5)] were 29.5(5) and 71.8(9)°, respectively. Again no significant deviations were found from the corresponding angles [27.7(5) and 70(1)°] reported for 1,4-oxatellurane(IV) 4,4-diiodide [9].

The intramolecular nonbonded distances Te(1)—Cl(3) and Te(1)—Cl(4) in **2** are 3.416(3) and 3.467(3) Å, respectively. Although the distances are clearly shorter than the sum of the corresponding van der Waals radii (4.00 Å), there are no suitable orbitals available for an interaction. This is further discussed in connection with the *ab initio* calculations.

Figure 2 depicts the short contacts between a molecule of **2** and its two neighbors. Additional information for the contact distances are listed in Table 2. Each Te atom has two Te···Cl contact distances shorter than the sum of van der Waals radii each with one adjacent molecule. The Cl atom bonded to the Te atom and the Cl atom of the CH_2Cl group participate in this network.

Ab initio *calculations*

Natural bond orbital (NBO) analysis has been used to estimate interactions between two water molecules [12]. In our recent article we used NBO analysis to evaluate secondary bonding between two anions of trichloro(ethane-1,2-diolato-*O*,*O*′)tellurate(IV) [13].

In the case of **2**, three successive asymmetric units of the ribbon involving Te—Cl interactions were included in the *ab initio* calculation. The partial crystal structure included in the *ab initio* calculations is depicted in Fig. 2. The numerical values calculated for the central molecule only are used in the subsequent discussion.

The chain can be described by alternating positive and negative charges residing on Te and Cl atoms, respectively. Obviously the chain formation explains the nonexistence of the symmetry plane going through Cl(1), Cl(2), Te(1) and O(1). Both Cl(1) and Cl(3) have an interaction with the Te atom of neighboring molecule, but not Cl(2) or Cl(4). The interacting Cl atoms carry a more negative charge than their noninteracting counterparts. This appears also in the respective bond length: the interacting Cl atom has a longer bond length than the noninteracting Cl atom.

The choice of basis set has a significant effect on the charges obtained as the results of the calculation. When the relativistic effect is taken into account, the central Te atom has a charge of 1.577, clearly more positive than 0.934 obtained at the RHF/STO-3G* level of theory. Also the Cl(1) atom has more negative charge than Cl(2). The noncoordinated Cl atoms carry less negative charge than the coordinated ones.

Natural localized molecular orbital (NLMO) [14] analysis was then carried out to evaluate the bonding. The summary for the NLMOs is given in Table S1 (Supplementary material).

The calculations also show that there is a lone pair of electrons in Te(1). The result is in accordance with our earlier finding for trichloro(ethane-1,2-diolato-*O,O′*)tellurate(IV). [13]

When the calculations were made at the HF/STO-3G* level of theory, no intermolecular interactions ($\geqslant 1$ kcal mol^{-1}) were found. When the calculations are carried out with the basis set LANL1DZ, the bonding system looks different. The main intermolecular interaction (1.1 kcal mol^{-1}) can be seen between the lone pair [LP(3)] of Cl(2) and the antibonding orbital (BD*) Te(1)′—C(1)′ (where the primed atoms belong to a neighboring unit). This type of interaction can be described as secondary bonding similar to that found in trichloro(ethane-1,2-diolato-*O,O′*)tellurate(IV). [13]

EXPERIMENTAL

Spectra

IR spectra were run on a Perkin–Elmer 1600 FTIR spectrometer. MS spectra were taken on a JEOL JMS-SX102 mass spectrometer.

Synthesis

cis-3,5-Di(chloromethyl)-1,4-oxatellurane(IV) 4,4-dichloride was synthesized by two different procedures. In procedure A tellurium tetrachloride (5.44 g, 20 mmol) was added to a stirred solution of diallyl ether (1.96 g, 20 mmol) in acetonitrile (20 cm^3) at 25°C. The clear solution was left for 24 h and the crystals formed were collected, 3.75 g (55%), m.pt 145°C (dec.). A second crop, 1.25 g (19%), was obtained by cooling (−30°C) the mother liquor.

IR: 2989(w), 2933(w), 1560, 1426, 1306, 1279, 1236, 1102, 1049, 968, 941, 732, 555 cm^{-1}. No molecular ion could be detected in normal EI-mode mass spectra. The isotopic pattern for the $[M-Cl]^{+}$ ion is very close to the theoretical pattern for the elemental composition $C_6H_{10}OTeCl_3$.

In procedure B tellurium tetrachloride (5.44 g, 20 mmol) was added to a stirred solution of diallyl ether (1.96 g, 20 mmol) in dry chloroform (30 cm^3). The clear solution was left overnight and the crystals formed were collected, 2.10 g (32%). Concentration into 10 cm^3 gave a second crop (2.60 g, 40%), the crystals formed according to both procedures were identical.

Crystal data

$C_6H_{10}Cl_4OTe$, $M = 367.56$, monoclinic, $a = 11.163(3)$, $b = 7.8504(13)$, $c = 13.4756(13)$ Å, $\beta = 107.348(10)^\circ$, $V = 1127.2(3)$ Å^3 (by least-squares refinement of diffractometer angles for 25 independent well-centred reflections, $\lambda = 0.71069$ Å), space group $P2_1/n$, no. 14, $Z = 4$, $D_c = 2.18$ g cm^{-3}, Crystal dimensions $0.26 \times 0.31 \times 0.45$ mm, $\mu = 3.65$ mm^{-1}.

Data collection and processing

Nicolet P3 diffractometer, ω scan mode, variable scan speed 2.0–20.0° min^{-1}, graphite monochromated Mo-K_α radiation, 6497 unique reflections measured ($3 \leqslant 2\theta \leqslant 75^\circ$), no absorption correction, giving 4018 independent reflections with $F > 6\sigma(F_0)$. No decay, but Lorentz and polarization corrections were made.

Structure analysis and refinement

Direct methods [15] *followed by difference Fourier techniques*. The structure was refined by full-matrix least-squares techniques with all nonhydrogen atoms anisotropic and the hydrogen atoms in their ideal fixed positions with $U_{iso} = 0.05$ Å^2. The highest peaks in the final difference maps were near to the Te and Cl atoms. Final R and R' (unit weights) values are 0.040 and 0.075, respectively. The neutral atom scattering factors and correction factors for anomalous scattering were those included in the program package. The calculations were carried out with XTAL software [16]. The neutral atom scattering factors were those included in the program. Supplementary material including nonhydrogen and hydrogen atomic coordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. Observed and calculated structure factors are available as Supplementary Material from the authors (MRS) on request.

Ab initio calculations. The calculations were carried out at the HF/STO-3G* and HF/LANL1DZ levels of theory by making use of the GAUSSIAN92 program package [17] installed on a CRAY-XMP supercomputer. The basis set STO-3G* includes single first polarization functions (*p* on H, *d* on the heavier elements) and the basis set LANL1DZ includes D95V (Dunning/Huzinaga valence double ζ) [18] on the first row as well as Los Alamos ECP+DZ on Na-Bi [19]. The electronic charges and the bonding properties were analyzed with the help of the NBO program [20], which is a subprogram in GAUSSIAN92. The atomic coordinates for a partial crystal structure shown in Fig. 2 were used as input data.

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