Tellurium(IV) Tetraalkoxides and Chlorotellurium(IV) Alkoxides Derived from β-Donor Alcohols

Holger Fleischer,*[a] Yvonne Dienes,[a] and Dieter Schollmeyer[b]

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$Te(OiPr)_3OCH_2CH_2XMe_n$ (**1a**–**1c**) and $Te(OCH_2CH_2NMe_2)_4$ (**2**) were synthesised by the reaction of $Te(OiPr)_4$ with $HOCH_2CH_2XMe_n$, while $TeCl_2(OCH_2CH_2OMe)_2$ (**3**) and $TeCl_3OCH_2CH_2XMe_n$ (**4a**–**4c**) resulted from the reaction of $TeCl_4$ with the corresponding silylated alcohols $Me_3SiOCH_2CH_2XMe_n$ (X = N, n = 2; X = O or S, n = 1). These compounds are the first known representatives of the hitherto unknown classes of tellurium(IV) tetraalkoxides and chlorotellurium(IV) alkoxides derived from β-donor-substituted alcohols. The donor atom X in the alkoxy ligand enables an intramolecular donor-acceptor Te···X interaction, which stabilises the di- and trichlorotellurium alkoxides, but reduces the reactivity of the tellurium atom towards nucleophiles, a result from which an associative-dissociative mechanism was inferred for the nucleophilic substitution in $TeCl_4$. In contrast to this, all O*i*Pr ligands of $Te(OiPr)_4$ can be exchanged by reaction with $HOCH_2CH_2XMe_n$. As was shown by multinuclear NMR studies, the kinetics and equilibrium of the reaction of $Te(OiPr)_4$ with $HOCH_2CH_2XMe_n$ depend substantially on X and thus demonstrate the presence of Te···X interactions in solution. The molecular and crystal structure of **3** was investigated by single-crystal X-ray diffraction. In the solid state of **3**, two kinds of molecules are present, differing in the coordination modes of the Te atoms. In each molecule, two intramolecular dative Te···O bonds [264.3(2)–267.7(2) pm] exist, approximately *trans* to the covalent Te–O bonds. Two C_1-symmetric molecules are linked by intermolecular Te···Cl contacts to a third, namely the C_2-symmetric molecule, giving coordination numbers of six and seven for the Te atoms of the C_2- and C_1-symmetric moieties, respectively. Ab initio (MP2/LANL2DZP) geometry optimizations and thermochemical calculations of the model compounds $TeCl_3OCH_2CH_2XH_n$ (**4α**–**4γ**) and $Te(OH)_3OCH_2CH_2XH_n$ (**1α**–**1γ**) as well as an analysis of the bonds in terms of natural bond orbitals were performed in order to study the nature of the Te···X bond and its dependence on conformational restraints. The donor power of the N atom was found to be greater than those of the O and S atoms and the Te···X interactions are stronger for $TeCl_3OCH_2CH_2XH_2$ than for $Te(OH)_3OCH_2CH_2XH_2$; σ-type n(X)–σ*(Te–E) interactions are important for the Te···X bond and compete with π-type n(O)–σ*(Te–E) interactions, which in turn are of importance for the E–Te–O–C conformation (E = O, Cl).

Introduction

In contrast to $SiCl_4$, $GeCl_4$ or $SnCl_4$, $TeCl_4$ does not react with alcohols themselves by means of partial or full exchange of the chloride ligands by alkoxy groups, but dissolves in many alcohols without decomposition.[1] In order to obtain tellurium(IV) tetraalkoxides, $Te(OR)_4$, from $TeCl_4$ and the appropriate alcohol, HOR, the latter has to be activated. This activation can either be achieved by *O*-silylation or *O*-metallation of the alcohol prior to the synthesis or by addition of tertiary amines which drive the reaction by formation of the corresponding ammonium chloride.[2–4] Alternatively, $Te(OR)_4$ can be derived from $Te(OR')_4$ and HOR by ligand exchange according to Equation (1).

$$Te(OR')_4 + 4\,HOR \rightleftarrows Te(OR)_4 + 4\,HOR' \qquad (1)$$

Gottlieb and co-workers showed that the equilibrium in Equation (1) is quickly reached for R, R′ = Me, Et in chloroform or benzene as solvents. They also found out that Equation (1) showed a statistical product distribution characteristic of thermally neutral reactions.[5] The equilibrium according to Equation (1) can be shifted towards the right if HOR′ can be removed by distillation or $Te(OR)_4$ is precipitated from the reaction mixture.[6,7]

Reaction of $TeCl_4$ with silylated alcohols according to Equation (2) represents a good approach to the synthesis of chlorotellurium(IV) alkoxides, $TeCl_{4-n}(OR)_n$.[3]

$$TeCl_4 + n\,Me_3SiOR \rightarrow TeCl_{4-n}(OR)_n + n\,Me_3SiCl \qquad (2)$$

The chlorotrimethylsilane which is formed as a by-product, can easily be distilled off together with the solvent. Trichlorotellurium(IV) alkoxides like trichlorotellurium(IV)

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[a] Institut für Anorganische Chemie und Analytische Chemie, Johannes Gutenberg Universität Mainz,
Duesbergweg 10−14, 55099 Mainz, Germany
[b] Institut für Organische Chemie, Johannes Gutenberg Universität Mainz,
Duesbergweg 10−14, 55099 Mainz, Germany

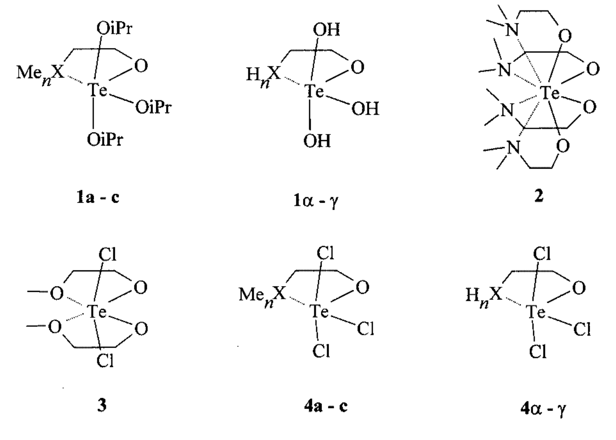
2-propoxide or ethoxide, which are reported to be unstable, could be stabilised as 1:1 adducts with THF or ethyl acetate.[7]

A number of tellurium compounds exhibit intramolecular donor-acceptor interactions, i.e. a Lewis acidic Te centre.[8,9] Concerning organotellurenyl halides, for example, these interactions enable the isolation of these otherwise unstable compounds. We were thus interested to see whether tellurium(IV) alkoxides and especially chlorotellurium(IV) alkoxides could be stabilised by such intramolecular donor-acceptor interactions and how these interactions would influence structure and reactivity.

Results and Discussion

Synthesis and ^{125}Te NMR Spectra

$Te(OiPr)_3OCH_2CH_2NMe_2$ (**1a**), $Te(OiPr)_3OCH_2CH_2OMe$ (**1b**) and $Te(OiPr)_3OCH_2CH_2SMe$ (**1c**) (Scheme 1) were prepared from equimolar amounts of $Te(OiPr)_4$ and the β-donor alcohols $HOCH_2CH_2NMe_2$, $HOCH_2CH_2OMe$ and $HOCH_2CH_2SMe$, respectively, by means of stirring the reactants in benzene and distilling off all volatile products under reduced pressure. $Te(OCH_2CH_2NMe_2)_4$ (**2**) could be prepared in this way as well by treating $Te(OiPr)_4$ with 4 equiv. of $HOCH_2CH_2NMe_2$. Reactions of equimolar amounts of $TeCl_4$ and the silylated β-donor alcohols $Me_3SiOCH_2CH_2XMe_n$ ($X = N$, $n = 2$; $X = O$ or S, $n = 1$) resulted in good yields of the trichlorotellurium(IV) alkoxides $TeCl_3OCH_2CH_2NMe_2$ (**4a**), $TeCl_3OCH_2CH_2OMe$ (**4b**) and $TeCl_3OCH_2CH_2SMe$ (**4c**) (Scheme 1).

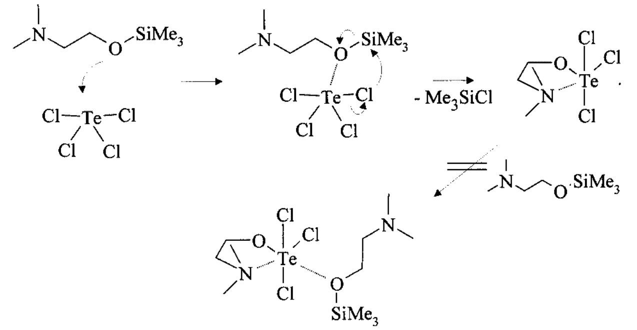


Scheme 1. Structural formulae of compounds and model compounds presented in this paper

Reaction of $TeCl_4$ with 2 or more equiv. of $Me_3SiOCH_2CH_2OMe$ resulted in the formation of $TeCl_2(OCH_2CH_2OMe)_2$ (**3**), whose crystal structure was solved and refined (see below).

At room temperature, **1a**−**c** and **2** are viscous colourless liquids that are quickly hydrolysed when exposed to air, whereas **3** and **4a**−**c** are colourless or slightly grey solids which are less sensitive to air, but decompose on melting. The positions of the ν(Te−Cl) bands in the Raman spectrum of **4a** indicate an aggregation in the solid state via Te−Cl···Te bridges. Whereas **4b** easily dissolves in chloroform, **4c** is soluble only in more polar solvents like THF. Compound **4a** is not soluble without decomposition, hence no high-resolution NMR spectra could be obtained for it.

When treating $TeCl_4$ with $Me_3SiOCH_2CH_2NMe_2$ and $Me_3SiOCH_2CH_2SMe$, no more than one Cl atom could be exchanged for an $OCH_2CH_2XMe_n$ group, even if an excess of the silylated alcohol was used and longer reaction times were applied. This is in contrast to the reaction of $Te(OiPr)_4$ with $HOCH_2CH_2NMe_2$, where all OiPr groups could be substituted by $OCH_2CH_2NMe_2$ groups, leading to compound **2**. Thus, the conclusion could be drawn that the nucleophilic substitution reactions with the Te atoms in $TeCl_4$ and $Te(OiPr)_4$ proceed with different mechanisms and that the intramolecular Te···N interactions in **1a** and **4a** exhibit different strengths (see also the ab initio studies below). For $TeCl_4$, an associative-dissociative mechanism (Scheme 2) is assumed, whereas for $Te(OiPr)_4$ a dissociative-associative mechanism (Scheme 3) is more likely.

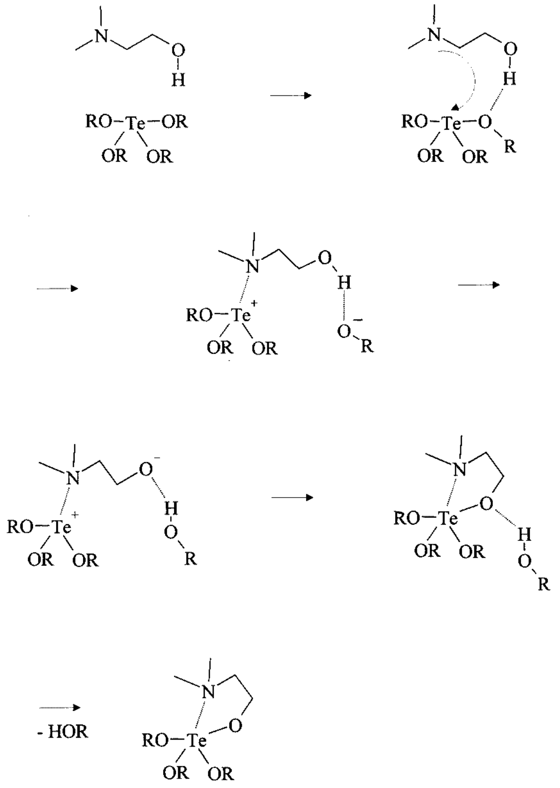


Scheme 2. Proposed associative-dissociative mechanism for the nucleophilic substitution at $TeCl_4$

In the associative-dissociative mechanism, the intramolecular Te···N bond shields the Te atom and reduces its Lewis acidity, so that interaction with the O atom of the silyl ether is not strong enough to cleave the O−Si bond.

For $Te(OiPr)_4$, a hydrogen bond assisted cleavage of a Te−O bond is supposed to precede the transfer of a proton from HOR^1 to OR^- and the addition of the thus formed OR^{1-} to $[Te(OR)_3]^+$. The different mechanisms of the nucleophilic substitution for $TeCl_4$ and $Te(OiPr)_4$ are due to a smaller Lewis acidity of $Te(OiPr)_4$ than $TeCl_4$ and a greater basicity of OR than the Cl ligand.

Whereas the ^{125}Te NMR shift of **1b** ($\delta = 1540$ ppm) is very similar to that of $Te(OiPr)_4$ ($\delta = 1538$ ppm), signals of **1c** ($\delta = 1519$ ppm), **1a** ($\delta = 1454$ ppm) and **2** ($\delta = 1410$ ppm) exhibit a significant high-field shift. This effect is attributed to an increased coordination number of the tellurium atom due to intramolecular Te···X interactions. This interpretation is supported by the observation that on addition of an equimolar amount of H_2SO_4 to a solution of **1a** in $CDCl_3$, the ^{125}Te NMR signal undergoes a low-field shift to $\delta = 1558$ ppm, an effect which is attributed to protonation of the nitrogen atom with subsequent cleavage of the Te···N bond, according to Equation (3).



Scheme 3. Proposed dissociative-associative mechanism for the nucleophilic substitution with Te(O*i*Pr)$_4$ (R = O*i*Pr)

$$\mathbf{1a} + H_2SO_4 \rightarrow [Te(OiPr)_3OCH_2CH_2NHMe_2][HSO_4] \quad (3)$$

The chemical shifts of **1a**, **1b** and **1c**, and their comparison with that of Te(O*i*Pr)$_4$ indicate an increase in Te···X bond strength in the order X = N > S > O. The difference between the ^{125}Te NMR shifts of **1a** and **2** is attributed to a further increase in the coordination number of the Te atom and to the different inductive effects of the O*i*Pr and the OCH$_2$CH$_2$NMe$_2$ groups. Each of the intramolecular Te···N interactions in **2** must be weaker than the one in **1a**, since the difference in the ^{125}Te NMR shifts of **1a** and **2** is only half as much as that between **1a** and Te(O*i*Pr)$_4$.

In order to investigate the molecular dynamics of the Te···X interactions, ^{125}Te NMR spectra of **1a**, **1b** and **1c** were recorded at different temperatures (Table 1). The data shows δ(^{125}Te) of **1a** to have a large, δ(^{125}Te) of **1c** a small, and δ(^{125}Te) of **1b** to have hardly any positive temperature gradient. As the temperature increases, the differences in δ(^{125}Te) of **1a**, **1b** and **1c** decrease, a fact attributed to a substantial weakening of the Te···X interactions at higher temperatures.

Table 1. ^{125}Te NMR shifts of **1a**−**c** at different temperatures

T/°C	1a	1b	1c
−30	1426	1538	1511
−10	1434	1538	1511
10	1445	1539	1516
25	1453	1540	1519
35	1458		

Ligand Exchange of Te(O*i*Pr)$_4$ with HOCH$_2$CH$_2$XMe$_n$

The equilibria and kinetics of the ligand-exchange reactions according to Equations (4a)−(4d) were investigated by means of NMR titration of solutions of Te(O*i*Pr)$_4$ in CDCl$_3$ with HOCH$_2$CH$_2$XMe$_n$ [X = N, n = 2; X = O or S, n = 1; in Equations (4a)−(4d), R′ = CH$_2$CH$_2$XMe$_n$].

$$Te(OiPr)_4 + HOR' \rightleftarrows Te(OiPr)_3OR' + HOiPr \quad (4a)$$

$$Te(OiPr)_3OR' + HOR' \rightleftarrows Te(OiPr)_2(OR')_2 + HOiPr \quad (4b)$$

$$Te(OiPr)_2(OR')_2 + HOR' \rightleftarrows Te(OiPr)(OR')_3 + HOiPr \quad (4c)$$

$$Te(OiPr)(OR')_3 + HOR' \rightleftarrows Te(OR')_4 + HOiPr \quad (4d)$$

With X = N, six solutions were investigated, containing a given amount of Te(O*i*Pr)$_4$ in CDCl$_3$ but different amounts of HOCH$_2$CH$_2$NMe$_2$. Figure 1 shows the ^{125}Te NMR spectra of these solutions, marked A−F. Five different signals can be observed, attributed to the five species of Te(O*i*Pr)$_{4-n}$(OCH$_2$CH$_2$NMe$_2$)$_n$ (n = 0−4), with the signals of Te(O*i*Pr)$_4$ (n = 0), **1a** (n = 1) and **2** (n = 4) known from the spectra of the pure compounds. The single species of Te(O*i*Pr)$_{4-n}$(OCH$_2$CH$_2$NMe$_2$)$_n$ are sufficiently stable on the NMR time scale towards ligand exchange among each other or with free alcohol, so that no coalescence of their ^{125}Te NMR signals occurs. Unlike these results, the ligand exchange between Te(O*i*Pr)$_4$ and HOMe, HOEt or HO*i*Pr, respectively,[5] and that between Te(O*i*Pr)$_4$ and Te(OMe)$_4$,[10] proceed at such a rate at room temperature that only averaged ^{125}Te NMR signals could be observed.

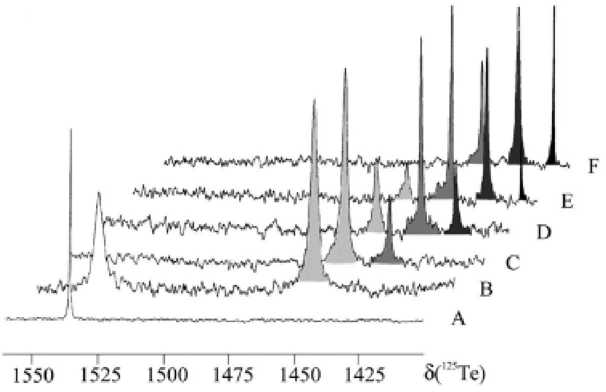


Figure 1. ^{125}Te NMR spectra of a solution of Te(O*i*Pr)$_4$ in CDCl$_3$ with 0.00 (A), 0.65 (B), 1.26 (C), 1.97 (D), 2.77 (E) and 3.89 (F) equiv. of HOCH$_2$CH$_2$NMe$_2$; the different signals correspond to the entire species of Te(O*i*Pr)$_{4-n}$(OCH$_2$CH$_2$NMe$_2$)$_n$ (n = 0−4); the darkening of the peaks' grey shadings corresponds to an increase in n

The ^{1}H NMR spectrum of solution B lacks any signal attributable to HOCH$_2$CH$_2$NMe$_2$, showing that the equilibrium according to Equation (4a) with X = N is shifted far towards the right side. Thus, formation of **1a** from Te(O*i*Pr)$_4$ and $HOCH_2CH_2NMe_2$ is favoured thermodynamically. Since the signal of $HOCH_2CH_2NMe_2$ is missing, no equilibrium constant could be obtained from the spectral intensities.

The equilibrium constants for Equations (4b)−(4d) were estimated considering the relative abundance of Te(*i*PrO)$_{4-n}$($OCH_2CH_2NMe_2$)$_n$, HO*i*Pr and $HOCH_2CH_2NMe_2$ in solutions C−F, derived from the intensities of their signals. Due to experimental errors, the values obtained for K_{4b}, K_{4c} and K_{4d} vary between the different solutions as described in the following: $35 < K_{4b} < 44$, $5.4 < K_{4c} < 8.1$, and $1.1 < K_{4d} < 1.4$. Hence, substitution of O*i*Pr for $OCH_2CH_2NMe_2$ is favoured for all compounds Te(O*i*Pr)$_{4-n}$($OCH_2CH_2NMe_2$)$_n$ (n = 0−3). The more $OCH_2CH_2NMe_2$ groups, however, are bound to the Te atom, the less favourably substitution takes place.

Information about the kinetics of reactions according to Equations (4a) and (4b) was obtained from ^1H NMR spectra. Sample B contains the following three moieties with isopropoxy groups: Te(O*i*Pr)$_4$, **1a** and HO*i*Pr. Nevertheless, only a single set of isopropoxy signals was observed, leading to the assumption of a rapid exchange of O*i*Pr groups between the different species. As the concentration of $HOCH_2CH_2NMe_2$ increases, two sets of signals were observed for each of the O*i*Pr and the $OCH_2CH_2NMe_2$ groups. One set of each could be attributed to the free alcohols, HO*i*Pr and $HOCH_2CH_2NMe_2$, the other one was due to an O*i*Pr and $OCH_2CH_2NMe_2$ group, respectively, both being bound to the Te atom.

Hence it follows that the exchange rate of O*i*Pr between HO*i*Pr and Te(O*i*Pr)$_{4-n}$($OCH_2CH_2NMe_2$)$_n$ decreases with increasing n, a fact attributed to the shielding of the tellurium atom by the $OCH_2CH_2NMe_2$ ligands. This is also reflected in the widths of the ^{125}Te signals, which become sharper with increasing n. It is noteworthy that each of the NMe_2, NCH_2 and OCH_2 groups of **2** gives rise to more than a single signal in the ^1H NMR spectrum, with the NMe_2 and OCH_2 groups also giving two signals each in the ^{13}C NMR spectrum. This is seen to be due to differences between equatorial and apical ligands and due to differences between coordinating and noncoordinating $OCH_2CH_2NMe_2$ groups.

In contrast to the NMR titration of Te(O*i*Pr)$_4$ with $HOCH_2CH_2NMe_2$, neither titration of Te(O*i*Pr)$_4$ with $HOCH_2CH_2OMe$ nor with $HOCH_2CH_2SMe$ leads to separated signals for Te(O*i*Pr)$_{4-n}$(OCH_2CH_2XMe)$_n$ (X = O or S, n = 0−4) in the ^{125}Te NMR spectra of the respective solutions (not depicted). The addition of $HOCH_2CH_2OMe$ to a solution of Te(O*i*Pr)$_4$ in $CDCl_3$ led to an enormous line broadening with hardly any change of the chemical shift. This result is presumably due to a fast exchange between the O*i*Pr and the OCH_2CH_2OMe ligands, assuming that all species Te(O*i*Pr)$_{4-n}$(OCH_2CH_2OMe)$_n$ (n = 0−4) have a similar chemical shift, which could at least be shown for n = 0 [Te(O*i*Pr)$_4$, δ = 1538 ppm] and n = 1 (**1b**, δ = 1540 ppm). Titration of a solution of Te(O*i*Pr)$_4$ in $CDCl_3$ with $HOCH_2CH_2SMe$ led to a significant broadening and a high-field shift of the ^{125}Te NMR signal. At room temperature, no signal could be observed with 5.5 equiv. of the alcohol added, while at −20 °C a single broad signal appeared at δ = 1480 ppm. These results are explained as well through a rapid exchange between the O*i*Pr and the OCH_2CH_2SMe ligands, the high-field shift being due to the different chemical shifts of Te(O*i*Pr)$_4$ and **1c** (δ = 1519 ppm). Similar to the ^{125}Te NMR spectra, the ^1H NMR spectra of the solutions of Te(O*i*Pr)$_4$ with either $HOCH_2CH_2OMe$ or $HOCH_2CH_2SMe$ give only averaged signals for chemically different O*i*Pr or OCH_2CH_2XMe groups.

Crystal and Molecular Structures of 3

In Figure 2, a section of the crystal structure of **3** is shown, illustrating the coordination of the Te atoms and the intermolecular association of the molecules. In the solid state, there are two nonequivalent molecules of **3**, differing in the coordination modes of the Te atoms as well as in their conformations.

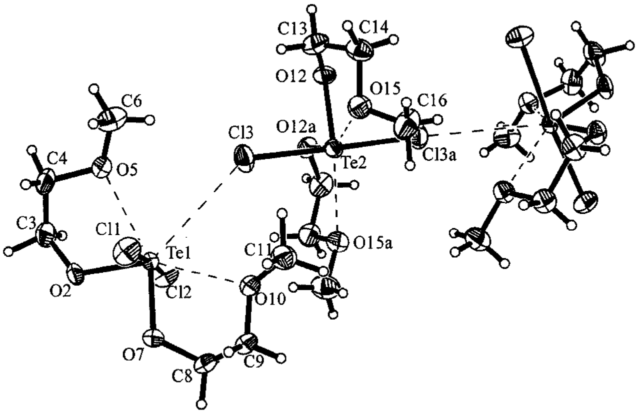


Figure 2. Molecular structure of **3** in the solid state; displacement ellipsoids are at the 50% probability level

Te1 exhibits heptacoordination with a distorted pentagonal-bipyramidal configuration (see bond angles in Table 2); Te1, O2, O5, O7 and O10 are nearly in a plane. Due to the effect of the lone pair of Te1, Cl3 lies slightly outside the plane. The two methyl groups bound to O5 and O10, respectively, are *cis* with respect to the O5−Te1−O10 plane. In contrast to Te1, Te2 is hexacoordinate with a stereochemically active lone pair, leading to a distorted pseudo-pentagonal-bipyramidal configuration; Te2 lies on a twofold axis and the entire molecule exhibits C_2 symmetry. Hence, the methyl groups bound to O15 and O15a, respectively, are *trans* with respect to the O15−Te2−O15a plane. Considering the covalent bonds of the Te atoms only, Te1 and Te2 exhibit pseudo-trigonal-bipyramidal configurations, in accordance with the VSEPR rules; the Cl atoms are in the apical positions, the O atoms and the lone pair are situated in the equatorial positions.

Table 2. Selected XRD and ab initio (MP2/LANL2DZP) atomic distances (in pm) and bonding angles (in °) of **3**

	XRD		XRD	Ab initio
Te1−O2	191.2(2)	Te2−O12	191.5(2)	193.4
Te1−O7	192.4(2)	Te2−Cl3	248.5(1)	249.0
Te1−Cl1	247.5(1)	Te2···O15	266.6(2)	268.0
Te1−Cl2	253.2(1)	O12−Te2−O12a	84.4(1)	84.2
Te1···O5	264.3(2)	Cl3−Te2−Cl3a	178.3(1)	178.2
Te1···O10	267.4(2)	O15···Te2−O12a	155.9(1)	154.7
Te1···Cl3	357.7(1)	O15···Te2···O15a	131.9(1)	133.4
O2−Te1−O7	84.4(1)	Cl3−Te2−O12	88.8(1)	89.8
Cl1−Te1−Cl2	175.1(1)			
O2−Te1···O5	71.7(1)			
O7−Te1···O10	71.8(1)			
O5···Te1···O10	130.5(1)			
Cl1−Te1−O2	88.2(1)			
Cl2−Te1−O7	89.0(1)			
Cl1−Te1···Cl3	104.1(1)			
Cl2−Te1···Cl3	80.7(1)			
O5−Te1···Cl3	69.5(1)			
O10−Te1···Cl3	67.4(1)			

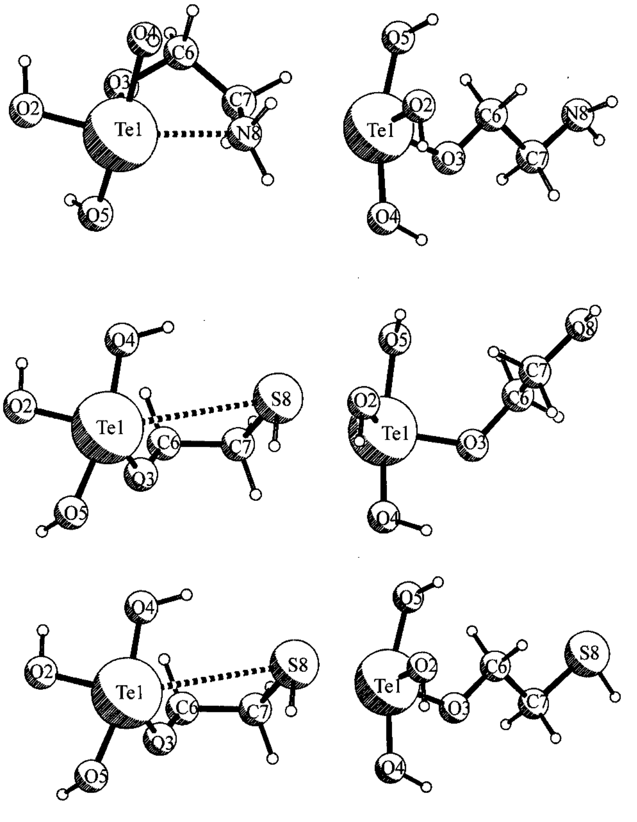


Figure 3. Ab initio molecular structures of model compounds $Te(OH)_3OCH_2CH_2NH_2$ (**1α**), $Te(OH)_3OCH_2CH_2OH$ (**1β**) and $Te(OH)_3OCH_2CH_2SH$ (**1γ**) with Te···X bond (on the left) and without Te···X bond (on the right; X = N8, O8, S8)

The molecular structure of **3**, restrained to C_2 symmetry, was optimised by ab initio methods (MP2/LANL2DZP). The optimised molecular structure agrees quite well with that of the C_2-symmetric unit in the solid state, despite the different phases (isolated vs. solid state) and the different structural types (r_e vs. r_α). An analysis of the Te···O bonds in terms of natural bond orbital interactions shows that these bonds are mainly due to n(O)−σ*(Te−O) interactions between one nonbonding orbital of the donor O atom and the antibonding orbital of the Te−O bond in *trans* position to it. The energy for both of these interactions was estimated to be 72 kJ·mol^{-1}.

Ab initio Studies

With the model compounds $Te(OH)_3OCH_2CH_2NH_2$ (**1α**), $Te(OH)_3OCH_2CH_2OH$ (**1β**), $Te(OH)_3OCH_2CH_2SH$ (**1γ**), $TeCl_3OCH_2CH_2NH_2$ (**4α**), $TeCl_3OCH_2CH_2OH$ (**4β**), and $TeCl_3OCH_2CH_2SH$ (**4γ**), the intramolecular Te···X (X = N, O, S) interactions were investigated in detail. The following two conformations were taken into consideration for each of the model compounds: one exhibiting a Te···X bond, and the second without such an interaction. The optimised molecular structures are depicted in Figures 3 and 4, and structural and energy data are given in Tables 3 and 4.

If only the covalently bound ligands are considered, the Te atoms exhibit pseudo-trigonal-bipyramidal configurations, in accordance with the VSEPR rules. The lone pair of the Te atom occupies an equatorial position, and for **4α**, **4β** and **4γ**, the apical positions are occupied by two Cl atoms which exhibit a greater distance to the Te atom than the equatorial Cl atom. An exothermal process for all model compounds is the conversion of the conformation without the Te···X bond into the conformation with the Te···X bond. From the ΔH^{298} values given in Tables 3 and 4 it follows that Te···X bonds are stronger for the trichlorotellurium(IV) alkoxides **4α**−**4γ** than for the tellurium(IV) tetraalkoxides **1α**−**1γ**, i.e. the Te atom is a better electron-pair acceptor in the former than in the latter. Furthermore, the N atom is a much better donor than the O or the S atom.

The results derived from thermochemical data are confirmed by an NBO analysis of the Te···X bond and by the structural parameters. The interaction of an occupied, nonbonding orbital of the donor atom, n(X), with the unoccupied, anti-bonding orbital of the Te−O or Te−Cl bond in the *trans* position, $\sigma^*(Te-O_{trans})$ or $\sigma^*(Te-Cl_{trans})$, is important for the Te···X bonds in $Te(OH)_3OCH_2CH_2XH_n$ and $TeCl_3OCH_2CH_2XH_n$, respectively. The energies of the $n(X)-\sigma^*(Te-Cl_{trans})$ interactions in **4α**−γ are higher than those of the $n(X)-\sigma^*(Te-O_{trans})$ interactions in **1α**−γ, and also higher when X is N than when X is O or S. According to second-order perturbation theory, the smaller the energy difference and the greater the overlap integral between two orbitals, the greater is the energy of their interaction. Both factors favour the interaction of n(N) compared to n(O) or n(S) with $\sigma^*(Te-Cl_{trans})$ or $\sigma^*(Te-O_{trans})$.

The structural parameters and their differences between the two conformations of the same model compound also serve as a measure of the strength of the Te···X bond. In the conformations of **1α**, **1β** and **4α**−γ with a Te···X

Table 3. Selected ab initio structural parameters (distances in pm, angles in °), $n_p(O)-\sigma^*(Te-O)$ and $n(X)-\sigma^*(Te-O)$ energies of interaction and thermochemical data (in kJ·mol^{-1}) of the model compounds **1α**, **1β** and **1γ**, with (a) and without (b) Te···X bond (X = N, O, S, see Figure 3)

(a)[a]	**1α** with Te···N bond	**1β** with Te···O bond	**1γ** with Te···S bond
Te1−O2/Te1−O3	194.2/196.6	192.8/195.8	192.6/195.5
Te1−O4/Te1−O5	205.7/198.7	202.9/196.4	203.1/195.9
Te1···X	261.4	312.3	385.6
l[b]	1.26	1.54	1.60
O2−Te1−O3	87.8	101.5	102.4
O2−Te1···X	159.6	137.9	135.1
O3−C6−C7−X	−56.0	−64.2	−63.4
C6−O3−Te1−O2	147.1	100.5	79.4
$n_p(O3)-\sigma^*(Te1-O2)$	13	29	31
$n(X)-\sigma^*(Te1-O2)$	68	[c]	[c]
ΔH^{298}[d]	−18	−15	−6

(b)	**1α** without Te···N bond	**1β** without Te···O bond	**1γ** without Te···S bond
Te1−O2/Te1−O3	194.1/194.9	194.2/195.1	193.9/195.5
Te1−O4/Te1−O5	200.3/198.0	200.2/198.2	200.0/198.1
O2−Te1−O3	103.8	104.6	104.3
O4−Te1−O5	163.5	162.8	162.9
O3−C6−C7−X	−178.2	177.2	−179.4
C6−O3−Te1−O2	−80.5	−79.1	−80.3
$n_p(O3)-\sigma^*(Te1-O2)$	32	32	31

[a] X = N8, O8 and S8 for **1α**, **1β** and **1γ**, respectively. [b] l = (Te···X)/[r_{cov}(Te) + r_{cov}(X)]. Covalent radii, r_{kov}, according to Sutton (70, 66, 104 and 137 pm for N, O, S and Te, respectively).[11] [c] Less than 5 kJ·mol^{-1}. [d] ΔH^{298} = H^{298}(with Te···X-bond) − H^{298}(without Te···X-bond).

Table 4. Selected ab initio structural parameters (distances in pm, angles in °), $n_p(O)-\sigma^*(Te-Cl)$ and $n(X)-\sigma^*(Te-Cl)$ energies of interaction and thermochemical data (in kJ·mol^{-1}) of the model compounds **4α**, **4β** and **4γ**, with (a) and without (b) Te···X bond (X = N, O, S, see Figure 4)

(a)[a]	**4α** with Te···N bond	**4β** with Te···O bond	**4γ** with Te···S bond
Te1−Cl2	236.5	232.8	233.5
Te1−Cl3/Te1−Cl4	246.7/249.3	247.8/245.0	245.7/245.8
Te1−O5	194.6	193.7	194.1
Te1···X	240.2	251.5	302.2
l[b]	1.16	1.24	1.25
Cl2−Te1−O5	85.2	88.8	89.8
Cl2−Te1···X	162.3	161.8	164.9
O3−C6−C7−X	−53.4	−57.9	−63.6
Cl2−Te1−O5−C6	161.5	161.2	149.1
$n_p(O3)-\sigma^*(Te1-Cl2)$	4	6	16
$n(X)-\sigma^*(Te1-Cl2)$	184	89	111
ΔH^{298} [c]	−84	−42	−19

(b)	**4α** without Te···N bond	**4β** without Te···O bond	**4γ** without Te···S bond
Te1−Cl2	233.1	232.9	232.9
Te1−Cl3/Te1−Cl4	245.1/241.1	244.3/241.5	241.2/244.8
Te1−O5	191.2	191.1	191.4
Cl2−Te1−O5	99.7	99.8	100.0
O3−C6−C7−X	178.9	177.8	179.1
Cl2−Te1−O5−C6	−62.5	−63.0	61.9
$n_p(O3)-\sigma^*(Te1-Cl2)$	45	45	44

[a] X = N8, O8 and S8 for **4α**, **4β** and **4γ**, respectively. [b] l = (Te···X)/[r_{cov}(Te) + r_{cov}(X)]. Covalent radii, r_{kov}, according to Sutton (70, 66, 104 and 137 pm for N, O, S and Te, respectively).[11] [c] ΔH^{298} = H^{298}(with Te···X-bond) − H^{298}(without Te···X-bond).

Table 5. Crystal data, data collection and correction, structure solution and refinement for **3**

Empirical formula	$C_6H_{14}O_4Cl_2Te$
M/g·mol^{-1}	348.67
Cryst. size/mm	0.06 × 0.19 × 0.35
Cryst. system	monoclinic
Space group	$C2/c$
Z	12
θ range and limiting indices	$4° \leq 2\theta \leq 54°$ $-37 \leq h \leq 37$ $-9 \leq k \leq 9$ $-29 \leq l \leq 29$
T/K	185
$\rho_{calcd.}$/g·cm^{-3}	1.958
a/nm	2.82632(4)
b/nm	0.72874(3)
c/nm	2.22623(11)
β/°	129.285(1)
V/nm^3	3.54903(11)
Reflections meas.[a]	45588
Unique reflections	4407
μ/mm^{-1}	2.95
Reflections observed	3709
Refined parameters	186
R [$\lvert F\rvert > 4\sigma(F)$][b]	0.0275
$wR2$[c]	0.0642
Goodness-of-fit on F^2	1.136
Max./min. peak in diff. Fourier synthesis/10^{-3} e·nm^{-3}	−1.55/0.78

[a] Lorentz and polarisation corrections were performed on the data. Absorption correction was performed with the MULABS program.[17] Hydrogen atoms were localised and isotropically refined by using a riding model. All non-hydrogen atoms were refined anisotropically. [b] $R = \Sigma\lVert F_o\rvert - \lvert F_c\rVert/\Sigma\lvert F_o\rvert$. [c] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o)^2]^2\}^{1/2}$.

"bond", all Te···X distances are smaller than the sum of the van der Waals radii (155, 152, 180 and 206 pm for N, O, S and Te, respectively[12]). The Te···N distance in **4α** corresponds quite well to that in *o*-$TeCl_3[C_6H_4CH(Me)NMe_2]$ [241.1(7) pm].[13] The Te···S bond in **1γ** nearly equals the sum of the van der Waals radii and the term "bond" has to be dealt with carefully. To compare the Te···X distance for different donor atoms with different covalent radii, the relative length, *l*, is used (for definition see Tables 3 and 4).[14] Since the bond with the smaller *l* is the stronger one, the Te···X bonds are again found to be stronger with X = N than with X = O or S and stronger in **4α−γ** than in **1α−γ**. Accordingly, the Te1−Cl2 bond in the *trans* position to the Te1···X8 bond is significantly longer in **4α** than in **4β** or **4γ**, demonstrating the stronger *trans* effect of the N atom compared to the O or S atom.

Optimal π-type n_p(O3)−σ*(Te1−E2) (**1α−γ**: E = O; **4α−γ**: E = Cl) interactions are not compatible with optimal σ-type n(X8)−σ*(Te1−E2) interactions (see Figure 5). In the conformation without a Te···X "bond", the absolute values of the C6−O3−Te1−E2 torsion angles are between 60 and 80° and permit a good overlap between n_p(O3) and σ*(Te1−E2). In the conformations with a Te···X "bond" the five-membered ring formed requires enlarged C6−O3−Te1−E2 torsion angles in order to obtain X in *trans* position to the Te1−E2 bond for a good σ-type n(X8)−σ*(Te1−E2) interaction. The π-type n_p(O3)−σ*(Te1−E2) interaction is significantly reduced in such a conformation (see Tables 3 and 4, b), but at least for **1α** and **4α−γ** it is more than compensated by the n(X8)−σ*(Te1−E2) interaction.

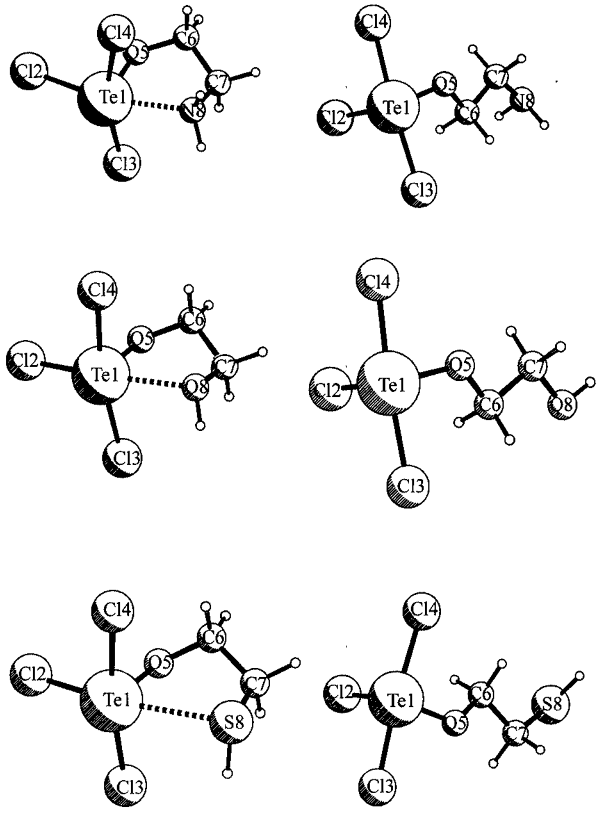


Figure 4. Ab initio molecular structures of model compounds $TeCl_3OCH_2CH_2NH_2$ (**4α**) $TeCl_3OCH_2CH_2OH$ (**4β**) and $TeCl_3OCH_2CH_2SH$ (**4γ**) with Te···X bond (on the left) and without Te···X bond (on the right; X = N8, O8, S8)

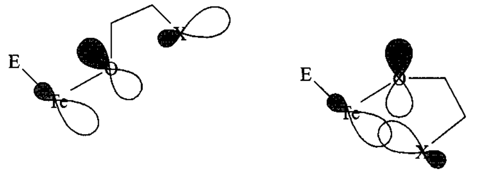


Figure 5. Conformations of the $ETeOCH_2CH_2X$ fragment for optimum π-type n_p(O)−σ*(Te−E) (on the left) and σ-type n(X)−σ*(Te−E) interactions (on the right), respectively

Conclusion

Tellurium(IV) tetraalkoxides, dichlorotellurium(IV) dialkoxides and trichlorotellurium(IV) alkoxides derived from β-donor-substituted alcohols are stabilised kinetically and thermodynamically by intramolecular Te···X interactions. In the trichlorotellurium(IV) alkoxides, this interaction reduces the reactivity of the Te atom towards nucleophiles and only with X = O substitution of a second Cl atom was feasible, leading to $TeCl_2(OCH_2CH_2OMe)_2$. Of all donor atoms investigated, nitrogen forms the strongest Te···X interaction. Substitution of Cl for alkoxide ligands substantially reduces the acceptor power of the Te atom; π-type $n_p(O)-\sigma^*(Te-E)$ interactions and σ-type $n(X)-\sigma^*(Te-E)$ interactions compete with each other in $TeCl_3(OCH_2CH_2XH_n)$ (E = Cl) and $Te(OH)_3(OCH_2CH_2XH_n)$ (E = O), and the stronger one determines the conformation.

Experimental Section

General Procedures: All procedures were carried out under an inert gas or under vacuum, using carefully dried glassware and solvents purified according to standard methods. Te(O*i*Pr)$_4$ was prepared according to Mehrotra et al.[6] NMR: Bruker DRX 400, $B_1(^1H) = 400.000$, $B_1(^{13}C) = 100.577$, $B_1(^{125}Te) = 126.387$ MHz; standards: TMS (^{1}H, ^{13}C) and $Te(CH_3)_2$ (^{125}Te). Raman: SPEX 1402, excitation with a Kr Laser (647 nm). CHNS analyses were performed with an Elemental Vario EL2.

Syntheses

Tellurium 2-(Dimethylamino)ethoxide Tris(2-propoxide), Te(O*i*Pr)$_3$-$OCH_2CH_2NMe_2$ (1a): A solution of 2-(dimethylamino)ethanol, $HOCH_2CH_2NMe_2$ (0.48 g, 5.3 mmol), in 30 mL of benzene was slowly added to a stirred solution of Te(O*i*Pr)$_4$ (1.94 g, 5.3 mmol) in 50 mL of benzene. Subsequently, the benzene and 2-propanol formed during the reaction were distilled off in a slight vacuum; **1a** was isolated from the crude product by a fractionated distillation under high vacuum (113 °C/1.5 10^{-2} mbar, partial decomp.). Yield: 1.54 g (73.9%). ^{1}H NMR (CDCl$_3$): δ = 1.16 [d, $^3J_{H,H}$ = 6.12 Hz, 18 H, OCH(CH_3)$_2$], 2.41 [s, 6 H, N(CH_3)$_2$], 2.66 (t, $^3J_{H,H}$ = 5.2 Hz, 2 H, NCH_2), 4.17 (t, $^3J_{H,H}$ = 5.2 Hz, 2 H, OCH_2), 4.40 [m, 3 H, OCH(CH$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 26.2 [OCH(CH$_3$)$_2$], 44.0 [N(CH$_3$)$_2$], 59.2 (NCH$_2$), 61.5 (OCH$_2$), 64.9 [OCH(CH$_3$)$_2$] ppm. ^{125}Te{^{1}H} NMR (CDCl$_3$): δ = 1454 ppm. $C_{13}H_{31}NO_4Te$ (393.00): calcd. C 39.73, H 7.95, N 3.56 ; found C 40.47, H 7.74 N 3.24.

Tellurium 2-(Methoxy)ethoxide Tris(2-propoxide), Te(O*i*Pr)$_3$OCH$_2$CH$_2$OMe (1b): The preparation was carried out by analogy to that of **1a**, using 2-(methoxy)ethanol, $HOCH_2CH_2OMe$ (0.28 g, 3.7 mmol), and Te(O*i*Pr)$_4$ (1.35 g, 3.7 mmol). The colourless and viscous crude product was washed with a small amount of dietyl ether and dried in vacuo. Yield: 1.25 g (88.9%). ^{1}H NMR (C$_6$D$_6$): δ = 1.33 [d, $^3J_{H,H}$ = 6.1 Hz, 18 H, OCH(CH_3)$_2$], 3.13 (s, 3 H, OCH_3), 3.30 (t, $^3J_{H,H}$ = 4.7 Hz, 2 H, H$_3$COCH_2), 4.21 (t, $^3J_{H,H}$ = 4.7 Hz, 2 H, TeOCH_2), 4.76 [sept, $^3J_{H,H}$ = 6.1 Hz, 3 H, OCH(CH$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ = 26.1 [OCH(CH$_3$)$_2$], 57.9 (H$_3$$C$O), 62.6 (TeO$CH_2$), 65.4 [O$C$H(CH$_3$)$_2$], 74.2 (H$_3COCH_2$) ppm. ^{125}Te{^{1}H} NMR (C$_6$D$_6$): δ = 1540 ppm. $C_{12}H_{28}O_5Te$ (379.94): C 37.94, H 7.43; found C 33.68, H 6.34%. The deviation between calculated and found data for the C,H analysis of compound **1b** is due to the thermal instability of the compound and its sensitivity to air.

Tellurium 2-(Methylsulfenyl)ethoxide Tris(2-propoxide), Te(O*i*Pr)$_3$-OCH$_2$CH$_2$SMe (1c): The preparation was carried out by analogy to that of **1a**, using (2-methylsulfenyl)ethanol, $HOCH_2CH_2SMe$ (0.37 g, 4.0 mmol), and Te(O*i*Pr)$_4$ (1.48 g, 4.1 mmol). The colourless and viscous crude product was washed with a small amount of diethyl ether and dried in vacuo. Yield: 1.62 g (98.2%). ^{1}H NMR (C$_6$D$_6$): δ = 1.30 [d, $^3J_{H,H}$ = 6.1 Hz, 18 H, OCH(CH_3)$_2$], 1.85 (s, 3 H, SCH_3), 2.54 (t, $^3J_{H,H}$ = 6.2 Hz, 2 H, SCH_2), 4.17 (t, $^3J_{H,H}$ = 6.2 Hz, 2 H, OCH_2), 4.71 [sept, $^3J_{H,H}$ = 6.1 Hz, 3 H, OCH(CH$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ = 26.1 [OCH(CH$_3$)$_2$], 37.9 (SCH$_2$), 61.4 (OCH$_2$), 65.7 [OCH(CH$_3$)$_2$] ppm; the signal of (H$_3$$C$S) was not observed. ^{125}Te{^{1}H} NMR (C$_6$D$_6$): δ = 1519 ppm. $C_{12}H_{28}O_4STe$ (396.02): C 36.40, H 7.13, S 8.10; found C 35.36, H 6.70, S 8.32.

Tellurium Tetrakis[2-(dimethylamino)ethoxide], $Te(OCH_2CH_2NMe_2)_4$ (2): The preparation was carried out by analogy to that of **1a**, using Te(O*i*Pr)$_4$ (1.15 g, 3.2 mmol), 2-(dimetylamino)ethanol, $HOCH_2CH_2NMe_2$ (1.16 g, 13.0 mmol), and 50 mL of benzene. The colourless and viscous crude product was washed with a small amount of diethyl ether and dried in vacuo. Yield: 1.21 g (80.0%). ^{1}H NMR (CDCl$_3$): δ = 2.36 + 2.25 + 2.21 [3 s, 24 H, N(CH_3)$_2$], 2.83 + 2.68 + 2.45 + 2.41 (4 m, 8 H, NCH_2), 4.36 + 4.09 + 4.01 + 3.54 (4 m, 8 H, OCH_2) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 43.5 + 44.9 [N(CH$_3$)$_2$], 58.4 (NCH$_2$), 60.3 + 62.4 (OCH$_2$) ppm. ^{125}Te{^{1}H} NMR (CDCl$_3$): δ = 1410 ppm. Raman: $\tilde{\nu}$ = 2941 [vs, ν(C−H)], 2863 [s, ν(C−H)], 2827 [s, ν(C−H)], 2784 [s, ν(C−H)], 2766 [s, ν(C−H)], 781 [m, ν(Te−O)], 711 [w, ν(Te−O)], 571 [m, ν(Te−O)], 533 [vs, ν(Te−O)] cm^{-1}. $C_{16}H_{40}N_4O_4Te$ (480.10): C 40.02, H 8.40, N 11.67; found C 41.02, H 8.48, N 11.79.

Tellurium Dichloride Bis[2-(methoxy)ethoxide], $TeCl_2(OCH_2CH_2OMe)_2$ (3): TeCl$_4$ (1.05 g, 3.9 mmol) and $Me_3SiOCH_2CH_2OMe$ (2.35 g, 15.9 mmol) were dissolved in 20 mL of benzene. The major part of the solvent together with the chlorotrimethylsilane formed during the reaction was then distilled off under normal pressure. The brown viscous residue was dissolved in 10 mL of toluene. From this solution **3** precipitated at −45 °C as colourless crystals. Yield: 1.27 g (93.3%). M.p. 102 °C. ^{1}H NMR ([D$_8$]THF): δ = 3.50 (s, 3 H, H_3CO), 3.65 (t, $^3J_{H,H}$ = 4.4 Hz, 2 H, H$_3$COCH_2), 4.58 (t, $^3J_{H,H}$ = 4.5 Hz, 2 H, TeOCH_2) ppm. ^{13}C{^{1}H} NMR ([D$_8$]THF): δ = 55.8 (OCH$_3$), 70.2 (MeOCH$_2$), 72.5 (TeOCH$_2$) ppm. ^{125}Te{^{1}H} NMR ([D$_8$]THF): δ = 1759 ppm. $C_6H_{14}Cl_2O_4Te$ (348.68): C 20.67, H 4.05; found C 18.93, H 3.72.

Tellurium Trichloride 2-(Dimethylamino)ethoxide, $TeCl_3OCH_2CH_2NMe_2$ (4a): $Me_3SiOCH_2CH_2NMe_2$ (3.20 g, 19.8 mmol) and TeCl$_4$ (5.32 g, 19.7 mmol) were dissolved in 80 mL of THF. The major part of the solvent together with the chlorotrimethylsilane formed during the reaction was then distilled off under normal pressure. A brownish solid precipitated which was isolated, washed several times with petroleum ether and dried in vacuo. Yield: 5.56 g (87.6%). M.p. 130 °C (decomp.). Raman: $\tilde{\nu}$ = 2975 [m, ν(C−H)], 2935 [w, ν(C−H)], 2919 [w, ν(C−H)], 1259 [w, δ(CH$_2$)], 1172 [w, δ(CH$_3$)], 764 [w, ρ(CH$_2$)], 590 (w), 560 [s, ν(Te−O)], 473 (m), 399 (m), 289 [s, ν(Te−Cl)], 270 [s, ν(Te−Cl)], 232 [m, ν(Te−Cl)] cm^{-1}. $C_4H_{10}Cl_3NOTe$ (322.08): C 14.92, H 3.13, N 4.35; found C 14.87, H 3.12, N 4.37.

Tellurium Trichloride 2-(Methoxy)ethoxide, $TeCl_3OCH_2CH_2OMe$ (4b): The preparation was carried out by analogy to that of **4a**, using TeCl$_4$ (2.51 g, 9.3 mmol), $Me_3SiOCH_2CH_2OMe$ (1.38 g, 9.3 mmol) and 30 mL of THF. The brown viscous residue was dissolved in 10 mL of toluene. From this solution **4b** precipitated at −45 °C as a colourless solid. Yield: 2.31 g (80.4%). M.p. 148−150 °C (decomp.). MS (field ionisation): *m*/*z* (%) = 309.8 (12) [M$^+$], 274.9 (100) [M − Cl]$^+$. ^{1}H NMR (CDCl$_3$): δ = 3.76 (s, 3 H, OCH_3), 4.03 (m, 2 H, MeOCH_2), 4.82 (m, 2 H, TeOCH_2) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 46.2 (OCH$_3$), 65.4 (MeOCH$_2$), 72.7

(TeO*C*H_2) ppm. $^{125}Te\{^1H\}$ NMR ($CDCl_3$): δ = 1747 ppm. $C_3H_7Cl_3O_2Te$ (309.04): C 11.66, H 2.28; found C 11.98, H 2.05.

Tellurium Trichloride 2-(Methylsulfenyl)ethoxide, $TeCl_3OCH_2CH_2$-SMe (4c): The preparation was carried out by analogy to that of **4a**, using $TeCl_4$ (2.30 g, 8.5 mmol), $Me_3SiOCH_2CH_2SMe$ (1.42 g, 8.6 mmol) and 30 mL of THF. From the yellow solution, which remained after distillation of the main part of the solvent and the chlorotrimethylsilane, a colourless solid precipitated which was washed with petroleum ether and dried in vacuo. Yield: 1.71 g (61.6%). M.p. 170−173 °C (decomp.). MS (field ionisation): *m/z* (%) = 325.8 (100) [M^+], 288.8 (22) [M − Cl]$^+$. ^1H NMR ([D_8]THF): δ = 2.52 (s, 3 H, SCH_3), 3.18 (t, $^3J_{H,H}$ = 5.2 Hz, 2 H, SCH_2), 5.04 (t, $^3J_{H,H}$ = 5.2 Hz, 2 H, OCH_2) ppm. $^{13}C\{^1H\}$ NMR ([D_8]THF): δ = 16.4 (S*C*H_3), 39.2 (S*C*H_2), 64.7 (O*C*H_2) ppm. $^{125}Te\{^1H\}$ NMR ([D_8]THF): δ = 1693 ppm. $C_3H_7Cl_3OSTe$ (325.10): C 11.08, H 2.17, S 9.86; found C 11.36, H 2.36, S 10.04.

Single-Crystal X-ray Diffraction: The single-crystal X-ray diffraction experiment was performed with a SMART CCD (Bruker AXS) diffractometer with low-temperature unit, employing Mo-K_α radiation (λ = 71.073 pm). The crystal structure was solved with direct methods and difference Fourier analysis (SIR-92)[15] and refined against F^2 (SHELXL-97).[16] For further details, see Table 5. CCDC-173865 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@-ccdc.cam.ac.uk].

Theoretical Methods: The ab initio calculations were performed by using the GAUSSIAN-94 and GAUSSIAN-98 software packages.[18,19] For these the following procedure was applied: Starting from a molecular structure with reasonable atomic distances, bond and torsion angles, the energy was calculated at the Hartree Fock level, using an effective core double-zeta pseudopotential basis set,[20,21] augmented by d-type polarisation functions for all non-hydrogen atoms, with exponents for Te, S and Cl according to Höllwarth et al,[22] and 0.75, 0.80 and 0.85 for C, N and O, respectively (HF/LANL2DZP). The geometry was optimised by using energy gradients obtained according to the algorithm of Schlegel,[23] and the HF/LANL2DZP energy of the stationary point reached at the end of the optimisation was calculated. The HF/LANL2DZP-optimised geometry was re-optimised by using energy gradients from second-order perturbation calculation according to Møller and Plesset using the above-mentioned basis set (MP2/LANL2DZP). Again, the energy of the stationary point at the end of the optimisation was calculated. The chemical bonds of the optimised molecule were analysed in terms of natural bond orbitals (NBO).[24,25] The normal modes of vibration were then calculated from numerical (GAUSSIAN94) or analytical (GAUSSIAN98) force constants. By means of statistical thermodynamics, the enthalpy at 298 K, H^{298}, was calculated. Only MP2/LANL2DZP molecular structures, energies, and enthalpies are given in this paper.

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[1] N. N. Greenwood, B. P. Straughan, A. E. Wilson, *J. Chem. Soc. A* **1968**, 2209−2212.

[2] D. B. Denney, D. Z. Denney, P. J. Hammond, Y. F. Hsu, *J. Am. Chem. Soc.* **1981**, *103*, 2340−2347.

[3] K. C. Malhotra, N. Sharma, R. Sharma, S. C. Chaudhry, *J. Indian Chem. Soc.* **1990**, *67*, 793−795.

[4] H. Meerwein, T. Bersin, *Justus Liebigs Ann. Chem.* **1929**, *476*, 139.

[5] H. E. Gottlieb, S. Hoz, I. Elyashiv, M. Albeck, *Inorg. Chem.* **1994**, *33*, 808−811.

[6] R. C. Mehrotra, S. N. Mathur, *J. Indian Chem. Soc.* **1965**, *42*, 1−4.

[7] R. C. Mehrotra, S. N. Mathur, *J. Indian Chem. Soc.* **1967**, *44*, 216−218.

[8] N. Sudha, H. B. Singh, *Coordination Chemistry Reviews* **1994**, *135/136*, 469−515 and references cited therein.

[9] A. Panda, G. Mugesh, H. B. Singh, R. J. Butcher, *Organometallics* **1999**, *18*, 1986−1993.

[10] H. Fleischer, D. Schollmeyer, *Inorg. Chem.* **2001**, *40*, 324−328.

[11] *Tables of Interatomic Distances and Configurations in Molecules and Ions* (Ed.: L. Sutton), Spec. Publ. no. 11 and 18, The Chemical Society, London, **1958** and **1965**.

[12] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441−451.

[13] H. B. Singh, N. Sudha, R. J. Butcher, *Inorg. Chem.* **1992**, *31*, 1431−1435.

[14] H. Fleischer, *Eur. J. Inorg. Chem.* **2001**, 393−404.

[15] *SIR − A Program for the Automatic Solution fo Crystal Structures by Direct Methods:* A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.* **1994**, *27*, 435−436.

[16] G. M. Sheldrick, SHELXL-97 *Program for crystal structure refinement*, University of Göttingen, Germany, **1997**.

[17] R. Blessing, *Acta Crystallogr., Sect. A* **1995**, *51*, 33−38.

[18] M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, *GAUSSIAN 94*, Revision E.2, Gaussian, Inc., Pittsburgh PA, **1995**.

[19] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, *GAUSSIAN 98*, Revision A.6, Gaussian, Inc., Pittsburgh PA, **1998**.

[20] L. Szasz, *Pseudopotential Theory of Atoms and Molecules*, Wiley, New York, Chichester, Brisbane, Toronto, Singapore, **1985**.

[21] W. R. Wadt, P. J. Hay, *J. Chem. Phys.* **1985**, *82*, 284−298.

[22] A. Höllwarth, M. Böhme, S. Dapprich, A. W. Ehlers, A. Gobbi, V. Jonas, K. F. Köhler, R. Stegmann, A. Veldkamp, G. Frenking, *Chem. Phys. Lett.* **1993**, *208*, 237−240.

[23] H. B. Schlegel, *J. Comp. Chem.* **1982**, *3*, 214−218.

[24] A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 735−746.

[25] A. E. Reed, L A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899−926.

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