Spectroscopic Investigation of the System $TeCl_4$/[NEt_4]PF_6 in Solution and the Crystal Structure of [NEt_4]$_2$[Te_2Cl_{10}]

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday

Solutions containing $TeCl_4$ and [NEt_4][PF_6] in CH_2Cl_2 were investigated by means of UV/vis and NMR spectroscopy in order to study the complex chemistry of $TeCl_4$ with the [PF_6]$^-$ anion. The results show formation of [$TeCl_5$]$^-$ and strong interactions of [PF_6]$^-$ with a tellurium containing species, presumably [$TeCl_3$]$^+$. The life time of the Te^{IV}-PF_6 complex is long enough to give different signals in the ^{19}F NMR spectrum of a solution containing excess [PF_6]$^-$. Even a fivefold excess of Cl^- ions over [PF_6]$^-$ does hardly lead to a dissociation of [$TeCl_3 \cdots PF_6$]. Crystals of [NEt_4]$_2$[Te_2Cl_{10}] were obtained from a 4:1 solution of [NEt_4]PF_6 and $TeCl_4$ in CH_2Cl_2. The compound crystallizes in the triclinic space group P$\bar{1}$, $a = 0.82626(7)$, $b = 1.04260(8)$, $c = 1.9915(3)$ nm, $\alpha = 84.641(9)$, $\beta = 84.891(9)$, $\gamma = 75.208(6)°$ ($T = 295$ K). Slight variations in the molecular environment can have a substantial influence on the interatomic distances within the Te_2Cl_2 bridge of the [Te_2Cl_{10}]$^{2-}$ ion. This conclusion is confirmed by *ab initio* calculations.

Key words: Tellurium, ^{19}F NMR Spectroscopy, UV/vis Spectroscopy, Single Crystal X-Ray
         Diffraction, *ab initio* Calculations

Introduction

Tellurium(IV) chloride, $TeCl_4$, displays a rich coordination chemistry in non-aqueous solvents [1, 2]. In donor solvents, formation of [$TeCl_3$]$^+$ is promoted, the ion being stabilized by donor acceptor interactions. The trichlorotelluronium ion is also the active electrophile in reactions of $TeCl_4$ with activated aromatic compounds like anisol or *N,N*-dimethylaniline, leading preferentially to the *p*-$TeCl_3$ substituted derivative [3]. Reactions with less reactive aromatic compounds are catalyzed by $AlCl_3$, which increases the electrophilicity of $TeCl_4$ by abstracting a chloride ion and increasing the concentration of [$TeCl_3$]$^+$ [4]. In CH_2Cl_2 solution, $TeCl_4$ was shown to be monomeric [5]. This is in accordance with findings in other non or slightly polar solvents like benzene and toluene [6]. On the other hand, several chloro tellurate(IV) complexes are known, *i.e.* [$TeCl_6$]$^{2-}$, [Te_2Cl_{10}]$^{2-}$ and [Te_3Cl_{13}]$^-$. The di- and trinuclear complexes can be regarded as adducts of two or one Cl^-, respectively, to the Te_2Cl_8

or Te_3Cl_{12} fragments of the ($TeCl_4$)$_4$ tetramer [2, 7]. A monomeric [$TeCl_5$]$^-$ anion, analogous to [TeF_5]$^-$ is hitherto unknown in the solid state. Ozin and Vander Voet [8a], as well as Creighton and Green [8b] proposed the existence of [$TeCl_5$]$^-$ in solid [NEt_4][$TeCl_5$] on the basis of IR and Raman data, but no single crystal X-ray diffraction data of the compound were available so far. We report here on UV/vis investigations of the system [NEt_4][PF_6] – $TeCl_4$ and on the single crystal X-ray structure of [NEt_4]$_2$[Te_2Cl_{10}].

Results and Discussion

UV/vis and NMR spectra: The UV/vis absorption of a solution of $TeCl_4$ in CH_2Cl_2 increases substantially on addition of [NEt_4][PF_6] (Fig. 1), while the spectra are qualitatively very similar and bands are shifted only slightly. The intense band at 232 nm and the weaker one at 295 nm can be attributed to [$TeCl_5$]$^-$, in accordance with the findings of Stufkens for [NBu_4][$TeCl_5$] [9]. Hence it might be questioned

Atoms	XRD	Atoms	XRD	C_{2h}	D_{2h}
Te1−Cl2	238.0(2)	Te2−Cl7	239.8(2)	237.4	243.5
Te1−Cl3	237.8(3)	Te2−Cl8	235.5(3)	251.5	243.5
Te1−Cl4	250.2(2)	Te2−Cl9	248.2(2)	249.9	250.9
Te1−Cl5	248.4(3)	Te2−Cl10	251.8(2)	249.9	250.9
Te1−Cl1	284.1(3)	Te1−Cl6	273.6(3)	252.3	279.6
Te2−Cl1#	280.1(3)	Te1−Cl6#	292.3(3)	342.6	279.6
N1A−C1A	150.4(10)	N1B−C1B	151.9(10)		
N1A−C3A	150.8(10)	N1B−C3B	149.3(12)		
N1A−C5A	151.5(11)	N1B−C5B	152.5(11)		
N1A−C7A	152.4(10)	N1B−C7B	154.5(12)		
C1A−C2A	152.6(15)	C1B−C2B	149.2(14)		
C3A−C4A	149.2(12)	C3B−C4B	146.0(14)		
C5A−C6A	150.5(13)	C5B−C6B	150.6(14)		
C7A−C8A	149.0(13)	C7B−C8B	150.8(17)		
Cl2−Te1−Cl1#	175.3(1)	Cl7−Te2−Cl6	176.4(1)	165.2	176.0
Cl3−Te1−Cl1	174.2(1)	Cl8−Te2−Cl6#	174.9(1)	174.9	176.0
Cl4−Te1−Cl5	176.6(1)	Cl9−Te2−Cl10	176.1(1)	172.8	174.4
Cl1−Te1−Cl4	90.9(1)	Cl6#−Te2−Cl9	90.4(1)	90.5	92.1
Cl1#−Te1−Cl4	89.5(1)	Cl6−Te2−Cl9	91.6(1)	93.6	92.1
Cl2−Te1−Cl4	89.1(1)	Cl7−Te2−Cl9	89.4(1)	86.4	88.1
Cl3−Te1−Cl4	88.9(1)	Cl8−Te2−Cl9	88.5(1)	89.2	88.1
Cl1−Te1−Cl1#	82.6(1)	Cl6−Te2−Cl6#	84.0(1)	78.0	84.2
Te1−Cl1−Te1#	97.4(1)	Te2−Cl6−Te2#	96.1(1)	102.0	95.8

Table 1. Selected structural data of [NEt$_4$]$_2$[Te$_2$Cl$_{10}$] from single crystal XRD and of [Te$_2$Cl$_{10}$]$^{2-}$ (C_{2h}-symmetry and D_{2h}-symmetry) from MP2/LANL2DZ(d) geometry optimizations. Distances are given in pm, angles in degree.

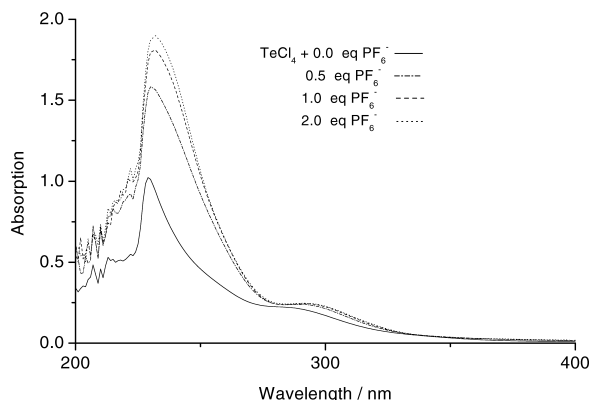# Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y+1, -z$; #2 $-x+2, -y, -z+1$.

Fig. 1. UV/vis spetra of TeCl$_4$ (0.22 mM in CH$_2$Cl$_2$) with different amounts of [NEt$_4$][PF$_6$] added.

whether TeCl$_4$ really dissolves as such in CH$_2$Cl$_2$, since its UV/vis spectrum suggests the presence of a substantial amount of [TeCl$_5$]$^-$. The following equilibria are hence assumed to be present in the system TeCl$_4$-[NEt$_4$][PF$_6$]:

$$2\,TeCl_4 \rightleftharpoons [TeCl_3]^+ + [TeCl_5]^- \tag{1}$$

$$[TeCl_3]^+ + [PF_6]^- \rightleftharpoons [TeCl_3 \cdots PF_6] \tag{2}$$

Obviously, even an excess of [NEt$_4$][PF$_6$] does not lead to the formation of [TeCl$_6$]$^{2-}$ according to equilibrium (3), as can be seen from the absence of bands at 385 and 321 nm [10].

$$3\,[TeCl_5]^- + [PF_6]^- \rightleftharpoons [TeCl_3 \cdots PF_6] + 2\,[TeCl_6]^{2-} \tag{3}$$

In the ^{19}F NMR spectrum of a 4:1 solution of [NEt$_4$][PF$_6$] and TeCl$_4$ in CH$_2$Cl$_2$, one intense and one weak doublet occur in addition to the doublet of the free [PF$_6$]$^-$ ion. The chemical shift (-72.9 ppm) and the $^1J(^{31}P,^{19}F)$ coupling constant (712 Hz) of the latter remained the same as in a solution of [NEt$_4$][PF$_6$] in CH$_2$Cl$_2$. The more intense of the new doublets [$\delta = -84.6$; $^1J(^{31}P,^{19}F) = 980$ Hz] represents about one eighth of all [PF$_6$]$^-$ ions and is assigned to the [TeCl$_3$$\cdots$PF$_6$] complex. Since no splitting due to a $^2J(^{19}F,^{19}F)$ coupling occurs, all F atoms in [TeCl$_3$$\cdots$PF$_6$] must be chemically (and hence magnetically) equivalent. This can either be due to rapid dissociation and formation of the complex or it can be explained *via* a fast rotation of the [PF$_6$]$^-$ relative to the [TeCl$_3$]$^+$. The increased $^1J(^{31}P,^{19}F)$ coupling of [TeCl$_3$$\cdots$PF$_6$] as compared to [PF$_6$]$^-$ can be explained by a higher s-character of the P–F bonds, due to an increased use of the fluorine atoms' *p*-orbitals in binding to Te. The weaker of the two doublets occurs at -89.0 ppm [$\delta = -84.6$; $^1J(^{31}P,^{19}F) = 1072$ Hz]. Its intensity is only 2–3% of that of the signal at -84.6 ppm. The increased $^1J(^{31}P,^{19}F)$ coupling might be due to an even stronger involvement of the *p*-orbitals of the F atoms in the interaction with the Te atom, as compared to [TeCl$_3$$\cdots$PF$_6$], but the origin of the signal remains unclear. It disappears on addition of an excess of [NEt$_4$]Cl, while the signal attributed to

Table 2. Comparison of selected structural parameters of compounds containing the [Te$_2$Cl$_{10}$]$^{2-}$ anion. Atomic distances are given in pm, bond angles are given in degree[a].

	[NEt$_4$][b]	[NEt$_4$][c]	[B[a]PT][d]	[Me$_3$NPh][e]	[Ni(MeCN)$_6$]	(C$_3$Cl$_3$Te$_2$)
Te−Cl^{br,1}	280.1(3)	273.6(3)	271.5(2)	272.1(3)	278.3(1)	274.5(4)
Te−Cl^{br,2}	284.1(3)	293.3(3)	293.7(2)	298.0(3)	290.9(1)	290.0(3)
Te−Cl^{tr,1}	238.0(2)	239.8(2)	241.3(2)	240.5(3)	238.3(1)	238.5(3)
Te−Cl^{tr,2}	237.8(3)	235.5(3)	234.9(2)	234.7(3)	235.2(1)	234.1(3)
(Te−Cl$^{\circ}$)$_{av}$	249.3	250.0	249.9	248.7	249.3	253.0
Te–Cl br/tr [f]	1.186	1.193	1.187	1.200	1.202	1.194
Te–Cl br^2/br^1 [g]	1.014	1.072	1.082	1.095	1.045	1.056
Reference	This work	This work	[11]	[12]	[13]	[14]

[a] Only the corresponding cation is given in the headline of the table. Te−Cl^{br,1} and Te−Cl^{br,2} denote the short and long Te−Cl distances in the centrosymmetric Te$_2$Cl$_2$ cyclus, respectively, (Te−Cl^{tr,1}) and (Te−Cl^{tr,2}) represent the distance of the Te−Cl bonds trans to Te–Cl^{br,1} and Te–Cl^{br,2}, respectively, and (Te−Cl$^{\circ}$)$_{av}$ is the average distances of the two Te−Cl bonds which are more or less orthogonal to the plane of the Te$_2$Cl$_2$ cyclus; [b] molecule containing Te1; [c] molecule containing Te2; [d] B[a]PT = benzo[a]phenothiazinium; [e] [Me$_3$NPh]$_2$[Te$_2$Cl$_{10}$] is part of the more complex compound [Me$_3$NPh]$_4$[Te$_2$Cl$_9$][Te$_2$Cl$_{10}$][ICl$_2$]; [f] ratio (Te–Cl^{br})$_{av}$ / (Te–Cl^{tr})$_{av}$; [g] Ratio (Te–Cl^{br,2}) / (Te–Cl^{br,1}).
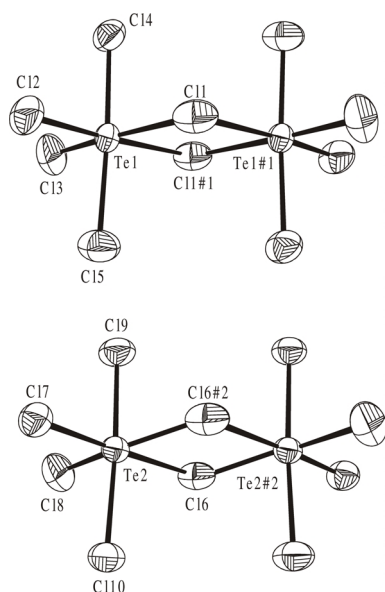

Fig. 2. Molecular structures of the two crystallographically different [Te$_2$Cl$_{10}$]$^{2-}$ ions. Top: molecule 1, bottom: molecule 2. Displacement ellipsoids are at the 50% probability level.

Fig. 3. Crystal structure of [NEt$_4$]$_2$[Te$_2$Cl$_{10}$], showing short Cl···H contacts.

[TeCl$_3$···PF$_6$] loses about 20% of its intensity and is shifted to −81.5 ppm, with $^1J(^{31}$P,^{19}F) being reduced to 954 Hz. Thus, an excess of Cl$^-$ shifts equilibrium (2) only slightly to the left side, presumably by reaction with [TeCl$_3$]$^+$. Unfortunately, no signals were observed in the ^{125}Te NMR spectra of these solutions and hence no details about the tellurium containing species could be obtained.

Single crystal X-ray diffraction and ab initio geometry optimization: Crystals of [NEt$_4$]$_2$[Te$_2$Cl$_{10}$] were obtained from a 4:1 solution of [NEt$_4$][PF$_6$] and TeCl$_4$ in CH$_2$Cl$_2$ by slow evaporation of the solvent. The molecular structures of the [Te$_2$Cl$_{10}$]$^{2-}$ ions are shown in Fig. 2, the crystal structure of [NEt$_4$]$_2$[Te$_2$Cl$_{10}$] is depicted in Fig. 3, selected structural parameters are given in Table 1.

Both [Te$_2$Cl$_{10}$]$^{2-}$ ions have inversion symmetry. Molecule 1 (Fig. 2 and Table 1) exhibits a much more symmetric Te$_2$Cl$_2$ bridge than molecule 2 and any of the other compounds listed in Table 2, as can be seen from the entries in line "Te–Cl br^2/br^1". For an exactly symmetric bridge, this parameter adopts a value of one. Regarding the Te–Cl distances of the equatorial terminal bonds given in Table 2, the longer of the two is always *trans* to the shorter Te–Cl bond in the

bridge, and the difference between the two correlates to the difference between the length of the two bridging Te–Cl bonds. The ratios of the average Te–Cl distances of bridging and equatorial terminal bonds, for molecules 1 and 2 are in good agreement with those found for other compounds containing the $[Te_2Cl_{10}]^{2-}$ ion (see entries in line "Te–Cl br/tr" of Table 2) [2].

There is a good agreement between the different XRD structures and the *ab initio* values concerning $(Te-Cl°)_{av}$ (see Table 2) [15]. This seems to be a rather "hard" parameter in the $[Te_2Cl_{10}]^{2-}$ structure, *i.e.* one with a nearly constant value in different environments. In contrast to the C_{2h}-symmetric form, D_{2h}-symmetric $[Te_2Cl_{10}]^{2-}$ does not represent a minimum but a first order saddle point on the potential energy surface, *i.e.* a symmetric Te–Cl–Te bridge is not stable for the isolated molecule and the C_{2h} form was calculated to be 11 kJmol⁻¹ lower in energy than the D_{2h} form. This corresponds to a highly asymmetric Te_2Cl_2 bridge in the C_{2h} symmetric form, the two respective Te–Cl bonds differing by more than 90 pm in their lengths. The *ab initio* results suggest that the position of the bridging Cl atom can substantially be shifted with only a small amount of energy.

Conclusion

$[PF_6]^-$ ions react with $TeCl_4$ in CH_2Cl_2 solution. The life time of the Te^{IV}-PF_6 complex, presumably $[TeCl_3 \cdots PF_6]^+$, is long enough to give different signals in the ¹⁹F NMR spectrum of a solution containing excess $[PF_6]^-$. Even a fivefold excess of Cl^- ions over $[PF_6]^-$ does hardly lead to a dissociation of $[TeCl_3 \cdots PF_6]$. On the basis of single crystal X-ray diffraction data, the compound $[NEt_4][TeCl_5]$ is better described as $[NEt_4]_2[Te_2Cl_{10}]$. Slight variations in the crystal environment can have a substantial influence on the interatomic distances within the Te_2Cl_2 bridge of the $[Te_2Cl_{10}]^{2-}$ ion. This conclusion is confirmed by *ab initio* calculations.

Experimental Section

General procedures: All procedures were carried out under an inert gas atmosphere, CH_2Cl_2 was purified by distillation from $LiAlH_4$. NMR: Bruker DRX 400, $B_1(^{19}F) = 376.480$ MHz. Standard: CCl_3F. UV/vis: JASCO V-570 double beam spectrometer, 190–900 nm, quartz-cuvettes, $d = 1$ cm, spectral step width 1 nm.

Crystal structure determination: The diffraction experiment was performed on a Nonius Turbo CAD4 diffractometer. The crystal structure was solved by direct methods and

Table 3. Crystal data for compound $[NEt_4]_2[Te_2Cl_{10}]$.

Empirical formula	$C_8H_{20}NCl_5Te$
a [nm]	0.82626(7)
b [nm]	1.04260(8)
c [nm]	1.9915(3)
α [deg]	84.641(9)
β [deg]	84.891(9)
γ [deg]	75.208(6)
V [nm³]	1.6477(3)
FW [g mol⁻¹]	435.10
Crystal system	triclinic
Space group	P$\bar{1}$
Z	4
Crystal size [mm]	$0.039 \times 0.159 \times 0.23$
Temperature [K]	295
$\rho_{calcd.}$ [g cm⁻³]	1.754
Radiation	Cu-K$_\alpha$, $\lambda = 1.54179$ Å
θ-Range	$2° \le \theta \le 74°$
Limiting indices	$-10 \le h \le 9, -12 \le k \le 0,$ $-24 \le l \le 24$
μ [mm⁻¹][a]	21.51
Reflections meas.	7061
Unique reflections	6678
Refl. $|F| > 4\sigma(F)$	5039
$F(000)$	848
R[$|F| > 4\sigma(F)$][b]	0.0661
Goodness-of-fit on F^2	1.040
Largest diff. peak and hole [10^{-3}e·nm⁻³]	$-1.94/1.67$

[a] Numeric absorption correction was performed using six planes [20]; [b] $R = \Sigma \parallel F_o \mid - \mid F_c \parallel / \Sigma |F_o|$.

difference Fourier technique (SIR-92) [17], structural refinement was against F^2 (SHELXL-97) [18]. Details of the crystal structure determination of and the crystal data for $[NEt_4]_2[Te_2Cl_{10}]$ are given in Table 3 [19].

UV/vis titrations: $TeCl_4$ (23.6 mg, 8.8 10^{-2} mmol) was dissolved in 400 ml CH_2Cl_2, giving a 0.22 mM solution. To three portions containing 2.0 ml of this solution, 0.025 ml (0.5 equivalents), 0.05 ml (1.0 equivalent) and 0.10 ml (2.0 equivalents), respectively, of an 8.8 mM solution of $[NEt_4][PF_6]$ in CH_2Cl_2 were added. The UV/vis spectra of all solutions were recorded in the range 200–800 nm.

¹⁹F NMR spectra: $[NEt_4][PF_6]$ (30 mg, 0.11 mmol) was dissolved in 0.5 ml of CH_2Cl_2 and a ¹⁹F NMR spectrum was recorded. Another ¹⁹F NMR experiment was performed after addition of $TeCl_4$ (7 mg, 0.03 mmol) in 0.5 ml of CH_2Cl_2. Finally, the solution was poured into a solution of $[NEt_4]Cl$ (83 mg, 0.50 mmol) in 0.5 ml of CH_2Cl_2 and 0.5 ml of the combined solution were taken for the third ¹⁹F NMR experiment. To all solutions under investigation, D_2O sealed in a capillary had been added in order to get a lock signal.

Theoretical methods: Quantum chemical *ab initio* investigations were performed with the GAUSSIAN98 program package [21]. Geometry optimizations, single point energy calculations and calculation of thermochemical data were

performed at the MP2 level, using relativistic effective core potentials and the corresponding double zeta valence basis sets [22], augmented by appropriate polarization functions, with exponents according to Höllwarth *et al.* [23], the method

being designated as MP2/LANL2DZ(d). Starting structures for geometry optimizations were set up using standard bond lengths, bond angles and torsion angles. Applied symmetry restrictions are given in the text.

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