Preparation and Characterization of F_3Te(map) and the Structure of Cl_3Te(map) (map = 2-(methylamino)pyridinato)

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2-(Methylamino)pyridinato-tellurium(IV) Halides, Tellurium(IV)-Nitrogen Compound, Pentacoordinate Tellurium(IV)

The tellurium-nitrogen compounds Cl_3Te(map) (**1**) and F_3Te(map) (**2**) (map = 2-(methylamino)pyridinato), derived from N-silylated map and the corresponding tellurium(IV) halide, have been prepared and characterized. The crystal structure of **1** reveals a dimeric species with two five-coordinate Te(IV) centers that are bridged by longer Te···Cl contacts (356 pm average). Crystal data for **1:** triclinic, a = 7.280(1), b = 9.512(1), c = 16.004(2) Å, α = 96.67(1), β = 91.95(1), γ = 105.79(1)°, V = 1057(1) Å^3, T = 293 K, space group P$\bar{1}$, Z = 2. Final R and R_w values for **1** are 0.026 and 0.033, respectively.

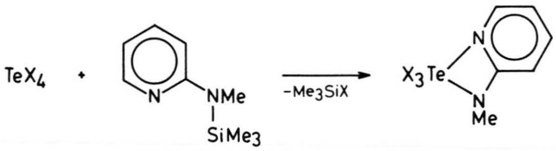
Introduction

The chemistry of S–N compounds has been studied quite extensively over the past few decades [1]. In contrast to this, Se–N and in particular Te–N chemistry has received comparatively little attention [2]. One of the main reasons for this is that suitable precursors to generate Se–N and Te–N compounds in a rational manner have not been available. With the exception of newly developed starting materials such as $Se[N(SiMe_3)_2]_2$ and $Te[N(SiMe_3)_2]_2$ the preparations of Se–N and Te–N compounds have often been limited to reactions of amine derivatives with corresponding chalcogen halogenides or by the use of explosive Se_4N_4.

In our continuing investigations on Te–N systems we previously described the formation of a four-membered planar Te_2N_2 heterocycle $(Cl_3TeNPPh_3)_2$ [3], which contains two five-coordinate Te(IV) centers. Herein we report the formation of two novel five-coordinate Te(IV) compounds Cl_3Te(map) (**1**) and F_3Te(map) (**2**) (map = 2-(methylamino)pyridinato).

Results and Discussion

A suspension of $TeCl_4$ in CH_2Cl_2 was treated with Me_3Si(map) at room temperature to obtain **1** (Scheme). The ^{1}H NMR spectrum of the volatiles removed under vacuum indicates that Me_3SiCl is formed in the reaction.



(1) X = Cl
(2) X = F

Yellow single crystals of **1** suitable for X-ray analysis were obtained from the CH_2Cl_2 solution. Details of the data collection, solution and refinement are given in the Experimental Section, and selected bond lengths and angles and atomic coordinates are given in Tables I and II, respectively.

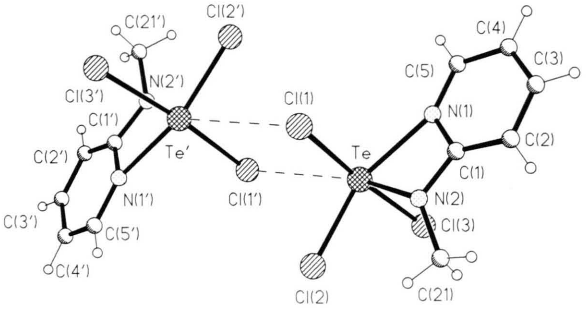


Fig. 1. Perspective view of the Cl_3Te(map) dimer in the unit cell.

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Table I. Selected bond lengths (pm) and angles (°) for Cl_3Te(map) (**1**).

Te−Cl(1)	249.1(1)	Te−Cl(2)	237.0(1)
Te−Cl(3)	252.5(2)	Te−N(1)	235.2(3)
Te−N(2)	203.9(3)	N(1)−C(1)	134.0(5)
N(1)−C(5)	134.5(5)	C(1)−N(2)	137.4(4)
N(2)−C(21)	145.5(5)	Te′−Cl(1′)	251.4(1)
Te′−Cl(2′)	238.4(1)	Te′−Cl(3′)	250.4(2)
Te′−N(1′)	232.8(3)	Te′−N(2′)	204.6(3)
N(1′)−C(1′)	133.5(5)	N(1′)−C(5′)	134.3(5)
C(1′)−N(2′)	137.1(4)	N(2′)−C(21′)	143.3(5)
Cl(1)−Te−Cl(2)	90.4(1)	Cl(1)−Te−Cl(3)	174.2(1)
Cl(2)−Te−Cl(3)	92.5(1)	Cl(1)−Te−N(1)	86.7(1)
Cl(2)−Te−N(1)	148.4(1)	Cl(3)−Te−N(1)	88.2(1)
Cl(1)−Te−N(2)	88.7(1)	Cl(2)−Te−N(2)	88.4(1)
Cl(3)−Te−N(2)	86.4(1)	N(1)−Te−N(2)	60.1(1)
Te−N(1)−C(1)	88.6(2)	Te−N(1)−C(5)	150.6(3)
C(1)−N(1)−C(5)	120.8(4)	N(1)−C(1)−C(2)	122.0(3)
N(1)−C(1)−N(2)	109.4(3)	C(2)−C(1)−N(2)	128.5(4)
Te−N(2)−C(1)	101.6(2)	Te−N(2)−C(21)	126.3(3)
C(1)−N(2)−C(21)	122.2(3)	Cl(1′)−Te′−Cl(2′)	91.3(1)
Cl(1′)−Te′−Cl(3′)	172.7(1)	Cl(2′)−Te′−Cl(3′)	92.9(1)
Cl(1′)−Te′−N(1′)	85.3(1)	Cl(2′)−Te′−N(1′)	147.6(1)
Cl(3′)−Te′−N(1′)	88.0(1)	Cl(1′)−Te′−N(2′)	87.6(1)
Cl(2′)−Te′−N(2′)	87.4(1)	Cl(3′)−Te′−N(2′)	86.7(1)
N(1′)−Te′−N(2′)	60.3(1)	Te′−N(1′)−C(1′)	89.2(2)
Te′−N(1′)−C(5′)	149.4(3)	C(1′)−N(1′)−C(5′)	121.2(3)
N(1′)−C(1′)−C(2′)	121.2(3)	N(1′)−C(1′)−N(2′)	109.5(3)
C(2′)−C(1′)−N(2′)	129.1(3)	Te′−N(2′)−C(1′)	100.8(2)
Te′−N(2′)−C(21′)	128.5(3)	C(1′)−N(2′)−C(21′)	124.1(3)

Table II. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($pm^2 \times 10^{-1}$) for Cl_3Te(map) (**1**).

Atom	*x*	*y*	*z*	U_{eq}
Te	5423(1)	2416(1)	3358(1)	40(1)
Cl(1)	7641(2)	831(1)	3205(1)	57(1)
Cl(2)	7771(2)	4248(1)	4247(1)	64(1)
Cl(3)	2947(2)	3814(1)	3574(1)	63(1)
N(1)	2919(5)	218(3)	3219(2)	50(1)
C(1)	2986(6)	303(4)	4061(3)	46(2)
C(2)	1744(6)	− 745(5)	4475(3)	63(2)
C(3)	501(8)	−1889(5)	3975(5)	83(3)
C(4)	436(8)	−1992(5)	3105(5)	84(3)
C(5)	1674(7)	− 914(5)	2734(3)	67(2)
N(2)	4483(4)	1477(3)	4403(2)	44(1)
C(21)	4479(7)	2250(5)	5243(3)	55(2)
Te′	10623(1)	2819(1)	1654(1)	40(1)
Cl(1′)	8241(2)	4268(1)	1931(1)	52(1)
Cl(2′)	8224(2)	815(1)	889(1)	65(1)
Cl(3′)	13246(2)	1654(2)	1302(1)	67(1)
N(1′)	12834(4)	5102(3)	1641(2)	45(1)
C(1′)	12477(5)	4972(4)	808(2)	41(2)
C(2′)	13390(5)	6086(4)	340(3)	46(2)
C(3′)	14599(6)	7314(5)	772(3)	58(2)
C(4′)	14939(7)	7451(5)	1637(3)	64(2)
C(5′)	14044(6)	6323(5)	2064(3)	55(2)
N(2′)	11063(4)	3697(3)	545(2)	41(1)
C(21′)	10785(6)	2944(5)	− 298(2)	47(2)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Compound **1** exists as a dimer in the solid state with long Te ··· Cl contacts (Te ··· Cl(1′) = 344(1) pm, Te′ ··· Cl(1) = 369(1) pm) between the two Te centers. These contacts are within the sum of the van der Waal's radii (370 pm) for Te and Cl atoms. Each Te atom is also directly bonded to two N atoms of the map ligand and three Cl atoms, which together with the lone pair of electrons at Te form a distorted pseudo-octahedral geometry about the Te center. The axial chlorines are bent slightly away from the "open face" containing the lone pair of electrons and towards the plane of the map ligand, forming angles Cl(1)−Te−Cl(3) and Cl(1′)−Te−Cl(3′) of 174.2(1) and 172.7(1)°, respectively. The map chelate forms a small four-membered ring at Te with an average N−Te−N angle of 60.2(1)°, which is smaller than, but still comparable to the N−Te−N angle (62.8(4)°) found in $Cl_3Te(Me_3SiN)_2CPh$ [4].

In each half of the dimer, all the atoms, with the exception of the axial chlorines and the methyl groups, are coplanar. (The largest deviation from the least-squares plane is 8.4 pm.) This is due not only to the π-delocalization within the pyridine ring itself, but also to the exocyclic delocalization involving N(1)−C(1)−N(2). The bond distances of both the endocyclic C(1)−N(1) (134.0(5) pm) and the exocyclic C(1)−N(2) (137.4(4) pm) are significantly shorter than the average C−N single bond length (145 pm), and also indicate partial delocalization of this N(1)−C(1)−N(2) segment. In addition, an absorption at 1594 cm^{-1}, corresponding to a partial C=N double bond, was observed in the IR spectrum of **1**. Similar N−C−N π-delocalizations have been reported for $Cl_3Te(Me_3SiN)_2CPh$ [4] and the phosphorus analogue $Cl_4P(map)$ [5].

The Te−N(2) bond distance of 203.9(3) pm is shorter than either that expected for a Te−N single bond estimated from covalent radii (207 pm) [6] or the Te−N bond length (209.6(4) pm) found in $Cl_3Te(Me_3SiN)_2CPh$ [4]. In contrast, the Te−N(1) distance (235.2(3) pm) to the ring nitrogen is much longer, reflecting a more coordinative nature of this Te−N bond. Similar Te−N distances involving the coordination of a pyridine nitrogen to a Cl_3Te center have been reported for $Cl_3Te[-2\text{-}CH_2C(O)-6\text{-}CH_3C(O)C_5H_3N]$ [7] (240.2(3) pm) and $Cl_3Te[-2\text{-}C_6H_4N{=}NPh]$ [8] (241.7(4) pm).

$F_3Te(map)$ (**2**) was prepared in a similar manner (Scheme) and the elimination of Me_3SiF could be observed by ^1H and ^{19}F NMR spectroscopy. The isotope pattern of the parent ion $[M^+]$ found in the mass spectrum of **2** is identical to the calculated pattern.

Suitable crystals of **2** for X-ray analysis could not be grown, but it is reasonable to expect that **2** also has five-coordinate F_3TeN_2 centers with weaker Te···F contacts to other F_3TeN_2 centers. The tendency for the Te center to interact with distant Cl or F atoms is reflected in the halogen bridging nature of the precursors to **1** and **2.** Both the $TeCl_4$ tetramer [9] and the TeF_4 polymer [10] possess a network of bridging halogen atoms between Te centers. An absorption at 1587 cm^{-1} corresponding to a partial C=N double bond was observed in the IR spectrum of **2.**

The broad singlet signal at −44.5 ppm in the ^{19}F NMR spectrum of **2** is consistent with fast fluorine exchange on the NMR time scale. Even at a temperature as low as −80 °C ($CDCl_3/CH_2Cl_2$) this fluorine exchange could not be slowed down sufficiently. Fast fluorine exchange has also been observed for TeF_4 [11] at −100 °C. The ^{125}Te NMR spectra of **1** and **2** show resonance signals at 1450.8 and 1155.8 ppm, respectively. As expected, these signals are shifted to lower frequency as compared to the signals of their precursors $TeCl_4$ (1736.2 ppm) and TeF_4 (1285.3 ppm) in the same solvent [12].

Experimental

The reactants TeF_4 [13] and $Me_3Si(map)$ [5] were prepared according to published methods. $TeCl_4$ was obtained from Merck and was further purified by vacuum sublimation. CH_2Cl_2 was dried and distilled before use. The NMR spectra were recorded with a Bruker AM-250 spectrometer for solutions of the compounds with TMS, $CFCl_3$ and $TeMe_2$ as external references for ^1H, ^{19}F and ^{125}Te NMR, respectively. Infrared spectra were recorded with a BIORAD FTS7 spectrometer using halo oil or nujol mull and KBr plates. The mass spectrum was recorded with a Finnigan MAT-8230 spectrometer operating at an ionizing voltage of 70 eV. All manipulations were carried out either on a vacuum line or in a dry box with exclusion of moisture. The melting points were determined on samples sealed in capillaries.

$Cl_3Te(map)$ (**1**)

To a suspension of $TeCl_4$ (1.20 g, 4.44 mmol) in 50 ml of CH_2Cl_2, a solution of $Me_3Si(map)$ (0.80 g, 4.45 mmol in 25 ml of CH_2Cl_2) was added dropwise at room temperature. After completion of the slow addition, the reaction mixture became clear and yellow. The solution was reduced to 30 ml, cooled to −36 °C, and kept for crystallization for several days. The yellow crystals (m.p. 137–140 °C) were filtered off, washed with CH_2Cl_2, and dried in a vacuum. Yield 1.25 g, 83%. MS (EI) *m/z* (%) = 342 [M] (11), 307 [M−Cl] (66), 271 [M−2Cl] (3), 235 [M−3Cl] (100), 200 [$TeCl_2$] (76), 165 [TeCl] (72), 107 [map] (71). – ^1H NMR ($CDCl_3$): δ = 8.30–6.71 (m, 4H, aromatic H), 3.66 (s, 3H, NMe). – ^{125}Te NMR ($MeCN/C_6D_6$): δ = 1450.8 (br s, Te).

$C_{12}H_{14}N_4Cl_6Te_2$ (682.2)

Calcd	C 21.1	H 2.1	Cl 31.2	N 8.2,
Found	C 20.9	H 2.1	Cl 31.4	N 7.8.

$F_3Te(map)$ (**2**)

To a suspension of TeF_4 (1.77 g, 8.68 mmol) in 30 ml of CH_2Cl_2, a solution of $Me_3Si(map)$ (1.55 g, 8.61 mmol in 25 ml of CH_2Cl_2) was added dropwise at room temperature. The reaction mixture was then stirred for 30 min to ensure complete reaction. The resulting clear light yellow solution was reduced to 20 ml and allowed to stand at −36 °C for several days. This produced colorless microcrystals (m.p. 125−127 °C) which were filtered off, washed with CH_2Cl_2, and dried in a vacuum. Yield 1.9 g, 76%. MS (EI) m/z (%) = 292 [M] (11), 273 [M−F] (6), 254 [M−2F] (2), 185 [TeF_3] (10), 107 [map] (100). − ^1H NMR ($CDCl_3$): δ = 8.12−6.51 (m, 4H, aromatic H), 3.23 (s, 3H, NMe). − ^{19}F NMR ($CDCl_3$): δ = −44.5 (br s, TeF_3). − ^{125}Te NMR ($MeCN/C_6D_6$): δ = 1155.8 (br s, Te).

$C_6H_7N_2F_3Te$ (291.7)

Calcd	C 24.7	H 2.4	N 9.6,
Found	C 24.7	H 2.6	N 9.5.

Crystal structure of **1**

Yellow prismatic single crystals of **1**, suitable for X-ray analysis, were obtained as described above and sealed into glass capillaries in a dry nitrogen atmosphere. Data were collected at 293 K on a Siemens-Stoe AED 2 diffractometer using graphite monochromated Mo−Kα radiation. 2θ-scans with online profile fitting and variable scan speeds were employed. The structure was solved by Patterson methods and refined by full-matrix least squares techniques (SHELX-76).

Crystallographic data for **1:** $C_{12}H_{14}N_4Cl_6Te_2$ Mr = 682.2, a = 7.280(1), b = 9.512(1), c = 16.004(2) Å, α = 96.67(1), β = 91.95(1), γ = 105.79(1)°, V = 1057(1) Å^3, space group $P\bar{1}$, Z = 2, F(000) = 640, d_{calc} = 2.14 g/cm^{-3}, μ = 3.54 mm^{-1}, 5128 reflections collected ($7 < 2\theta < 45°$), 2745 unique and 2614 observed reflections with $F > 3.0\,\sigma(F)$. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted at calculated positions and refined using a riding model. The full-matrix refinement of 217 parameters converged with R = 0.026, R_w = 0.033, $w^{-1} = \sigma^2(F) + 0.0002\,F^2$ and maximum/minimum residual electron density +0.4/−0.9 eÅ^{-3}. Further details of the crystal structure investigation are available on request from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD 55393, the names of the authors, and the journal citation.

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