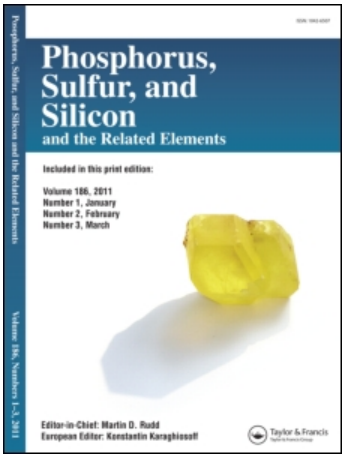

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THE CRYSTAL STRUCTURE OF 2-[(*N*,*N*-DIMETHYLAMINO)METHYL]BENZENETELLURENYL CHLORIDE

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THE CRYSTAL STRUCTURE OF 2-[(*N*,*N*-DIMETHYLAMINO)METHYL]BENZENETELLURENYL CHLORIDE

L. Engman,[a] *A. Wojtoń,*[b] *B. J. Oleksyn,*[b] *and J. Śliwiński*[b]
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*The crystal structure of 2-[(*N,N-*dimethylamino)methyl]benzenetellurenyl chloride (**2**), a compound previously formulated as bis[[2-(*N,N-*dimethylamino)methyl]phenyl] ditelluride bis hydrochloride (**1a**), was determined. In the molecule **2**, tellurium is bonded to the carbon of the phenyl group [2.120(3) Å], the nitrogen of the* ortho *dimethylamino substituent [2.362(3) Å], and the chlorine atom [2.536(1) Å]. There also is an intermolecular interaction of the tellurium atom with the phenyl ring of a neighbouring molecule [3.655(1) Å], resulting in the formation of zigzag chains along the **b** axis. The noncentrosymmetric space group of the crystal can be explained by the chiral surrounding of tellurium.*

Keywords: Conformation; crystal structure; telluroorganic compounds

Some time ago,[1] one of us reported on the catalytic peroxide decomposing activity of diaryl ditellurides in the presence of stoichiometric amounts of thiol reducing agents (thiol peroxidase activity). One of the most active catalysts tested, bis[[2-(*N*,*N*-dimethylamino)methyl]phenyl] ditelluride bis hydrochloride (**1a**), was prepared in analogy with the synthesis of the corresponding diselenide **1b**.[2] Briefly the synthesis involved *ortho*-lithiation of *N*,*N*-dimethylbenzyl amine, insertion of tellurium into the carbon-lithium bond, oxidation of the resulting arene lithium tellurolate to a ditelluride, and final treatment with hydrochloric acid. However, as shown in this article, the product formed using this procedure is 2-[(*N*,*N*-dimethylamino) methyl] benzenetellurenyl chloride (**2**). Compound **2** is likely to form via decomposition of ditelluride **1a**, involving nucleophilic

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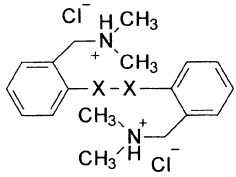
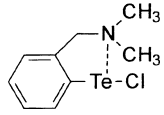
attack of chloride on the Te-Te bond accompanied by expulsion of a benzenetellurol.



1a X=Te
1b X=Se



2

EXPERIMENTAL SECTION

Yellow crystals of 2-[(*N*,*N*-dimethylamino)methyl]benzenetellurenyl chloride were obtained from ethanol by slow evaporation. A single crystal with dimensions $0.17 \times 0.15 \times 0.05$ mm, suitable for the diffraction measurement, was selected and mounted on a four-circle KM-4 diffractometer (KUMA Diffraction, Wrocław, Poland), equipped with molybdenum X-ray tube (MoKα, $\gamma = 0.71073$ Å) and a graphite monochromator. All measurements were performed at 293 (2) K. The lattice parameters were determined by the least squares analysis from the setting angles of 75 reflections, which were confined in the θ range of 2.41–27.03° The number of all measured reflections was 5272, while the number of unique reflections was 2358 (R(int) = 0.0280, R(sigma) = 0.0328). Data reduction with corrections for Lorentz and polarization effects, but not for absorption was performed using local KM-4 programs. The phase problem was solved by the direct methods using the SHELXS-97 program.

The positions of hydrogen atoms were found on subsequent difference Fourier maps. Full-matrix least squares refinement of atomic coordinates and anisotropic temperature parameters for nonhydrogen atoms was carried out, while for all hydrogens the coordinates and isotropic temperature parameters were refined. To this end SHELX-97 was used on F_o^2 with weighting scheme: $w^{-1} = \sigma^2(F_o{}^2) + (0.1P)^2 + 0.1P$, where $P = 1/3\,[\max(F_o^2, 0) + 2F_c^2]$.

The final values of the conventional discrepancy factor was R = 0.0234 for $F_o > 4$ (F_o) and 0.0270 for all 2358 unique reflections respectively; wR2 = 0.0516 for all unique reflections. Goodness of fit S = 1.006, shift/σ in the last cycle was 0.00, the largest peak on the difference Fourier map was 0.316 e/Å^3.

Crystal data:

$C_9H_{12}Cl\ N\ Te$, FW = 297.25, orthorhombic, $P2_12_12_1$,
a = 6.7638(11) Å, b = 9.9781(17) Å, c = 15.939(4) Å,
$\alpha = \beta = \gamma = 90^\circ$,
V = 1075.7(3)Å^3, Z = 4, D_x = 1.835 g/cm^3.

RESULTS AND DISCUSSION

Atomic coordinates, displacement parameters, and all bond lengths, bond angles, and torsion angles as well as the list of structure factors have been deposited with Cambridge Crystallographic Data Centre deposition number: CCDC 215223.

The structure of compound **2** together with the atom numbering, is depicted in Figure 1. Selected bond lengths, bond angles, and torsion angles are listed in Table I.

The C—C bond lenghts and angles in the phenyl ring, which is approximately planar (to within 0.008 Å), and in the dimethylaminomethyl substituent have typical values within 3σ. The bond length Te-C1, 2.120(3) Å, is similar to that observed in bis(aminophenyl)telluride.[3] The bond angle Cl-Te-C1 = 91.4(1)° in **2** is much smaller and close to the value 92.7(3)°, observed earlier for a similar compound.[3] The tellurium atom is linked by a bond of 2.362 (3) Å to the nitrogen atom of the dimethylaminomethyl group attached to the phenyl ring in *ortho* position with regard to the chlorotellurium substituent. This results in

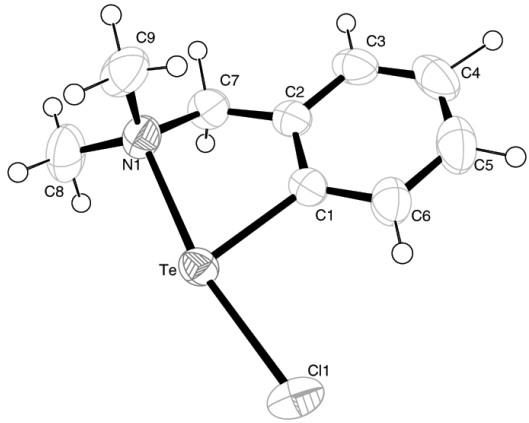
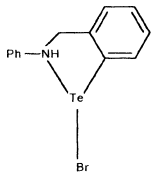


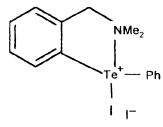
FIGURE 1 Molecular structure of 2-[(*N*,*N*-dimethylamino)methyl]benzenetellurenyl chloride.

formation of a C—C—N—Te—C five-membered ring fused with the phenyl group.

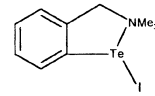
In order to compare the bond lengths and angles in **2** with the data collected hitherto we performed a CSD search[4] for compounds similar to **2**. This search provided only five structures with the refcodes: LIFNET,[5] SEPLUU,[6] SUHFUW,[7] ZIQPEU,[8] and ZISWON[9] with the following chemical formulae.



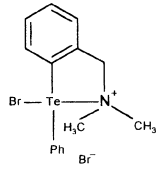
SUHFUW



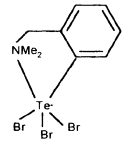
ZIQPEU



ZISWON



LIFNET



SEPLUU

The molecules of these compounds are shown in Figure 3. Only two of them, i.e., **b**. SUHFUW and **d**. ZISWON, seem strictly chemically relevant.[7,9] All the compounds found differ from **2** in the halogen atoms linked to Te and/or in the coordination number/valence of Te atom. In the compounds **a**-**e** (Figure 3) the coordination polyhedra of Te atom are distorted trigonal bipyramids. The vertical positions in all of them are occupied by weakly bonded nitrogen and halogen atoms (on mutually opposite vertices), while the equatorial position occupancy depends on the tellurium valence. Te(IV) in the compounds **a**, **c**, and **e** is equatorially surrounded by one lone electron pair and by two carbon atoms (in **c** and **e**) or one halogen and one carbon atom (**a**). Te(II) in the compounds **b** and **d** has only one carbon atom in the equatorial position, the other two being occupied by the lone electron pairs.

The bond lengths Te—C and Te—N do not seem to be affected by the substituents at tellurium and nitrogen atoms and vary in narrow ranges, i.e., 2.08–2.12 Å and 2.37–2.41 Å, respectively. The bond length values observed in the molecule **2** are found in the ranges mentioned above.

An interesting rule can be noticed for the angles of the type: C2-C1-Te and C6-C1-Te (numbering of **2**), namely the first of them is smaller than 120°, while the other is greater, so that the planarity of C1

TABLE I Bond Lengths (Å), Bond Angles, and Torsion Angles (°) for Nonhydrogen Atoms in Molecule (1) with e.s.d.s. in Parentheses

Te(1)-C(1)	2.120(3)	C(1)-C(2)	1.389(5)	C(4)-C(5)	1.385(7)
Te(1)-N(1)	2.362(3)	C(2)-C(3)	1.385(6)	C(5)-C(6)	1.396(6)
Te(1)-Cl(1)	2.5356(11)	C(2)-C(7)	1.490(6)	C(7)-N(1)	1.492(4)
C(1)-C(6)	1.371(5)	C(3)-C(4)	1.366(7)	C(8)-N(1)	1.469(6)
C(1)-Te(1)-N(1)		76.51(12)		C(3)-C(4)-C(5)	119.5(4)
C(1)-Te(1)-Cl(1)		91.40(9)		C(4)-C(5)-C(6)	120.4(5)
N(1)-Te(1)-Cl(1)		167.91(8)		C(1)-C(6)-C(5)	119.3(4)
C(6)-C(1)-C(2)		120.6(3)		C(2)-C(7)-N(1)	109.7(3)
C(6)-C(1)-Te(1)		124.8(3)		C(8)-N(1)-C(9)	110.4(4)
C(2)-C(1)-Te(1)		114.5(3)		C(8)-N(1)-C(7)	111.0(4)
C(3)-C(2)-C(1)		119.1(4)		C(9)-N(1)-C(7)	110.6(4)
C(3)-C(2)-C(7)		121.8(4)		C(8)-N(1)-Te(1)	110.9(3)
C(1)-C(2)-C(7)		119.0(3)		C(9)-N(1)-Te(1)	111.0(3)
C(4)-C(3)-C(2)		121.1(4)		C(7)-N(1)-Te(1)	102.66(19)
N(1)-Te(1)-C(1)-C(6)		162.3(3)		C(2)-C(1)-C(6)-C(5)	178.7(3)
Cl(1)-Te(1)-C(1)-C(6)		−17.9(3)		Te(1)-C(1)-C(6)-C(5)	1.3(7)
N(1)-Te(1)-C(1)-C(2)		−17.5(20		C(4)-C(5)-C(6)-C(1)	−148.8(3)
Cl(1)-Te(1)-C(1)-C(2)		162.2(2)		C(3)-C(2)-C(7)-N(1)	34.3(5)
C(6)-C(1)-C(2)-C(3)		0.8(5)		C(1)-C(2)-C(7)-N(1)	−161.8(4)
Te(1)-C(1)-C(2)-C(3)		−179.4(3)		C(2)-C(7)-N(1)-C(8)	75.3(4)
C(6)-C(1)-C(2)-C(7)		177.7(3)		C(2)-C(7)-N(1)-C(9)	−43.2(3)
Te(1)-C(1)-C(2)-C(7)		−2.5(4)		C(2)-C(7)-N(1)-Te(1)	151.8(3)
C(1)-C(2)-C(3)-C(4)		0.2(6)		C(1)-Te(1)-N(1)-C(8)	150.6(4)
C(7)-C(2)-C(3)-C(4)		−176.5(4)		Cl(1)-Te(1)-N(1)-C(8)	−85.1(3)
C(2)-C(3)-C(4)-C(5)		−0.5(7)		C(1)-Te(1)-N(1)-C(9)	−86.2(5)
C(3)-C(4)-C(5)-C(6)		−0.3(7)		Cl(1)-Te(1)-N(1)-C(9)	33.1(3)
Te(1)-C(1)-C(6)-C(5)		−1.5(6)		C(1)-Te(1)-N(1)-C(7)	32.0(6)

surrounding is maintained. In the all compounds these angles vary in the ranges: 114.6–116.1° and 123.8–124.7° respectively. A possible explanation of this behavior is the formation of the Te—N bond leading to the five-membered ring closure in all the compounds. The absolute values of torsion angles about the bonds in the five-membered rings, with the exception of Te-C1-C2-C7, are found in the wide range: 8.7–48.2°. The angle Te-C1-C2-C7, the absolute values of which vary in the range 0.1–8.6°, indicates a tendency of the bonds Te-C1, C1-C2, C2-C7 to be mutually coplanar. The corresponding torsion angles in **2** are found in the same range. The halogen atoms (X = Br, I, Cl), coordinated to Te, are displaced from the plane of phenyl ring as shown by the torsion angles X-Te-C1-C6. Their absolute values for the compounds compared are in the range: 14.7–26.9°, while for **2** this angle is 17.9(3)°.

An unexpected feature of the investigated crystal structure is its lack of centrosymmetry, which does not seem to result from the chirality of

the molecules. However, when the closest surroundings of the tellurium atom are examined, we can conclude that this atom may be treated as a stereogenic centre. There are four different ligands connected with this atom, namely C1, N1, Cl, and the phenyl ring (π) of the neighboring molecule in the position ($-x + 2$, $y - 0.5$, $-z + 1.5$).

The distance between the Te atom and the centroid (Ct) of π is 3.665(1) Å. This value is smaller than the sum of the tellurium atom van der Waals radius (2.2 Å) and the aromatic molecule thickness (1.85 Å).[10] The Te$\cdots\pi$ interactions lead to the formation of zigzag chains along b axis (Figure 2), similar to those described by Zukerman-Schpector and Haiduc in their review of the tellurium interactions with π-aryl moieties.[11]

The ligands around the Te atom are arranged in the vertices of a distorted square with the angles between bonds formed by the tellurium atom with Cl1 and Ct, i.e., Cl1-Te-Ct, N1-Te-Ct, being respectively: 95.58(9)° and 98.37(9)°. However, as suggested by the Referee, the coordination polyhedron of Te(II) in this compound should be a pseudo trigonal bipyramid like those in SEPLUU (Figure 3b) and

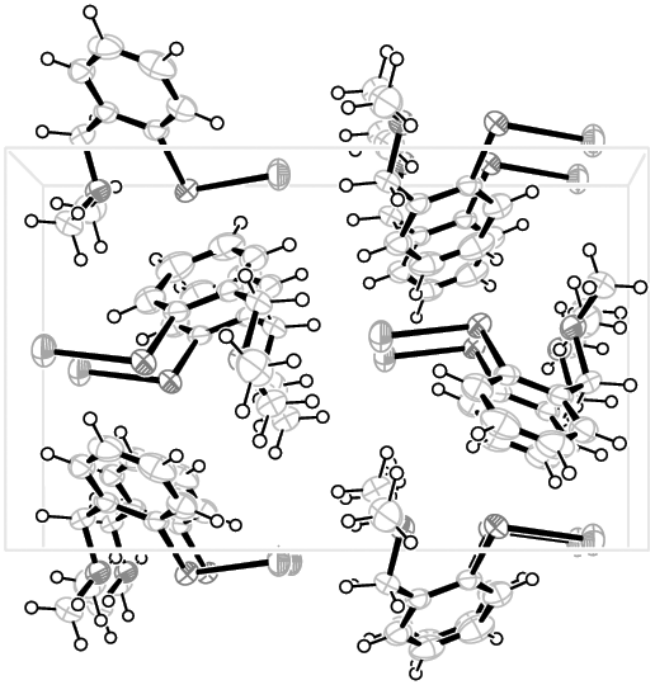


FIGURE 2 Unit cell of 2-[(*N*,*N*-dimethylamino)methyl]benzenetellurenyl chloride projected along a axis.

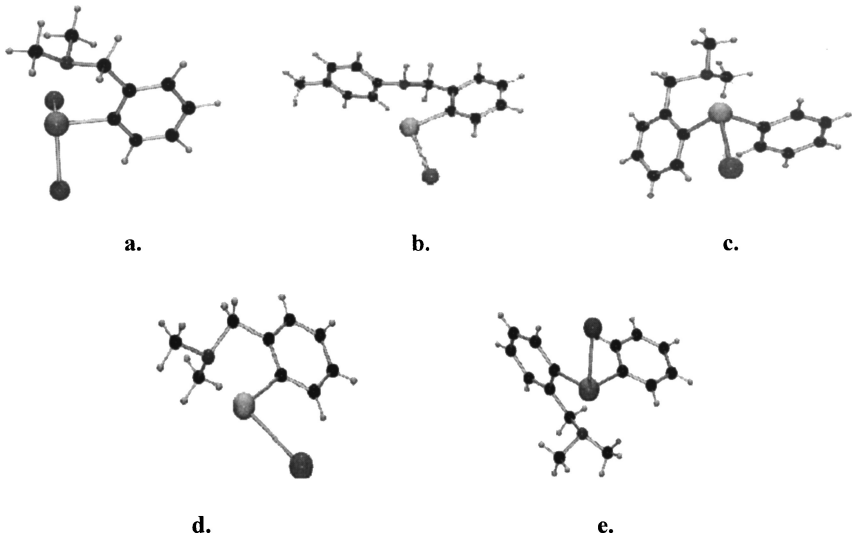


FIGURE 3 The molecular structures of the compounds found in CSD: **a.** SEPLUU, **b.** SUHFUW, **c.** ZIQPEU, **d.** ZISWON, and **e.** LIFNET.

ZISWON (Figure 3d). Thus, the Cl and N can be considered as the vertical ligands, while C1 and two lone pairs, one of which interacts with the π system of an adjoining phenyl, occupy the equatorial positions. If we assume the priority of the ligands: π, Cl1, N, C1, we can ascribe the absolute configuration S to the tellurium atom.

The glutathione peroxidase-like properties of tellurenyl chloride **2** can be nicely rationalized using the catalytic cycle originally proposed for ditellurides.[1] One only has to make the reasonable assumption that compound **2** in the presence of thiol is converted to a tellurosulfide.[12]

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