Synthesis and structure of pyridine-2-tellurenyl chloride

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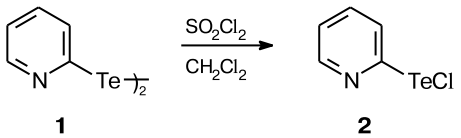
The structure of pyridine-2-tellurenyl chloride, the chlorination product of di(2-pyridyl) ditelluride by sulfuryl chloride, was studied by X-ray diffraction analysis.

Key words: organyltellurenyl halides, di(2-pyridyl) ditelluride, pyridine-2-tellurenyl chloride.

Two approaches to the synthesis of organyltellurenyl halides RTeHal as stable individual substances have been formed in chemistry of organotellurium compounds.[1—9] In terms of these approaches, the stabilization of alkane- and arenetellurenyl halides is achieved due to bulky substituents or functional groups (usually nitrogen- or oxygen-containing) capable of forming intramolecular coordination bonds O→Te and N→Te, which were introduced into the position adjacent to the tellurium atom. Evidently, this intramolecular coordination provides the stability of unique, as far as we know, representatives of hetarenetellurenyl halides, namely, thiophenetellurenyl halides containing the pyridyl or acetyl fragment in the *ortho*-position to the halotellurenyl group.[10,11]

The present work is devoted to the synthesis of the first representative of hetarenetellurenyl halides bearing a nitrous base, pyridyl group as a hetaryl substituent. Di(2-pyridyl) ditelluride (**1**) synthesized according to a known procedure[12] was used as a precursor of the target tellurenyl chloride. We found that the reaction of sulfuryl chloride with ditelluride **1** in methylene chloride at 20 °C affords pyridine-2-tellurenyl chloride (**2**) in 96% yield (Scheme 1).

Scheme 1



1 **2**

The molecular structure of compound **2** was determined by X-ray diffraction analysis (Fig. 1). Selected bond lengths and bond angles are given in Table 1. In the crystalline state molecules of compound **2** are dimerized due to the intermolecular coordination of the nitrogen and tellurium atoms. The Te(1B)—N(1A) and Te(1A)—N(1B) distances are 2.329(4) and 2.309(3) Å, respectively, which is noticeably greater than the sum of covalent radii of the N and Te atoms (2.1 Å) but is substantially smaller than the sum of the van der Waals radii of these atoms (3.75 Å).[13] The Te(1B)—C(1B) and Te(1A)—C(1A) distances are 2.125(4) and 2.120(4) Å, which is comparable with the sum of covalent radii of the Te and C atoms (2.14 Å).[13] The direction of coordination of the N atom to the Te atom of the adjacent molecule almost coincides with the direction of the Te—Cl bond and is nearly perpendicular to the Te—C bond.

The Te(1A)Te(1B)C(1A—5A)N(1A) and Te(1A)-Te(1B)C(1B—5B)N(1B) fragments are planar, and the average shifts of the atoms are 0.014 and 0.021 Å, respectively. The angle between the planes of these fragments along the Te(1A)...Te(1B) line is 75.4°. The chlo-

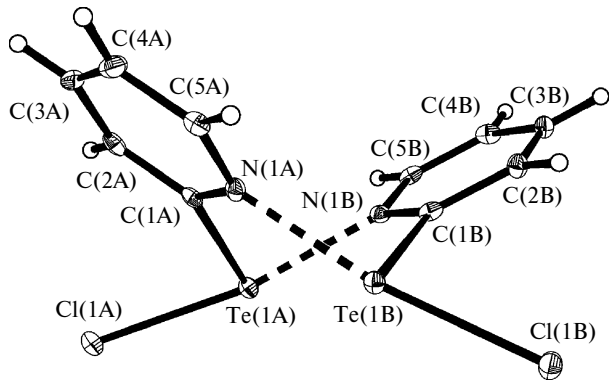


Fig. 1. Molecular structure of compound **2**. Thermal ellipsoids of non-hydrogen atoms are given with the 30% probability.

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Table 1. Selected bond lengths (*d*) and bond angles (ω) in the crystal structure of compound **2**

Bond	*d*/Å	Angle	ω/deg
Te(1B)—C(1B)	2.125(4)	C(1B)—Te(1B)—N(1A)	83.10(15)
Te(1B)—N(1A)	2.329(4)	C(1B)—Te(1B)—Cl(1B)	87.25(12)
Te(1B)—Cl(1B)	2.539(1)	N(1A)—Te(1B)—Cl(1B)	169.87(9)
Te(1A)—C(1A)	2.120(4)	C(1A)—Te(1A)—N(1B)	83.32(14)
Te(1A)—N(1B)	2.309(3)	C(1A)—Te(1A)—Cl(1A)	86.48(11)
Te(1A)—Cl(1A)	2.558(1)	N(1B)—Te(1A)—Cl(1A)	169.35(9)

rine atoms are in the *trans*-position relative to the inflection line Te(1A)...Te(1B). The torsion angle Cl(1A)—Te(1A)—Te(1B)—Cl(1B) is 126.0°. The shifts of the Cl(1A) and Cl(1B) atoms from the planes of the Te(1A)Te(1B)C(1B—5B)N(1B) and Te(1A)Te(1B)-C(1A—5A)N(1A) fragments are 0.343 and 0.352 Å toward the hydrogen atoms at C(2A) and C(2B), respectively. Perhaps, this is due to the intramolecular contacts Cl...H, being 2.991 and 2.936 Å (3.0 Å).[13]

In molecules of compound **2** the interatomic distances Te(1B)—Cl(1B) and Te(1A)—Cl(1A) are 2.539(1) and 2.558(1) Å, which is noticeably greater than the sum of covalent radii of the Te and Cl atoms (2.35 Å)[13] but is substantially smaller than the sum of their van der Waals radii (3.95 Å).[13] Most likely, this elongation of the Te—Cl distances compared to the sum of covalent radii indicates that additional interactions with the Cl atom exist in the crystal. Indeed, in the crystal packing molecules of compound **2** form the two-dimensional packing along the axis *a* of the unit cell in such a way that the layers of molecules —A—B—A— alternate in the direction perpendicular to the axis *a* (Fig. 2). The molecules of adjacent layers interact through the intermolecular contacts Te...Cl. The Te(2E)...Cl(1A), Te(2F)...Cl(1B), Te(2A)...Cl(1C), and Te(2B)...Cl(1D) distances are 3.521 Å, whereas the Te(1A)...Cl(2F) and Te(1D)...Cl(2A) distances are 3.552 Å, which is noticeably shorter than the sum of van der Waals radii of the Te and Cl atoms (3.95 Å).[13]

The detailed analysis of the crystal packing of compound **2** along with the intermolecular contacts Te...Cl designated in Fig. 2 showed additional intermolecular interactions involving the chlorine atom. The intermolecular distances Cl...C are 3.394 and 3.267 Å. This is appreciably smaller than the value of 3.45 Å,[14] indicating that specific interactions Cl...C take place. Among the intermolecular contacts Cl...H, the shortest are the contacts with distances of 2.717 and 2.790 Å, which are considerably less than the sum of van der Waals radii of the Cl and H atoms (3.0 Å)[13] and are close to the value of 2.67 Å characteristic[14] of the shortened Cl...H contacts.

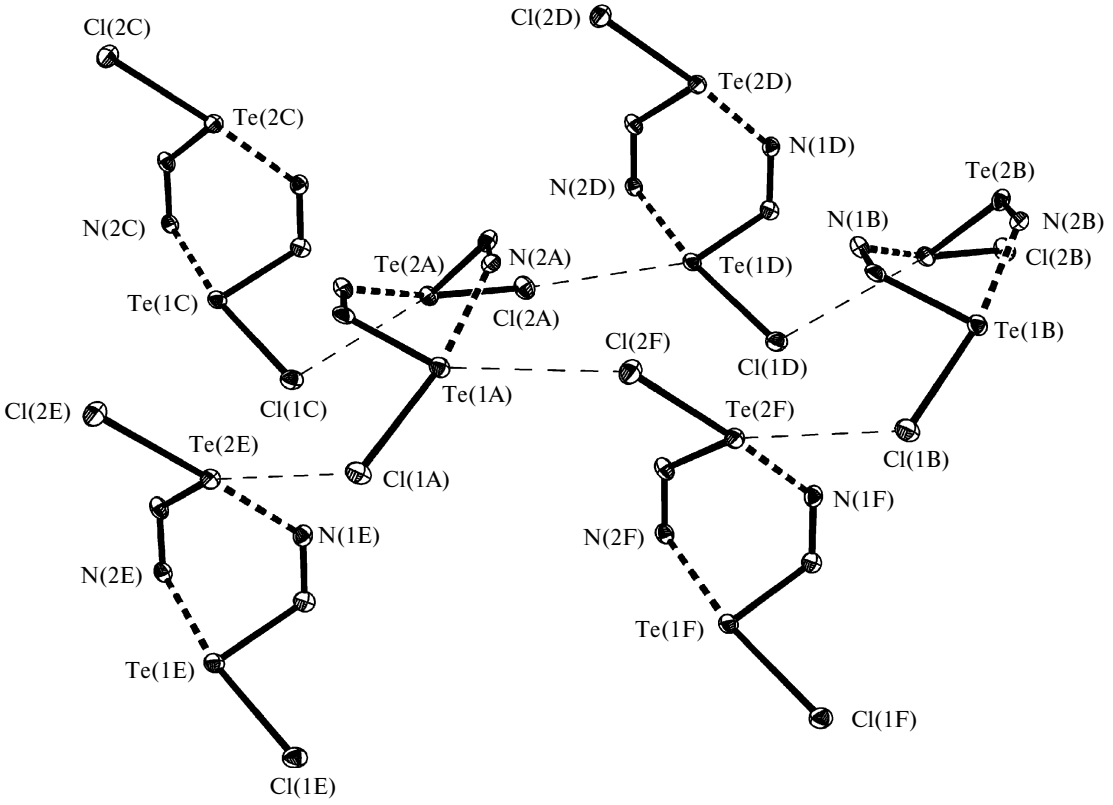

Fig. 2. Fragment of the crystal packing of molecules **2**. Thermal ellipsoids of non-hydrogen atoms are given with the 50% probability. Hydrogen atoms and pyridine fragments are omitted for clarity.

Thus, the dimers in crystalline compound **2** are stabilized by various intermolecular interactions with the neighboring molecules. This results in the supramolecular organization of the synthesized compound in crystal.

It seems interesting to analyze the structure of compound **2** from the viewpoint of the degree of filling of the coordination space of the Te atoms. To calculate the degree of filling of the coordination sphere of the metal atoms, we used the *G* parameter, where $G = (\Sigma\Omega_i/4\pi) \cdot 100\%$ ($\Sigma\Omega_i$ is the sum of solid angles of the ligands with allowance for the interligand overlapping in steradians).[15—18] The calculated values of the *G* parameter in the monomeric units of compound **2** are 28.1(2) and 28.3(2)% (for Te(1A) and Te(1B), respectively). Therefore, the ligands in the monomeric units of compound **2** insufficiently screen the Te atom from intermolecular interactions, which leads to the dimerization of molecules and, correspondingly, to an increase in the degree of screening of the Te(1A) and Te(1B) atoms to 46.3(2)%. The intermolecular interactions Te...L (L is the ligand of the dimer) in crystal also indicate an insufficient screening of the Te atoms. As a result, shortened intermolecular contacts Te...Cl occur in crystal. Taking into account these constants, the degree of filling of the coordination sphere of the Te atoms increases to approximately 73%, which is substantially higher than that in the monomeric unit. Note that in rare-earth metal complexes the shielding of Ln cations by ligands is substantially higher being 85(3)%.

Thus, we synthesized for the first time pyridine-2-tellurenyl chloride and showed that an insufficient shielding of the Te atom in this compound resulted in its dimerization.

Experimental

Pyridine-2-tellurenyl chloride (1). A solution of sulfuryl chloride (0.14 g, 1 mmol) in methylene chloride (10 mL) was added to a solution of di(2-pyridyl) ditelluride (0.41 g, 1 mmol) in methylene chloride (10 mL) at 20 °C. After 1 h, the precipitate of compound **1** (0.26 g, 54%) was filtered off, and the filtrate was evaporated *in vacuo*. The recrystallization of the residue from methylene chloride gave additionally 0.20 g (42%) of compound **1**. The crystals are orange, m.p. 195—197 °C. Found (%): C, 24.57; H, 1.59; N, 5.72. C_5H_4ClNTe. Calculated (%): C, 24.90; H, 1.67; N, 5.81.

X-ray diffraction analysis of compound 2. Experimental sets of intensities were measured on a Smart APEX automated diffractometer (graphite monochromator, Mo-Kα radiation, ω and φ scan modes). An absorption correction was applied using the SADABS program.[19] The structure of compound **2** was solved by a direct method and refined by least squares on F^2_{hkl} in the anisotropic approximation for all non-hydrogen atoms. Hydrogen atoms were fixed in geometrically calculated positions and refined in the riding model ($U_{iso}(H) = 1.2U_{eq}(C)$). All calculations were performed using the SHELXTL v.6.12 program package.[20] The crystals of $C_{10}H_8Cl_2N_2Te_2$ are monoclinic at 100 K, a = 10.0103(4), b = 8.0519(3), c = 16.4700(7) Å, β = = 103.8800(10)°, V = 1288.75(9) Å^3, Z = 4, space group $P2(1)/n$, d_{calc} = 2.486 g cm^{-3}, μ = 4.915 mm^{-1}, 2.55 ≤ θ ≤ 25.99°, 7357 measured reflections, of which 2524 reflections were independent (R_{int} = 0.0228), GOOF = 1.057, R_1 = 0.0278, wR_2 = 0.0625 ($I > 2\sigma(I)$), R_1 = 0.0357, wR_2 = 0.0646 (for all data), residual electron density 1.578/−0.772 eÅ^{-3}.

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