

Synthesis and Crystal Structures of new Complex Salts Containing both Cationic and Anionic Tellurium(IV) Species: The Role of Secondary Bonds in the Arrangement of Tellurium Based Tectons

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Neste trabalho divulgamos a síntese e a estrutura cristalina de uma série de três novos complexos de telúrio(IV), $[\text{Te}(\text{C}_6\text{H}_5)(\text{CH}_3)_2][\text{TeX}_4(\text{C}_6\text{H}_5)]$, X = Cl (**1**), Br (**2**) ou I (**3**). Nesses complexos, as ligações secundárias promovem diferentes arranjos estruturais, mostrando o caráter tectônico das espécies de telúrio. Em **1** e **2**, a interação $\text{Te}\cdots\text{X}$ promove um arranjo polimérico na forma de “zig-zag” para os ânions tetra-halofeniltelurato(IV). Em **3**, as ligações secundárias $\text{Te}\cdots\text{I}$ induzem um arranjo diferenciado para os ânions, que estão organizados de forma antiparalela.

We report herein the synthesis and the crystal structures of three new tellurium(IV) complexes, $[\text{Te}(\text{C}_6\text{H}_5)(\text{CH}_3)_2][\text{TeX}_4(\text{C}_6\text{H}_5)]$, X = Cl (**1**), Br (**2**), I (**3**). In these complexes, the secondary bonds promote different structural arrangements due to the tectonic character of the tellurium species. In **1** and **2**, the $\text{Te}\cdots\text{X}$ interactions create a polymeric “zig-zag” chain of the tetrahalo-phenyltellurate(IV) anions. In **3**, the secondary $\text{Te}\cdots\text{I}$ bonds induce a different arrangement for the anions that are organized in a pseudo-dimeric antiparallel fashion.

Keywords: organotellurium halides, tectonic tetrahalo-organyltellurates, secondary bonding

Introduction

Several classes of organytellurium halide compounds are known, including species of general formula TeX_3R , TeX_2R_2 and TeXR_3 (R=alkyl, aryl; X=Cl, Br, I). The solid state structures of the tellurium(IV) compounds are themselves very interesting owing to the occurrence of secondary tellurium-halogen bonds ($\text{Te}\cdots\text{X}$),¹ which create exceptional supramolecular structures, leading to the formation of polymeric chains, dimeric structures, or monomers with fairly strong intermolecular interactions.²⁻⁶ We have been interested for some time in the synthesis and crystal structures of TeX_3R compounds and their derivatives, such as the $[\text{TeX}_4\text{R}]^-$ anions. These halogenated tellurates may be considered tectons (any species whose interactions are dominated by particular associative forces that induce the self-assembly of an organized network with specific architectural or functional features⁷) where the different packing arrangements in the crystal lattice of $[\text{TeX}_4\text{R}]^-$ salts are determined by the secondary bonds which complete the octahedral coordination

at tellurium. We have already observed this tendency in a great number of examples with cations of alkali metals or pyridonium and ammonium derivatives.⁸⁻¹¹ We now report the synthesis and crystal structures of $[\text{Te}(\text{C}_6\text{H}_5)(\text{CH}_3)_2][\text{TeX}_4(\text{C}_6\text{H}_5)]$, X = Cl (**1**), Br (**2**) and I (**3**), complexes in which organytellurium(IV) ion is found in both anionic and cationic species.

Experimental

All reactions were conducted under nitrogen, but recrystallizations of the complexes were done in air. Methanol was dried with Mg/I_2 and acetonitrile with CaH_2 , and both were distilled prior to use.¹² The compound iododimethylphenyltellurium(IV) was prepared according to Reid's procedure;¹³ the analogous chloride and bromide derivatives were prepared by ion exchange with the appropriate silver halide in hot methanol. Trihalophenyltellurium(IV) compounds were prepared following literature procedures.¹⁴ Melting points were recorded in a Microquímica equipment and are uncorrected. Elemental analyses (C, H) were

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performed at the Microanalytical Laboratory of the Chemistry Institute – University of São Paulo.

¹H and ¹²⁵Te NMR

The NMR spectral data were obtained in a Varian Mercury Plus 7.05 T spectrometer with 300.07 MHz (¹H) and 94.74 MHz (¹²⁵Te). The samples were dissolved in a 9:1 mixture of acetone-*d*₆ and DMSO-*d*₆, respectively. The solutions were measured in NMR tubes of 5 mm, at 300 K. The ¹H NMR chemical shifts are relative to Si(CH₃)₄ as internal reference. The ¹²⁵Te NMR spectra were taken with reference to Te(CH₃)₂. A capillary containing Te₂(C₆H₅)₂ dissolved in CDCl₃ (δ 450) was used as external reference. By convention, the chemical shift is positive when the resonance occurs at higher frequency than that of the reference.

General procedure for the preparation of dimethylphenyltellurium(IV) tetrahalophenyltellurates(IV) (general formula [Te(C₆H₅)(CH₃)₂][TeX₄(C₆H₅)])

To a solution of 1.3 mmol of TeX₃(C₆H₅), trihalophenyltellurium(IV), in 20 mL of methanol cooled to 0 °C, 1.3 mmol of TeX(C₆H₅)(CH₃)₂, halodimethylphenyltellurium(IV), dissolved in 20 mL of methanol were added dropwise. Precipitation of the desired products occurs immediately. After stirring for 30 min, the powdered products were collected by filtration and recrystallized from acetonitrile.

[Te(C₆H₅)(CH₃)₂][TeCl₄(C₆H₅)] (**1**). Properties: air stable, yellow crystalline substance; C₁₄H₁₆Te₂Cl₄ (581.30 g mol⁻¹). Yield: 90% based on TeCl₃(C₆H₅); mp: 158 - 159 °C; C and H Elemental Analysis: Found (%): C, 29.01; H, 3.25; Calc. (%): C, 28.92; H, 2.78. ¹H NMR (ppm): δ 2.53 (s, Me), 7.44-8.63 (m, aryl); ¹²⁵Te NMR (ppm): δ 581.88 (cation), 1234.81 (anion).

[Te(C₆H₅)(CH₃)₂][TeBr₄(C₆H₅)] (**2**). Properties: air stable, orange-reddish crystalline substance; C₁₄H₁₆Te₂Br₄ (759.10 g mol⁻¹). Yield: 94% based on TeBr₃(C₆H₅); mp: 125 - 126 °C; C and H Elemental Analysis: Found (%): C, 21.74; H, 2.85; Calc. (%): C, 22.15; H, 2.13. ¹H NMR (ppm): δ 2.54 (s, Me), 7.39-8.77 (m, aryl); ¹²⁵Te NMR (ppm): δ 581.04 (cation), 1203.87 (anion).

[Te(C₆H₅)(CH₃)₂][Te(C₆H₅)I₄] (**3**). Properties: air stable, black crystalline substance; C₁₄H₁₆Te₂I₄ (947.10 g mol⁻¹). Yield: 85% based on TeI₃(C₆H₅); mp: 119 - 120 °C; C and H Elemental Analysis: Found (%): C, 17.36; H, 2.22;

Calc. (%): C, 17.75; H, 1.71. ¹H NMR (ppm): δ 2.51 (s, Me), 7.14-8.58 (m, aryl); ¹²⁵Te NMR (ppm): δ 584.02 (cation), 951.08 (anion).

Crystallography

X-ray data were collected on a Bruker X8 APEX II diffractometer using Mo Kα radiation (0.71073 Å). The crystallographic structures of **1**, **2** and **3** were solved by direct methods (SHELXS-97).¹⁵ Refinements were carried out with the SHELXL-97 package.¹⁶ All refinements were made by full-matrix least-squares on *F*² with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were included in the refinement in calculated positions.

Results and Discussion

The new tellurium(IV) complexes were obtained in good yields by the reactions of methanolic solutions of the halodimethylphenyltellurium(IV) with the appropriate trihalophenyltellurium(IV) to afford microcrystalline solids. In order to examine the occurrence and extent of Te...X secondary bonds, and the effect of these interactions on the environment at tellurium atoms, crystallographic analyses were carried out on single crystals of the products obtained from the slow evaporation of acetonitrile solutions. Crystal data and details of the data collection are given in Table 1. Solution NMR spectra confirm the ionic nature of the product.

The solution ¹²⁵Te NMR spectra show two peaks for each compound. The low frequency peak, around δ 580, is attributed to the cationic [Te(C₆H₅)(CH₃)₂]⁺ species, which corresponds well to the value found for [Te(C₆H₅)(CH₃)₂]I (δ 550 in DMSO).¹⁷ The lower field peak, attributed to the anionic [TeX₄Ph]⁻ species, show chemical shifts at δ 1234.81, 1203.87 and 951.08 for **1**, **2** and **3** respectively. The chlorine atom, being the most electronegative of the halides, deshields best the tellurium atom.¹⁷

The crystal structures of **1**, **2** and **3** confirm that the compounds are essentially ionic. Within the crystals, the packing is determined by Te...X secondary bonds between anion-anion and cation-anion pairs. The primary coordination geometries of the tellurium cations, as well as the tellurate anions, are similar in all structures. The geometry of the tellurium cation is trigonal pyramidal while the tellurate anion is square-pyramidal. When the two Te...X secondary bonds are considered, the tellurium cation has a distorted square pyramidal geometry with the phenyl group in the apical position. The resulting geometry is very similar to that of an equivalent tellurate anion. When the secondary

Table 1. Crystallographic data of the new complexes synthesized

	1	2	3
Empirical formula	C ₁₄ H ₁₆ Cl ₄ Te ₂	C ₁₄ H ₁₆ Br ₄ Te ₂	C ₁₄ H ₁₆ I ₄ Te ₂
Formula weight	581.27	759.11	947.07
T/(K)	295(2)	295(2)	295(2)
Radiation, λ/(Å)	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073
Crystal system, space group	Monoclinic, P2 ₁ /c	Monoclinic, P2 ₁ /c	Monoclinic, P2 ₁ /n
Unit cell dimensions			
a/(Å)	12.2002(2)	12.5780(4)	9.6060(4)
b/(Å)	9.1126(2)	9.3793(4)	9.5067(4)
c/(Å)	16.8918(3)	17.3082(6)	23.3779(9)
β/(°)	92.7170(10)	91.934(2)	91.567(2)
V/(Å ³)	1875.84(6)	2040.73(13)	2134.10(15)
Z, calculated density/(g cm ⁻³)	4, 2.058	4, 2.471	4, 2.948
Absorption coefficient/(mm ⁻¹)	3.668	10.681	8.511
F(000)	1088	1376	1664
Crystal size/(mm)	0.304×0.175×0.136	0.0596×0.054×0.054	0.25×0.22×0.20
θ range/(°)	1.67 to 30.53	1.62 to 30.26	3.02 to 30.13
Index ranges	-17 ≤ h ≤ 17 -12 ≤ k ≤ 13 -24 ≤ l ≤ 24	-17 ≤ h ≤ 17 -13 ≤ k ≤ 13 -14 ≤ l ≤ 24	-10 ≤ h ≤ 13 -13 ≤ k ≤ 11 -29 ≤ l ≤ 33
Reflections collected	26979	19724	24945
Reflections unique	5721	6055	6282
Completeness	99.8%	99.3%	99.7%
Refinement method	Full matrixLeast squares on F ²	Full matrixLeast squares on F ²	Full matrixLeast squares on F ²
Absorption correction	Multi-scan (SADABS)	Multi-scan (SADABS)	Multi-scan (SADABS)
Data/restraints/parameters	5721/0/181	6055/0/181	6282/0/181
Goodness-of-fit on F ²	1.235	1.021	1.086
Final R indices [I>2σ(I)]	R ₁ =0.0193, wR ₂ =0.0607	R ₁ =0.0405, wR ₂ =0.1129	R ₁ =0.0340, wR ₂ =0.0777
R indices (all data)*	R ₁ =0.0256, wR ₂ =0.0756	R ₁ =0.0665, wR ₂ =0.1277	R ₁ =0.0492, wR ₂ =0.0824
Largest difference peak and hole/(e Å ⁻³)	0.963 and -0.884	1.444 and -1.309	1.392 and -1.284

$$* R_1 = |F_o - F_c|/|F_o|; wR_2 = [w(F_o^2 - F_c^2)^2/(wF_o^2)]^{-1/2}.$$

bonds are considered for the tellurate anion, the resulting geometry is a distorted octahedron, with the secondary bond in the *trans* position to the phenyl group, forming a structure similar to an equivalent tellurate dianion. Table 2 shows selected primary and secondary bonding distances within the compounds.

The structures of **1** and **2** are isotypic. In these structures, there are two sets of secondary bonds: one with anion-anion interactions and another with cation-anion

interactions. The first set of secondary bonds is formed by non-reciprocal Te1...X4' interactions between the tellurium atoms and the halogen atoms of the tellurate anions to create a polymeric "zig-zag" chain parallel to the *b* crystallographic axis (see Figure 1). In **1**, the Te1...Cl4' distance is 3.4600(1) Å, around 0.350 Å less than the sum of the van der Waals radii; in **2**, the Te1...Br4' distance is 3.5257(1) Å, around 0.384 Å less than the sum of the van der Waals radii. The second set of secondary

Table 2. Selected bond lengths. The covalent bonds are represented by — and the secondary bonds by ... Symmetry operations are depicted under the respective columns

1	2	3
Te1—C1 = 2.135(2)	Te1—C1 = 2.145(5)	Te1—C7 = 2.158(5)
Te1—Cl1 = 2.5442(7)	Te1—Br1 = 2.7239(7)	Te1—I1 = 2.9712(5)
Te1—Cl2 = 2.5003(7)	Te1—Br2 = 2.7001(7)	Te1—I2 = 2.9859(5)
Te1—Cl3 = 2.5377(7)	Te1—Br3 = 2.7211(7)	Te1—I3 = 2.9204(5)
Te1—Cl4 = 2.5240(7)	Te1—Br4 = 2.6906(7)	Te1—I4 = 2.8845(5)
Te1...Cl4' = 3.4600(1)	Te1...Br4' = 3.5257(1)	Te1...I2' = 3.7766(1)
Te2—C7 = 2.107(3)	Te2—C7 = 2.099(6)	Te2—C1 = 2.133(6)
Te2—C8 = 2.114(3)	Te2—C8 = 2.112(7)	Te2—C2 = 2.103(6)
Te2—C9 = 2.113(3)	Te2—C9 = 2.138(7)	Te2—C3 = 2.118(6)
Te2...Cl1' = 3.5105(1)	Te2...Br1' = 3.6786(1)	Te2...I2 = 3.9018(2)
Te2...Cl3 = 3.4477(1)	Te2...Br3 = 3.5619(1)	Te1...I3'' = 4.0096(1)

$$' = 1-x; -0.5+y; 0.5-z.$$

$$' = 1-x; -0.5+y; 0.5-z.$$

$$' = 1-x, 1-y, -z; '' = x, 1+y, z.$$

bonds are created by $\text{Te2}\cdots\text{X1}'$ and $\text{Te2}\cdots\text{X3}$ interactions between the tellurium cations and tellurate anions. The tellurium cations are arranged along the polymeric tellurate anionic chain.

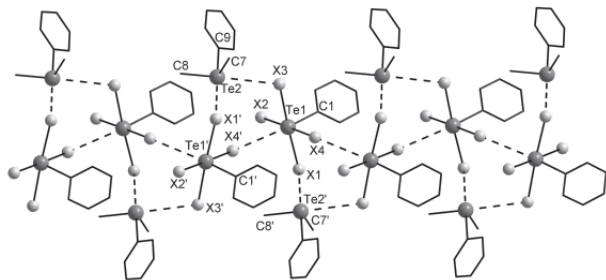


Figure 1. General representation for the structures of **1** and **2**, emphasizing the zig-zag architecture along the *b* axis promoted by the secondary bonds $\text{Te}\cdots\text{X}$ ($\text{X}=\text{Cl}, \text{Br}$). Symmetry operations to generate equivalent atoms: $' = 1-x; -0.5+y; 0.5-z$.

The structure of **3** is different from those of **1** and **2**. The strong reciprocal $\text{Te}\cdots\text{I}$ secondary interactions between the tellurate anions in **3** form tellurate dimers. These are united by secondary bonding to the tellurium cations made up from $\text{Te1}\cdots\text{I2}'$ and $\text{Te1}'\cdots\text{I2}$ interactions to form a polymeric chain in the direction of the crystallographic *b* axis (Figure 2). Additional interactions between the iodide atoms of the tellurate anions, $\text{I1}\cdots\text{I3}$ (3.771(1) Å) and $\text{I2}\cdots\text{I4}$ (3.859(1) Å), create a lamellar structure perpendicular to the crystallographic *c* axis. The tellurate dimers form a square net into which the tellurium cations pack. Small spaces between the dimers form perpendicular tunnels along the crystallographic *a* and *b* axes.

The secondary bonding $\text{Te}\cdots\text{X}$ exhibited by **1**, **2** and **3** in the solid state allow these compounds to be viewed as a supramolecular assembly of tellurium cations and tellurate anions. These three new structures with different architectures confirm the tectonic character of the tellurium

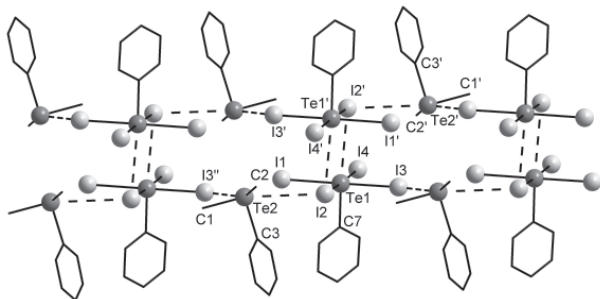


Figure 2. Representation of the structure of **3**, emphasizing the dimeric antiparallel architecture to the anions, promoted by the secondary bonds $\text{Te}\cdots\text{I}$. Symmetry operations to generate equivalent atoms: $' = 1-x, 1-y, -z$; $'' = x, 1+y, z$.

and tellurate ions in which the secondary bonds play a fundamental role in the architecture of the crystal structures.

Supplementary Information

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre CCDC nos. CSD 610462, 610463 and 610464 for compounds **1**, **2** and **3**. Further details of the crystal structures investigations are available free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk). Proton and Tellurium NMR spectra of compounds are available free of charge at <http://jbc.sbq.org.br>, as a PDF file.

Acknowledgments

The authors thank Professor S. S. Lemos (UnB) for access to the NMR Varian Mercury Plus spectrometer. The authors gratefully acknowledge financial support from CNPq, CAPES e FAPERGS via PRONEX and a scholarship from CNPq (S.S.S.).

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Received: June 12, 2006

Published on the web: December 1, 2006

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The NMR spectral data were obtained in a Varian Mercury Plus 7.05 T spectrometer with 300.07 MHz (^1H) and 94.74 MHz (^{125}Te). The samples were dissolved in a 9:1 mixture of acetone- d_6 and DMSO- d_6 , respectively. The solutions were measured in NMR tubes of 5 mm, at 300 K. The ^1H NMR chemical shifts are relative to $\text{Si}(\text{CH}_3)_4$

as internal reference. The ^{125}Te NMR spectra were taken with reference to $\text{Te}(\text{CH}_3)_2$. A capillary containing $\text{Te}_2(\text{C}_6\text{H}_5)_2$ dissolved in CDCl_3 (δ 450) was used as external reference. By convention, the chemical shift is positive when the resonance occurs at higher frequency than that of the reference.

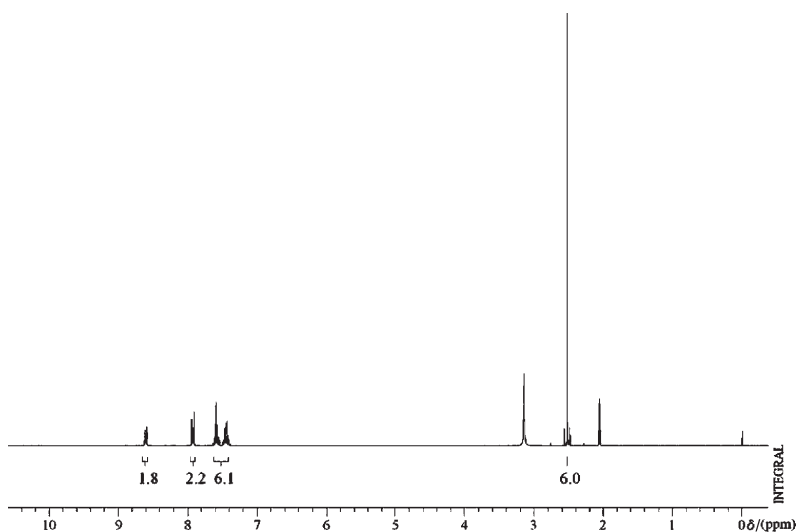


Figure S1. ^1H NMR spectrum of the compound 1.

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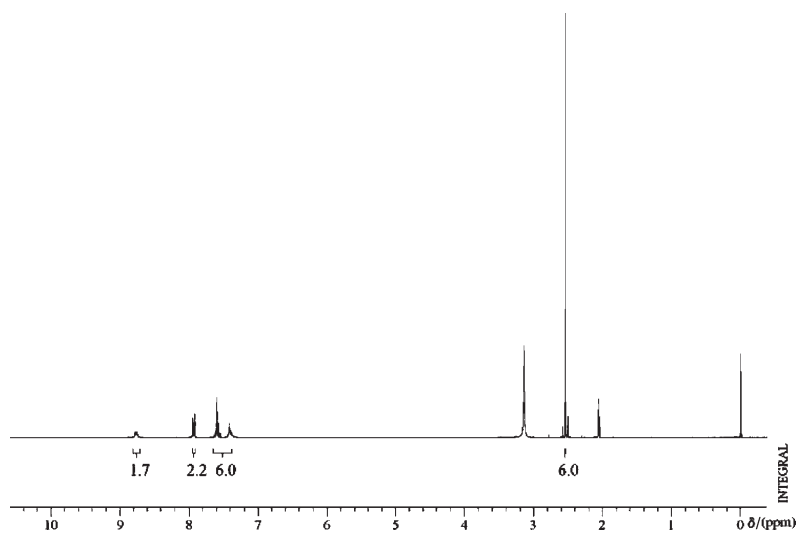


Figure S2. ¹H NMR spectrum of the compound 2.

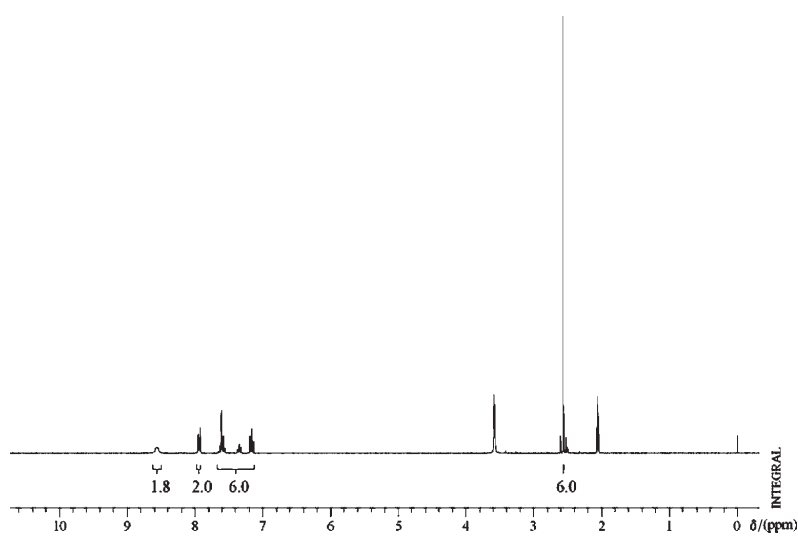


Figure S3. ¹H NMR spectrum of the compound 3.

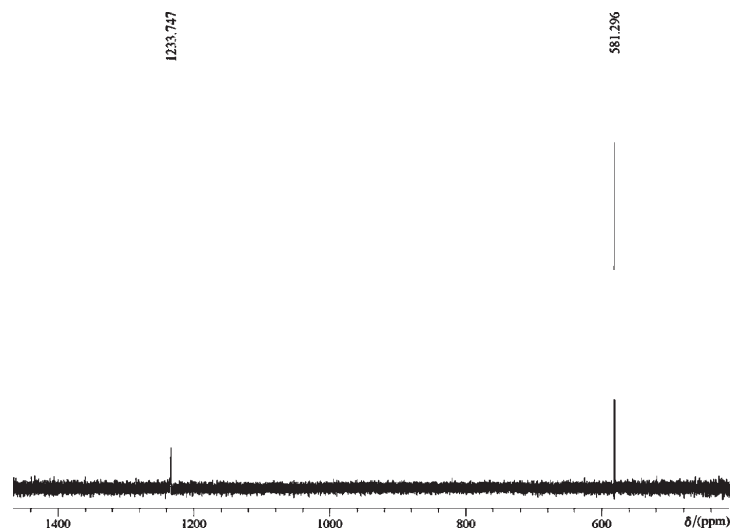


Figure S4. ^{125}Te NMR spectrum of the compound 1.

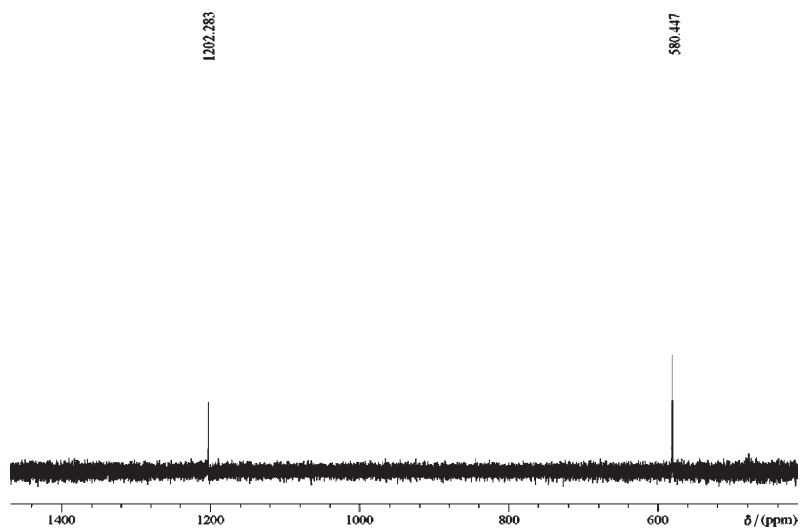


Figure S5. ^{125}Te NMR spectrum of the compound 2.

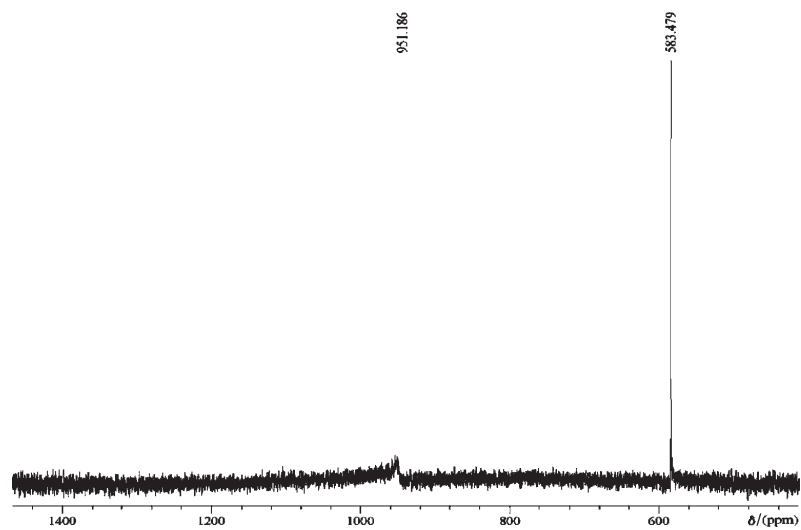


Figure S6. ^{125}Te NMR spectrum of the compound 3.