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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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 = \text{Cl} (1), \text{Br} (2) e \text{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 Te--X interactions create a polymeric “zig-zag” chain of the tetrahalo-phenyltellurate(IV) anions. In 3, the secondary Te--I bonds induce a different arrangement for the anions that are organized in a pseudo-dimeric antiparallel fashion.

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

Introduction

Several classes of organometalltellurium halide compounds are known, including species of general formula TeX₃R, TeX₂R₂ and TeXR, (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 (Te--X), which create exceptional supramolecular structures, leading to the formation of polymeric chains, dimeric structures, or monomers with fairly strong intermolecular interactions. We have been interested for some time in the synthesis and crystal structures of TeX₃R compounds and their derivatives, such as the [TeX₄]⁻ 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 features) where the different packing arrangements in the crystal lattice of [TeX₄]⁻ 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. 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 = \text{Cl} (1), \text{Br} (2) e \text{I} (3), complexes in which organometalltellurium(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/I₂ and acetonitrile with CaH₂, and both were distilled prior to use. The compound iododimethylphenyltellurium(IV) was prepared according to Reid’s procedure; the analogous chloride and bromide derivatives were prepared by ion exchange with the appropriate silver halide in hot methanol. Trihalo-phenyltellurium(IV) compounds were prepared following literature procedures. Melting points were recorded in a Microquimica 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.

\(^{1}\text{H}\) and \(^{125}\text{Te}\) NMR

The NMR spectral data were obtained in a Varian Mercury Plus 7.05 T spectrometer with 300.07 MHz (\(^{1}\text{H}\)) and 94.74 MHz (\(^{125}\text{Te}\)). The samples were dissolved in a 9:1 mixture of acetone-\(\text{d}_6\) and DMSO-\(\text{d}_6\), respectively. The solutions were measured in NMR tubes of 5 mm, at 300 K. The \(^{1}\text{H}\) NMR chemical shifts are relative to Si(\(\text{CH}_3\))\(_4\) as internal reference. The \(^{125}\text{Te}\) NMR spectra were taken with reference to Te(\(\text{CH}_3\))\(_2\). A capillary containing Te\(_2\)(\(\text{C}_6\text{H}_5\))\(_2\) dissolved in CDCl\(_3\) (\(\delta 450\)) 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(\(\text{C}_6\text{H}_5\))\(_2\)]\([\text{TeX}_4\text{Ph}]\))

To a solution of 1.3 mmol of TeX\(_3\)(\(\text{C}_6\text{H}_5\)), trihalophenyltellurium(IV), in 20 mL of methanol cooled to 0 °C, 1.3 mmol of TeX(\(\text{C}_6\text{H}_5\))\(_2\)(\(\text{CH}_3\))\(_2\), 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.

\([\text{Te}(\text{C}_6\text{H}_5\text{J}_2)(\text{CH}_3)_2\text{I}])/[\text{Te}(\text{C}_6\text{H}_5\text{J}_2\text{Cl})]/[\text{Te}(\text{C}_6\text{H}_5\text{J}_2\text{Br})] (1)\). Properties: air stable, yellow crystalline substance; C\(_{14}\)H\(_{16}\)Te\(_2\)Cl\(_4\) (581.30 g mol\(^{-1}\)). Yield: 90% based on TeCl\(_3\)(\(\text{C}_6\text{H}_5\)); mp: 158 - 159 °C; C and H Elemental Analysis: Found (%): C, 21.74; H, 3.25; Yield: 90% based on TeBr\(_3\)(\(\text{C}_6\text{H}_5\)); mp: 125 - 126 °C; C and H Elemental Analysis: Found (%): C, 17.75; H, 1.71. \(^{1}\text{H}\) NMR (ppm): \(\delta 2.51\) (s, Me), 7.14-8.58 (m, aryl); \(^{125}\text{Te}\) NMR (ppm): \(\delta 584.02\) (cation), 951.08 (anion).

\(^{1}\text{H}\) and \(^{125}\text{Te}\) NMR

X-ray data were collected on a Bruker X8 APEX II diffractometer using Mo K\(\alpha\) 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 \(^{125}\text{Te}\) NMR spectra show two peaks for each compound. The low frequency peak, around \(\delta 580\), is attributed to the cationic [Te(\(\text{C}_6\text{H}_5\))\(_2\)]\(_{2}\)\(^{+}\) species, which corresponds well to the value found for [Te(\(\text{C}_6\text{H}_5\))\(_2\)]\(_{2}\)\(_{2}\)\(^{+}\) in DMSO.\(^{17}\) The lower field peak, attributed to the anionic [TeX\(_3\)\(_{2}\)\(_{2}\)]\(_{2}\)\(^{-}\) species, shows chemical shifts at \(\delta 1234.81, 1203.87\) 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
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 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.

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

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<th>2</th>
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<tr>
<td>Te1—C1'</td>
<td>2.544(7)</td>
<td>Te1—Br1</td>
<td>2.7239(7)</td>
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<td>Te1—Br2</td>
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* R1 = |Fo - Fc|/|Fo|; wR2 = [w(Fo2 - Fc2)2/(wFo2)] -1/2.

Table 1. Crystallographic data of the new complexes synthesized
bonds are created by Te2--X1' and Te2--X3 interactions between the tellurium cations and tellurate anions. The tellurium cations are arranged along the polymeric tellurate anionic chain.

The structure of 3 is different from those of 1 and 2. The strong reciprocal Te···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 Te1···I2' and Te1'···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, I1···I3 (3.771(1) Å) and I2···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.

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://jbcs.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 (125Te). The samples were dissolved in a 9:1 mixture of acetone-\textit{d}_6 and DMSO-\textit{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(CH\textsubscript{3})\textsubscript{4} as internal reference. The 125Te NMR spectra were taken with reference to Te(CH\textsubscript{3})\textsubscript{2}. A capillary containing Te\textsubscript{2}(C\textsubscript{6}H\textsubscript{5})\textsubscript{2} dissolved in CDCl\textsubscript{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. $^1$H NMR spectrum of the compound 2.

Figure S3. $^1$H NMR spectrum of the compound 3.
Figure S4. $^{125}\text{Te}$ NMR spectrum of the compound 1.

Figure S5. $^{125}\text{Te}$ NMR spectrum of the compound 2.
Figure S6. $^{125}$Te NMR spectrum of the compound 3.