X-Ray Structure of Triphenyltelluronium Thiocyanate: an Oligomeric Organotelluronium Salt

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Summary *X*-Ray structural results shows that the solid organo-tellurium salt $Ph_3Te(NCS)$ exists as discrete dimers and tetramers formed from bridging NCS groups with intra Te · · · N and Te · · · S distances significantly shorter than respective van der Waals distances.

ORGANO-CHALCOGENONIUM salts R_3XY ($X = S$, Se, Te; $Y =$ anion) in the solid state are generally thought of as simple ionic solids of the $R_3X^+Y^-$ form.[1] The structures of Me_3SI[2] and Me_3SeI,[3] for example, consist of isolated ion pairs having X · · · I distances slightly shorter than the respective van der Waals distances. During an investigation of the interaction of ambidentate nitrogen-containing pseudohalide ions with the triphenyltelluronium cation, however, we found spectroscopic evidence suggesting structures far more complicated than the $R_3Te^+Y^-$ ion-pair model.[4] $Ph_3Te(NCS)$, for example, shows three C–N i.r. stretching vibrations at 2058, 2064, and 2070 cm^{-1}. We have therefore determined the crystal and molecular structure of $Ph_3Te(NCS)$, and report here the first structural data for an organo-telluronium salt, R_3TeY, where Y is a simple, non-tellurium-containing anion.

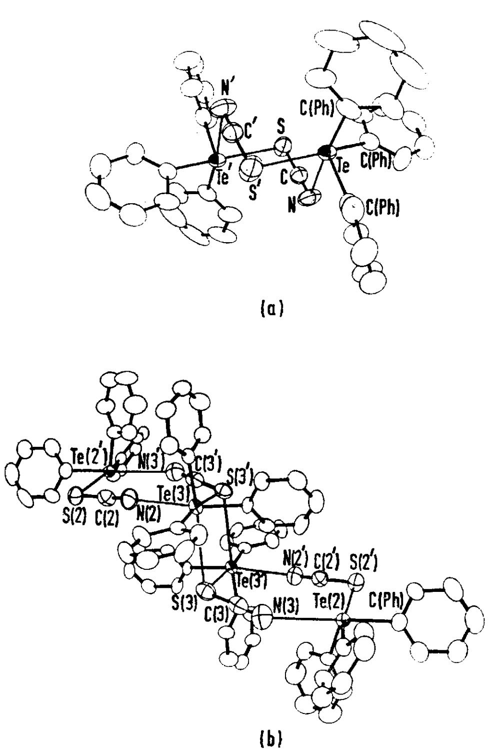

FIGURE. Structure of (a) $Ph_3Te(NCS)$ dimer and (b) $Ph_3Te(NCS)$ tetramer; selected interatomic distances and angles: Te–N, 3·153(6); Te–S′, 3·256(3); Te(2)–N(3), 3·182(8); Te(2)–S(2), 3·348(3); Te(3)–N(2), 2·963(8); Te(3)–S(3), 3·527(3); N–C, 1·148(10); C–S, 1·621(8); N(2)–C(2), 1·147(11); C(2)–S(2), 1·643(8); N(3)–C(3), 1·163(12); C(3)–S(3), 1·658(9); Te–Te′, 4·660(4); Te(3)–Te(3′), 4·955(4); Te(2)–Te(3), 7·446(5) Å; ∠N–C–S, 175·4(6); N(2)–C(2)–S(2), 179·1(6); N(3)–C(3)–S(3), 179·2(6)°.

$Ph_3Te(NCS)$ was precipitated by mixing aqueous solutions of Ph_3TeCl and excess of NaNCS, washed with water, and recrystallized from propan-2-ol.

$Ph_3Te(NCS)$ forms triclinic crystals of space group $P\bar{1}$ having $a = 13{\cdot}339(12)$, $b = 13{\cdot}885(10)$, $c = 14{\cdot}796(11)$ Å; $\alpha = 82{\cdot}53(6)$, $\beta = 76{\cdot}53(7)$, $\gamma = 78{\cdot}20(7)°$; $Z = 6$; $D_c = 1{\cdot}60$, $D_m = 1{\cdot}60(2)$ g cm^{-3}. Intensity data were collected on a Syntex $P\bar{1}$ automatic diffractometer using graphite-monochromatized Mo-K_α radiation. The intensities of 6690 reflections were measured and corrected for Lorentz and polarization effects, but not for absorption. The structure was solved by Patterson and Fourier techniques, and was refined by least-squares methods using 5543 reflections having $|F| > \sigma(F)$. Anisotropic thermal parameters were used for all non-hydrogen atoms. The refinement converged to a final R factor of 3·9% and a weighted R factor of 5·1%. The hydrogen atom contributions to the calculated structure factors were included as fixed contributions in the final cycles of refinement.

The structure consists of triphenyltelluronium cations bridged by thiocyanate anions to form dimers and tetramers separated by van der Waals distances. In the centrosymmetric dimer (Figure, a) the eight-membered ring is in a chair configuration with the dihedral angle of the chair being 93·2°. The centrosymmetric tetramer exhibits an overall step-type structure (Figure, b) formed by the interaction of two somewhat planar eight-membered rings. The dihedral angle of the step is 89·5°. The tellurium atoms in the dimer are 5-co-ordinate (~ square pyramidal) whereas both 5-co-ordination (~ square pyramidal) and 6-co-ordination (~ octahedral) occurs in the tetramer. Thiocyanate bridging is in the three-atom end-to-end mode with one of the groups bridging in the terminal single-atom mode as well.

The Te · · · N and Te · · · S distances are longer than those expected for a single covalent bond, 2·02 and 2·36 Å respectively, but are significantly shorter than the van der Waals distances[5] of 3·61 and 3·86 Å respectively. These interactions involve nearly linear C–Te · · · X (X = N, S) arrangements, and may be described as secondary bonding interactions.[6]

The three crystallographically independent triphenyltelluronium cations have a pyramidal shape with C–Te–C angles ranging from 92 to 103°. The C–N and C–S distances of the thiocyanate groups are normal with the C–S distances significantly shorter than that for the free ion [1·689(13) Å] in KNCS.[7] The three crystallographically independent NCS groups are responsible for the multiplicity of bands near 2064 cm^{-1} in the i.r. spectrum of $Ph_3Te(NCS)$.

We thank Dr. W. H. H. Günther for his interest in and support of this work.

(*Received*, *5th April* 1976; *Com.* 353.

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