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Structural Characterization of the Bioligomeric Triphenyltelluronium Thiocyanate Salt, $((C_6H_5)_3Te(NCS))_4((C_6H_5)_3Te(NCS))_2$

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The crystal and molecular structure of triphenyltelluronium thiocyanate, $(C_6H_5)_3Te(NCS)$, has been determined from three-dimensional x-ray data collected by counter techniques. The structure was refined by full-matrix least-squares methods. The refinement was carried out using 5543 nonzero reflections for which $F > \sigma(F)$ and assuming anisotropic thermal motion for all nonhydrogen atoms. The least-squares refinement led to a final value of the conventional R factor (on F) of 0.039. Crystal data are as follows: space group $P\bar{1}$; a = 13.339 (12), b = 13.885 (10), c = 14.796 (11) Å; α = 82.53 (6), β = 76.53 (7), γ = 78.20 (7)° (23 °C); V = 2599 Å^3. Triphenyltelluronium thiocyanate is bioligomeric in the solid state. The unit cell (Z = 6) consists of one dimer and one tetramer separated by van der Waals distances. The oligomers are predominantly ionic with tellurium–nitrogen and tellurium–sulfur distances significantly shorter than respective van der Waals distances. Te–N distances range from 2.963 (8) to 3.182 (8) Å; the Te–S distances range from 3.256 (4) to 3.616 (4) Å. Both end-to-end and terminally bridging NCS groups are present. The central eight-membered ring of the dimer is puckered and has a chair configuration with a dihedral angle of 93.2°. The overall configuration of the tetramer is that of a step with a dihedral angle of 99.9°. Five- and six-coordinate tellurium atoms are present in distorted square-pyramidal and distorted octahedral geometries, respectively. The three crystallographically independent triphenyltelluronium cations have a trigonal-pyramidal shape but possess no symmetry, due to the conformation adopted by the phenyl rings. The mean Te–C distance is 2.13 (2) Å and the mean C–Te–C angle is 97.3 (6)°. The thiocyanate groups are ionic with mean N–C and C–S distances of 1.15 (2) and 1.64 (1) Å, respectively.

Introduction

Organochalcogenonium salts, R_3XY (X = S, Se, Te; Y = anion), have been known for at least a century and are generally thought of as simple ionic solids of the $R_3X^+Y^-$ form.[2-6] Structural studies of $(CH_3)_3SI$[7] and $(CH_3)_3SeI$,[8] however, show that the compounds consist of isolated ion pairs having X···I distances shorter than respective van der Waals distances. Likewise, in the structure of the telluronium salt, $[(CH_3)_3Te]^+[CH_3TeI_4]^-$, four weak tellurium–iodine interactions occur.[9] This type of interaction, which frequently causes the chalcogen to have a coordination number higher than would be expected from the stoichiometry of the system, is called secondary bonding and has been reviewed by Alcock.[10]

During our investigation of the interaction of ambidentate nitrogen-containing pseudohalide ions with triorganotelluronium and triorganoselenonium ions, we found spectroscopic evidence suggesting structures for these compounds more complicated than the $R_3X^+Y^-$ ion-pair model.[11,12] $(C_6H_5)_3TeX$ (X = N_3, NCO, NCS, NCSe) compounds, for example, show multiple C–N or N–N stretching vibrations in the 2000–2200-cm^{-1} region of their infrared spectra.[11] As part of our effort to determine the structural relationships among these compounds[13,14] we have determined the crystal structure of triphenyltelluronium thiocyanate, $(C_6H_5)_3Te(NCS)$. The structural results reported herein have appeared in preliminary form.[15]

Experimental Section

The compound was prepared as a precipitate by mixing aqueous solutions of $(C_6H_5)_3TeCl$ and excess NaNCS.[11] The $(C_6H_5)_3Te(NCS)$, after being collected, was washed with water and recrystallized from 2-propanol.

Intensity data were collected by Molecular Structure Corporation (College Station, Texas) on a Syntex $P\bar{1}$ automatic diffractometer using graphite monochromatized Mo Kα radiation. The prism used for data collection measured 0.25 × 0.29 × 0.39 mm.

Unit cell parameters for $(C_6H_5)_3Te(NCS)$ obtained by computer-centering 25 reflections followed by least-squares refinement of the setting angles are as follows: a = 13.339 (12), b = 13.885 (10), c = 14.796 (11) Å; α = 82.53 (6), β = 76.53 (7), γ = 78.20 (7)°; V = 2599 Å^3 (temperature 23 °C). Reduction of the cell revealed no hidden symmetry, and the cell axes, obtained from the Baloshov and Ursell algorithm,[16] represent the three shortest noncoplanar translations (Dirichlet triplet). The measured density of 1.597 (10)

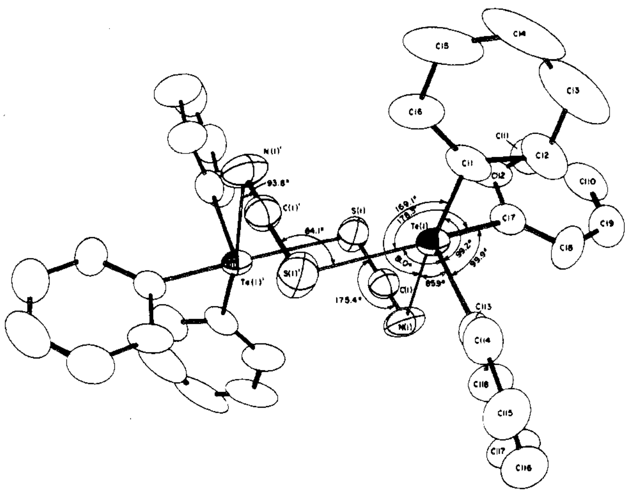

Figure 1. The $(C_6H_5)_3Te(NCS)$ dimer.

g/cm^3 agrees with the calculated value of 1.598 g/cm^3 for six formula units per unit cell.

A total of 6690 independent reflections were collected by the θ–2θ scan technique in the range $0 < 2\theta$ (Mo Kα) $\leq 45°$. A takeoff angle of 3° was used with a counter aperture width of 2 mm. A scan rate of 4–24°/min (in 2θ) was used with stationary crystal, stationary counter background counts where scan time per background time equaled 2.0.

Intensities and standard deviations of intensities were calculated using the following formulas

$$I = S(C - RB)$$

$$\sigma(I) = [S^2(C + R^2B) + (pI)^2]^{1/2}$$

where S is the scan rate, C is the total integrated peak count, R is the ratio of scan time of background counting time, B is the total background count, and p is a factor introduced to downweight intense reflections. Here, p was set to 0.07. No trends were observed in the intensities of three standard reflections. Lorentz and polarization corrections were applied to the data; extinction and absorption corrections were not deemed necessary. The calculated linear absorption coefficient (Mo Kα), μ, is 18.9 cm^{-1}.

Scattering factors were taken from the compilation of Hanson et al.;[17] those for Te and S were corrected for the real and imaginary components of anomalous dispersion using the values of Cromer.[18]

In addition to local programs, modified versions of the following programs were used: Zalkin's FORDAP Fourier program; Ibers' NUCLS least-sqaures program; Busing, Martin, and Levy's ORFFE error function program; and Johnson's ORTEP II thermal ellipsoid plotting program.

The three tellurium atoms and two of the sulfur atoms were located using a sharpened Patterson map. Subsequent calculations were carried out on a data set of 5543 reflections with $F > \sigma(F)$. The centric space group $P\bar{1}$ was assumed and confirmed by successful refinement of the structure. The function minimized in the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F)$. All nonhydrogen atoms were located from a Fourier map based upon the phases of the five heavy atoms. A cycle of least-squares refinement (isotropic temperature factors) reduced R_F $(\sum||F_o| - |F_c||/\sum|F_o|)$ to 0.076 and R_w $(\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)$ to 0.096. The hydrogen atoms were added as fixed contributions to subsequent structure factor calculations. Their postions were calculated, assuming an in-plane C–H distance of 0.95 Å. Temperature factors were set equal to that of the carbon to which the hydrogen was attached. Electron density was observed in all expected H positions using a difference Fourier map.

In subsequent cycles of least squares, all nonhydrogen atoms were allowed to vibrate anisotropically. Because of the large number of parameters, it was necessary to break the matrix into eight smaller groups. After three complete cycles (of eight refinements each) no parameter was found to shift by more than 0.1 of its standard deviation; refinement was considered complete. The final R_F was 0.039, the final R_w was 0.051, and the goodness of fit, $(\sum w(F_o - F_c)^2/(\text{no. of reflections} - \text{no. of variables}))^{1/2}$, was 1.04.

There were no unusual problems in the refinement. The final positional and anistropic thermal parameters for the nonhydrogen atoms are given in Table I. The observed and calculated structure factors are available as supplementary material.

Results and Discussion

Triphenyltelluronium thiocyanate is bioligomeric in the solid state. Three crystallographically independent $(C_6H_5)_3$-Te(NCS) units form discrete centrosymmetric dimers and tetramers separated by van der Waals distances. The configuration of the oligomers and the atom numbering schemes are depicted in Figures 1 and 2. Interatomic distances and additional angles are given in Table II.

The oligomers are built up primarily through interaction between the triphenyltelluronium cations and end-to-end bridging thiocyanate anions. The central eight-membered ring

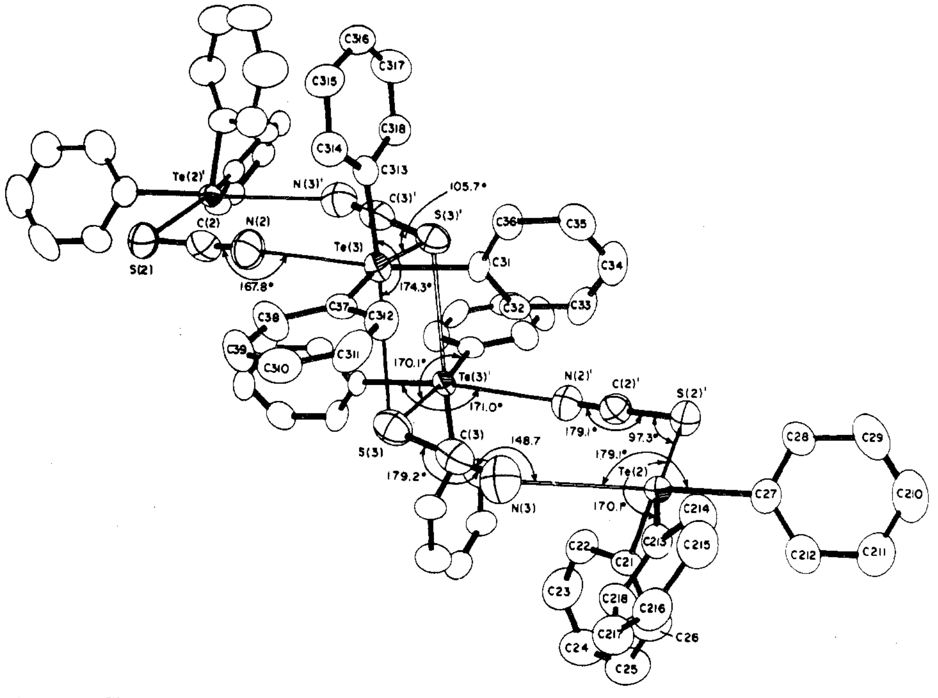

Figure 2. The $(C_6H_5)_3Te(NCS)$ tetramer.

Table I. Positional and Thermal Parameters (Å^2) of the Nonhydrogen Atoms[a-c]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Te(1)	4322 (0.3)	1190 (0.3)	1070 (0.2)	363 (2)	399 (2)	385 (2)	−69 (2)	111 (2)	69 (2)
Te(2)	2734 (0.3)	6453 (0.3)	2350 (0.3)	388 (2)	399 (2)	385 (2)	−60 (2)	65 (2)	89 (2)
Te(3)	328 (0.3)	3206 (0.3)	4522 (0.2)	289 (2)	399 (2)	344 (2)	−60 (2)	56 (2)	0 (2)
N(1)	6631 (5)	−12 (4)	1508 (4)	759 (49)	771 (37)	500 (31)	9 (35)	176 (37)	256 (30)
N(2)	−1579 (5)	2684 (5)	4884 (4)	602 (58)	1012 (56)	812 (42)	−209 (35)	232 (37)	197 (39)
N(3)	587 (6)	5771 (5)	2311 (5)	833 (58)	706 (46)	885 (52)	−148 (35)	213 (37)	−38 (39)
C(1)	6844 (5)	214 (4)	867 (4)	445 (49)	502 (37)	604 (42)	−17 (35)	19 (37)	59 (30)
C(2)	−2324 (5)	2636 (4)	5123 (4)	511 (58)	548 (37)	448 (42)	−87 (35)	102 (37)	20 (30)
C(3)	2 (6)	5610 (4)	2721 (4)	627 (58)	418 (37)	522 (42)	−8 (35)	−18 (37)	−78 (30)
S(1)	7098 (2)	464 (1)	−88 (1)	940 (16)	743 (9)	541 (10)	−419 (9)	204 (9)	30 (10)
S(2)	−3392 (2)	2551 (1)	5457 (1)	553 (16)	743 (9)	677 (10)	−218 (9)	241 (9)	30 (10)
S(3)	−836 (2)	5397 (1)	3308 (1)	643 (16)	632 (9)	531 (10)	−78 (9)	0 (9)	−19 (10)
C(11)	2912 (5)	2234 (5)	808 (5)	421 (49)	325 (37)	833 (52)	−69 (26)	167 (37)	148 (30)
C(12)	2651 (6)	2951 (5)	1497 (6)	511 (49)	437 (37)	1145 (62)	−130 (35)	398 (46)	−19 (39)
C(13)	1780 (7)	3679 (6)	1265 (9)	569 (74)	529 (56)	2238 (125)	−69 (53)	797 (74)	128 (69)
C(14)	1164 (6)	3685 (6)	384 (9)	454 (66)	455 (56)	2426 (146)	18 (44)	445 (74)	580 (79)
C(15)	1401 (6)	2961 (6)	−291 (7)	462 (58)	752 (65)	1686 (94)	−43 (44)	9 (56)	738 (69)
C(16)	228 (6)	222 (5)	−94 (6)	454 (49)	687 (46)	968 (62)	−104 (35)	−36 (37)	384 (39)
C(17)	5214 (5)	2300 (4)	1687 (4)	363 (41)	409 (37)	562 (42)	−87 (26)	130 (28)	79 (30)
C(18)	5444 (6)	2616 (5)	2628 (4)	759 (58)	715 (46)	500 (42)	−305 (44)	130 (37)	−78 (39)
C(19)	5987 (6)	3386 (6)	2909 (6)	800 (66)	669 (56)	781 (52)	−227 (44)	74 (46)	−156 (39)
C(110)	6320 (6)	3819 (5)	2269 (6)	610 (58)	529 (46)	1145 (73)	−200 (35)	120 (56)	39 (49)
C(111)	6094 (6)	3492 (6)	1356 (6)	627 (58)	715 (56)	979 (62)	−270 (44)	139 (46)	236 (49)
C(112)	5539 (5)	2742 (5)	1061 (5)	495 (49)	548 (37)	698 (42)	−60 (35)	139 (37)	236 (39)
C(113)	4139 (5)	650 (4)	2290 (4)	528 (49)	446 (36)	468 (42)	−139 (35)	241 (37)	−19 (30)
C(114)	3131 (6)	602 (5)	2367 (5)	660 (58)	604 (46)	593 (42)	−244 (35)	287 (37)	−117 (30)
C(115)	3017 (7)	142 (6)	3109 (5)	998 (74)	873 (56)	677 (52)	−428 (53)	380 (56)	−38 (49)
C(116)	3876 (8)	−214 (6)	3758 (5)	1476 (99)	752 (74)	614 (52)	−428 (61)	454 (56)	79 (39)
C(117)	4883 (7)	−175 (6)	3676 (5)	1105 (82)	1022 (65)	614 (52)	−165 (53)	176 (46)	374 (49)
C(118)	5018 (6)	274 (6)	2930 (5)	651 (58)	808 (56)	562 (42)	−69 (44)	167 (37)	207 (39)
C(21)	1618 (5)	7752 (4)	2122 (4)	412 (41)	372 (37)	427 (31)	−8 (26)	65 (28)	669 (30)
C(22)	912 (6)	8009 (5)	2707 (5)	577 (49)	632 (46)	677 (42)	−25 (35)	259 (37)	118 (39)
C(23)	148 (6)	8831 (5)	2572 (6)	767 (58)	632 (46)	916 (62)	96 (44)	454 (46)	0 (39)
C(24)	62 (6)	9400 (5)	1850 (6)	816 (66)	502 (46)	1083 (62)	201 (44)	259 (56)	216 (49)
C(25)	754 (6)	9159 (5)	1274 (5)	808 (58)	474 (46)	822 (52)	53 (35)	259 (46)	138 (39)
C(26)	1536 (6)	8336 (4)	1405 (4)	668 (49)	427 (37)	604 (42)	−17 (35)	195 (37)	69 (30)
C(27)	4184 (5)	6900 (4)	2357 (4)	412 (41)	464 (37)	437 (31)	−157 (26)	111 (28)	0 (30)
C(28)	5051 (5)	6461 (5)	2955 (5)	445 (58)	836 (56)	573 (42)	−78 (35)	74 (37)	177 (39)
C(29)	6040 (6)	6628 (7)	2964 (5)	363 (58)	1142 (65)	750 (52)	−104 (44)	−8 (37)	39 (49)
C(210)	6137 (6)	7269 (6)	2347 (5)	544 (58)	947 (56)	760 (52)	−304 (44)	241 (46)	−215 (49)
C(211)	5259 (6)	7727 (7)	1764 (5)	684 (74)	1124 (65)	750 (52)	−419 (53)	56 (46)	236 (49)
C(212)	4281 (6)	7518 (6)	1752 (5)	520 (66)	985 (56)	760 (52)	−262 (44)	−18 (37)	305 (49)
C(213)	2582 (5)	5834 (4)	931 (4)	355 (41)	372 (28)	458 (31)	−69 (26)	93 (28)	39 (30)
C(214)	3408 (5)	5096 (4)	751 (4)	478 (41)	511 (37)	458 (42)	−43 (35)	111 (28)	10 (30)
C(215)	3339 (5)	4618 (4)	−142 (5)	553 (49)	474 (37)	645 (42)	−122 (35)	213 (37)	−48 (30)
C(216)	2452 (5)	4869 (4)	−828 (4)	643 (49)	483 (37)	468 (42)	−253 (35)	111 (37)	−9 (30)
C(217)	1651 (5)	5599 (5)	−638 (4)	561 (49)	539 (37)	437 (42)	−157 (35)	83 (28)	10 (30)
C(218)	1712 (5)	6093 (4)	241 (4)	478 (49)	446 (37)	583 (42)	−95 (35)	0 (37)	118 (30)
C(31)	1841 (4)	3465 (4)	4449 (4)	239 (41)	483 (37)	396 (31)	−165 (26)	102 (28)	59 (30)
C(32)	1955 (5)	4440 (4)	4503 (4)	445 (49)	437 (37)	521 (42)	−34 (35)	56 (37)	98 (30)
C(33)	2940 (6)	4640 (5)	4505 (5)	569 (58)	650 (37)	750 (52)	−279 (35)	130 (37)	157 (39)
C(34)	3772 (6)	3886 (6)	4464 (5)	487 (49)	827 (46)	708 (52)	−262 (35)	158 (37)	59 (39)
C(35)	3639 (5)	2931 (5)	4416 (5)	371 (49)	706 (46)	656 (42)	88 (35)	167 (37)	69 (39)
C(36)	2672 (5)	2710 (4)	4411 (4)	330 (49)	539 (37)	604 (31)	−69 (35)	204 (37)	30 (30)
C(37)	−101 (5)	2602 (4)	3123 (4)	404 (41)	372 (37)	344 (31)	−78 (26)	−45 (28)	69 (30)
C(38)	−1114 (5)	2390 (5)	2826 (4)	429 (49)	567 (37)	552 (42)	−43 (35)	19 (28)	−97 (30)
C(39)	−1142 (5)	2012 (5)	1911 (5)	404 (58)	641 (46)	614 (52)	−148 (44)	−8 (37)	−78 (39)
C(310)	−759 (6)	1847 (4)	1315 (4)	709 (58)	427 (56)	416 (52)	−130 (44)	−55 (37)	0 (39)
C(311)	226 (6)	2066 (5)	1596 (4)	841 (58)	641 (46)	448 (42)	−340 (35)	213 (37)	−9 (39)
C(312)	559 (5)	2436 (5)	2510 (4)	536 (49)	752 (37)	354 (42)	−253 (79)	139 (28)	−48 (30)
C(313)	988 (4)	1824 (4)	5110 (4)	322 (41)	474 (28)	375 (31)	−78 (26)	74 (28)	39 (20)
C(314)	857 (4)	941 (5)	4591 (4)	569 (49)	567 (37)	510 (42)	−130 (35)	74 (37)	0 (30)
C(315)	1347 (6)	72 (5)	4985 (5)	775 (49)	409 (46)	739 (42)	−113 (35)	83 (37)	128 (39)
C(316)	1957 (5)	84 (5)	5876 (5)	511 (58)	594 (37)	781 (42)	−34 (35)	158 (37)	236 (30)
C(317)	2067 (6)	968 (5)	6365 (5)	660 (66)	613 (46)	625 (42)	−52 (44)	0 (37)	167 (30)
C(318)	1581 (5)	1848 (4)	5989 (4)	561 (49)	492 (46)	521 (31)	−130 (35)	9 (28)	79 (30)

[a] All values × 10^4. [b] Values in parentheses above and in Table II are estimated standard deviations in the last significant figure. [c] The temperature factors are of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$; the U_{ij} in Å^2 are related to the dimensionless β_{ij} employed during refinement as $U_{ij} = \beta_{ij}/2\pi^2 a_i^* a_j^*$.

of the dimer is puckered and has a chair configuration with the dihedral angle between the N(1)–Te(1)–S(1)′ plane (plane 15, Table III) and the six-membered thiocyanate plane (1) being 93.2° (Table IV). The NCS group is nearly linear and therefore nearly parallel to the other group in the dimer. No thiocyanate atom deviates by more than 0.03 Å from the six-membered thiocyanate least-squares plane. In the tetramer, the eight-membered ring of the dimeric subunit is nearly planar. The average deviation of the atoms from the least-squares plane (16) is 0.10 Å. The two dimeric subunits are

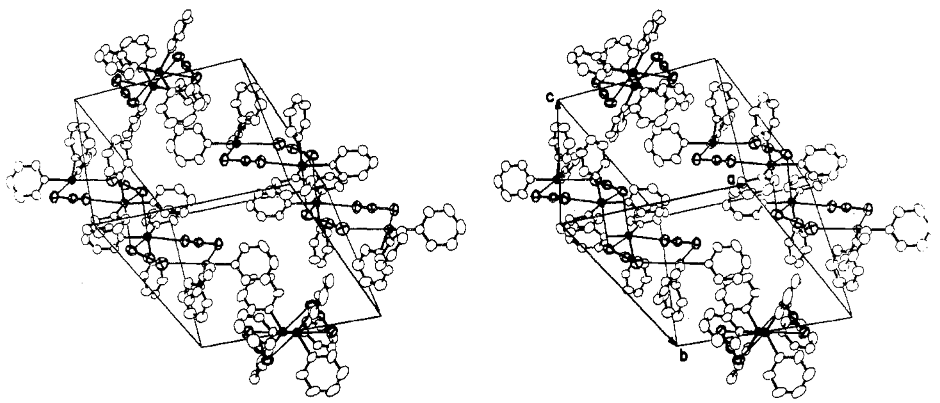

Figure 3. Stereoscopic unit cell view of $(C_6H_5)_3Te(NCS)$.

Table II. Interatomic Distances (Å) and Angles (deg)[a]

	Distances		
Te(1)-N(1)	3.153 (6)	Te(3)-S(3)	3.616 (4)
Te(1)-S(1)′	3.256 (4)	Te(3)-S(3)′	3.527 (3)
Te(1)-Te(1)′	4.660 (4)	Te(3)-Te(3)′	4.955 (4)
Te(1)-C(11)	2.117 (6)	Te(3)-C(31)	2.149 (6)
Te(1)-C(17)	2.121 (6)	Te(3)-C(37)	2.123 (5)
Te(1)-C(113)	2.125 (7)	Te(3)-C(313)	2.145 (6)
Te(2)-N(3)	3.182 (8)	Te(2)-Te(2)′	9.513 (9)
Te(2)-S(2)′	3.348 (3)	N(1)-C(1)	1.148 (10)
Te(2)-Te(3)′	6.767 (5)	C(1)-S(1)	1.621 (8)
Te(2)-C(21)	2.100 (6)	N(2)-C(2)	1.147 (11)
Te(2)-C(27)	2.145 (7)	C(2)-S(2)	1.643 (8)
Te(2)-C(213)	2.143 (6)	N(3)-C(3)	1.163 (12)
Te(3)-N(2)	2.963 (8)	C(3)-S(3)	1.658 (9)
	Angles		
N(1)-Te(1)-S(1)′	104.3 (1)	N(2)-Te(3)-S(3)′	92.9 (1)
N(1)-Te(1)-C(17)	77.2 (2)	N(2)-Te(3)-S(3)	99.8 (1)
C(11)-Te(1)-C(17)	92.4 (2)	N(2)-Te(3)-C(313)	79.9 (2)
C(11)-Te(1)-S(1)′	86.1 (2)	C(31)-Te(3)-C(37)	97.3 (2)
N(3)-Te(2)-S(2)′	103.0 (1)	C(31)-Te(3)-S(3)′	82.8 (2)
N(3)-Te(2)-C(213)	86.7 (2)	C(31)-Te(3)-S(3)	88.3 (2)
C(27)-Te(2)-C(213)	92.5 (2)	C(31)-Te(3)-C(313)	96.4 (2)
C(27)-Te(2)-S(2)′	77.8 (2)	C(37)-Te(3)-S(3)	78.0 (2)
C(21)-Te(2)-N(3)	76.7 (2)	C(37)-Te(3)-C(313)	96.3 (2)
C(21)-Te(2)-S(2)′	86.0 (2)	S(3)-Te(3)-S(3)′	92.2 (1)
C(21)-Te(2)-C(27)	103.6 (2)	S(3)′-Te(3)-C(313)	93.5 (2)
C(21)-Te(2)-C(213)	98.2 (2)	Te(3)-S(3)-Te(3)′	87.8 (8)
N(2)-Te(3)-C(37)	88.3 (2)	Te(3)-S(3)-C(3)	108.4 (2)

[a] The atom labeling scheme and additional angles are given in Figures 1 and 2.

joined by a long Te–S interaction (3.616 (4) Å) to give an overall step configuration to the tetramer. The dihedral angle between the vertical Te(3)–S(3)–S(3)′–Te(3)′ plane (5) and the horizontal eight-membered plane (16) is 99.9°.[19] Core atoms Te(2), (NCS)-(3), Te(3), and (NCS)-(2) define a second vertical plane forming the "side" of the step configuration with the average deviation of the atoms from the least-squares plane (4) being 0.22 Å. This plane is perpendicular to the other vertical plane with a dihedral angle of 89.5° and nearly perpendicular to the horizontal plane (16) with a dihedral angle of 95.0°. The packing of the dimers and tetramers is illustrated in Figure 3.

A summary of the Te···N and Te···S interactions in $(C_6H_5)_3Te(NCS)$ is given in Table V. The oligomers are predominantly ionic with tellurium–nitrogen and tellurium–sulfur distances significantly shorter than van der Waals distances. The mean Te···N distance is 3.10 (1) Å, slightly longer than that in $(C_6H_5)_3Te(NCO)$, 2.99 (2) Å.[13] The mean Te···S distance is 3.437 (7) Å. This type of interaction, called secondary bonding, has been reviewed by Alcock and is common to many Te(IV) (and Se(IV)) compounds with halogen or oxygen as ligands.[10] Reports of secondary bonding of Te(IV) (and Se(IV)) to nitrogen or sulfur, however, are not common. In the present structure the difference between the secondary value mean and the single-bond value (Te–N = 2.02 Å, Te–S = 2.36 Å)[20] is 1.08 Å in both cases. A similar Te···S difference value (0.95 Å) has been reported for a secondary interaction in $Te[S_2P(OCH_3)_2]_2$.[10] The C—Te···X (X = N, S) interactions are approximately linear and range from 169.1 (2) to 179.1 (2)°. Deviations of up to 15° from linearity in A—Y···X interactions are common.[10] We note that none of the secondary interactions is in the direction of the pseudo-threefold axis of the trigonal-pyramidal $(C_6H_5)_3Te^+$ cation. A similar situation exists in all of the $R_3(VI)X$ structures reported to date: $(CH_3)_3SI$,[7] $(CH_3)_3SeI$,[8] $(C_6H_5)_3SeCl\cdot H_2O$,[21] $(C_6H_5)_3SeCl\cdot 2H_2O$,[22] $(C_6H_5)_3Se(NCS)$,[14] $(CH_3)_3Te(CH_3TeI_4)$,[9] and $(C_6H_5)_3Te(NCO)\cdot {}^1/_2CHCl_3$.[13]

Table III. Least-Squares Planes in $((C_6H_5)_3Te(NCS))_6$[a]

Plane	Atoms	Equation
1	N(1), C(1), S(1), and primes	$2.623x - 12.384y - 2.839z = 1.312$
2	N(1), S(1)′, C(11), C(17)	$5.082x + 4.007y - 14.471z = 1.164$
3	C(27), C(213), N(3), S(2)′	$3.602x - 11.713y + 4.370z = -5.519$
4	(NCS)-(2), Te(2), Te(3), (NCS)-(3)	$1.314x + 6.793y + 11.566z = 7.454$
5	Te(3), S(3), and primes	$13.153x + 3.898y - 5.186z = -0.844$
6	C(11)-C(16)	$10.187x + 10.202y - 7.090z = 4.663$
7	C(17)-C(112)	$9.714x - 7.095y + 0.0910z = 3.449$
8	C(113)-C(118)	$0.0768x - 11.386y - 6.776z = -2.260$
9	C(21)-C(26)	$8.114x + 8.629y + 6.016z = 9.281$
10	C(27)-C(212)	$1.756x - 9.299y - 9.460z = -7.911$
11	C(213)-C(218)	$8.764x + 11.461y - 6.933z = 8.309$
12	C(31)-C(36)	$0.0616x - 0.725y + 14.365z = 6.154$
13	C(37)-C(312)	$1.292x - 12.722y + 4.812z = -1.823$
14	C(313)-C(318)	$12.402x + 3.166y - 8.501z = -2.543$
15	Te(1), N(1), S(1)′	$4.979x + 4.298y - 14.436z = 1.119$
16	(NCS)-(2)′, Te(2), Te(3)′, (NCS)-(3)	$3.998x - 11.193y + 5.136z = -4.914$

[a] Planes are defined in fractional triclinic coordinates (x, y, z) and are calculated using unit weights for all atoms.

Table IV. Summary of Dihedral Angles

Planes[a]	Angle, deg	Planes[a]	Angle, deg
1-15	93.2	9-10	45.4
4-5	89.5	9-11	63.6
4-16	95.0	9-16	93.0
5-16	99.9	10-11	76.5
6-7	82.8	12-13	70.9
6-8	51.7	12-14	68.7
7-8	59.8	13-14	87.2

[a] As defined in Table III.

Table V. Summary of C–Te· · ·X Secondary Interactions

C–Te· · ·X interaction	Angle, deg	Te· · ·X dist, Å	Sum of van der Waals radii[a]
C(11)-Te(1)-N(1)	169.1 (2)	3.153 (6)	Te· · ·N, 3.61 Å
C(27)-Te(2)-N(3)	179.1 (2)	3.182 (8)	
C(31)-Te(3)-N(2)	171.0 (2)	2.963 (8)	
C(17)-Te(1)-S(1)′	178.3 (1)	3.256 (4)	Te· · ·S, 3.86 Å
C(213)-Te(2)-S(2)′	170.1 (2)	3.348 (3)	
C(37)-Te(3)-S(3)′	170.1 (1)	3.527 (3)	
C(313)-Te(3)-S(3)	174.3 (1)	3.616 (4)	

[a] Reference 20.

As a result of the secondary interactions in $(C_6H_5)_3$-Te(NCS), the coordination of tellurium is higher than would be expected from the stoichiometry of the compound. Both five- and six-coordinate tellurium atoms are present in distorted square-pyramidal and distorted octahedral geometries, respectively. Alternatively, the geometry of the five-coordinate tellurium may be described as distorted octahedral with three primary bonds, two secondary bonds, and one vacant site.[10] An examination of Figure 3 shows no atoms near the vacant position. Unlike the five-coordinate tellurium atom in $(C_6H_5)_3$Te(NCO), which is displaced 0.6 Å toward the axial carbon atoms of its pyramid, the five-coordinate tellurium atoms in $(C_6H_5)_3$Te(NCS) are essentially in the equatorial plane of their respective square pyramids with no equatorial atom deviating by more than 0.04 Å from the least-squares plane (planes 2 and 3, Table III). Both Te(1) (dimer) and Te(2) (tetramer) have C_{ax}–Te–C_{eq} angles greater than 90° and C_{ax}–Te–$(N,S)_{eq}$ angles less than 90°. The axial carbon atom is, therefore, located off-axis toward the eight-membered ring. In the tetramer the axial C(21)–C(27) phenyl ring is bent toward and nearly perpendicular (93.0°) to the plane (16) of the Te(2)–Te(3)′ ring. The N(1)–Te–S(1)′ and N(3)–Te(2)–S(2)′ angles are 104.3 (1) and 103.0 (1)°, respectively. The N–Te–S angles for the six-coordinate tellurium atom (Te(3)) are smaller with N(2)–Te(3)–S(3) at 99.8 (1)° and N(2)–Te(3)–S(3)′ at 92.9 (1)°. The C–Te–C angles for Te(3) are greater than 90° and the C–Te–(N,S) angles less than 90° except C(313)–Te(3)–S(3)′ at 93.5 (2)°.

The tendency toward oligomerization in compounds of the heavier chalcogen(IV) elements has become apparent through recent structural studies. For example, $(C_6H_5)_3SeCl\cdot 2H_2O$, with its directed interactions, is dimeric,[22] and TeX_4 (X = Cl, Br, I) compounds are tetrameric.[23] The coexistence of two different oligomeric forms of a compound within the same unit cell, however, is atypical and, to our knowledge, is without precedent in the structural chemistry of organotellurium compounds. The coexistence of the oligomers is likely due to the combination of rather specific secondary interactions and packing effects, for we note that the unit cell of $(C_6H_5)_3$-Te(NCO) contains only tetramers and solvent of crystallization.[11,13]

A comparison of the thiocyanate and cyanate tetramers is illustrated in Figure 4. A comparison of the Te···X distances within the tetramers reveals that the cyanate tetramer has more integrity, but that both contain a discernibly dimeric subunit (vide supra). The Te···N and Te···O distances in the cyanate[13] suggest that the centrosymmetric center ring is the basic dimeric subunit, with two Te–NCO groups flanking it to complete the two outer, fused, eight-membered rings. The center ring has a chair configuration similar to that of the pure dimer in the present structure, but has a dihedral angle considerably larger at 132°, reflecting the mode of coordination of the outer Te–NCO groups. Contortions in the NCO tetramer remove any visage of the step-type core found in the thiocyanate. Interestingly, this step-type core appears in TeI_4.[23] Since the volume difference between the NCO^- and NCS^- anions is small (22 Å^3),[24] the differences in coordination and structure between the two compounds must be attributed, mainly, to differences in the electronic nature of the anions and to packing considerations thereof. In the thiocyanate, the relatively "soft" sulfur exhibits both two- and three-coordinate species. In the cyanate, the relatively "hard" oxygen exhibits only two-coordinate species while the bridging nitrogen becomes three-coordinate.

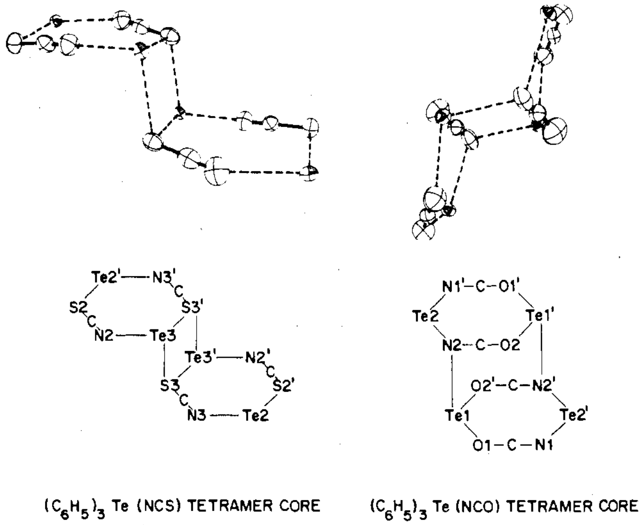

Figure 4. Comparison of the tetramer cores of $(C_6H_5)_3$Te(NCS) and $(C_6H_5)_3$Te(NCO). No correspondence in orientation is intended between the upper ORTEP drawings and the lower schematics which depict coordination modes.

Despite structural differences between the compounds, packing efficiencies are very similar. When the volume of $CHCl_3$ (104 Å^3, 185 K)[27] is substracted from the unit cell volume of $(C_6H_5)_3Te(NCO)\cdot {}^1/_2CHCl_3$, the $(C_6H_5)_3$Te(NCO) unit occupies 423 Å^3, Each $(C_6H_5)_3$Te(NCS) unit, by comparison, occupies a slightly larger volume, 433 Å^3. The efficiency of packing results from the adaptability of the bulky $(C_6H_5)_3Te^+$ cation. Although the cations appear structurally similar in the two compounds, with similar C–Te–C angles, the conformation of each cation is unique, as seen by differences in dihedral angles between the least-squares planes of the phenyl groups within each cation. The dihedral angles between the three phenyl groups in each of the three independent cations of the thiocyanate are listed in Table V. The angles range from 45.4 to 82.8° and show no recognizable pattern among the three cations. A similar situation occurs in $(C_6H_5)_3Te(NCO)\cdot {}^1/_2CHCl_3$. The adaptability of the cations, as manifested by the broad range of angles and by differences in conformation, is a direct result of the voluble nature of the phenyl groups. It is, in fact, the orientation of the phenyl rings in the thiocyanate that gives it a distinctly hydrophobic nature in the solid state.[11] By comparison, the cyanate has no envelope of aromatic rings surrounding its anions and is distinctly hydrophilic.[13]

The present structure and that of $(C_6H_5)_3Te(NCO)\cdot {}^1/_2CHCl_3$[13] establish the conformation of the triphenyltelluronium cation. The three crystallographically independent cations have the expected trigonal-pyramidal shape but possess no symmetry due to the conformation adopted by the phenyl rings. The assignment of a pseudo-threefold axis to the cation is purely heuristic. The mean Te–C distance (2.13 (2) Å) is identical with that in the cyanate structure[13] and is within the range of other reported Te–C distances.[28] For reference, the sum of the single bond radii is 2.14 Å.[20] The C–Te–C angles range from 92 to 103° and have a mean value of 97.3 (6)°, comparable to the C–Te–C mean values in the cyanate (95.7 (8)°)[13] and $(CH_3)_3Te(CH_3TeI_4)$ (95 (2)°).[9] Recently the conformation of the triphenylselenonium cation was established.[14,22] It is similar to that of the triphenyltelluronium cation. In the latter, the C–Te–C angles are slightly smaller than the C–Se–C angles in $(C_6H_5)_3Se^+$. Accompanying this expected decrease in C–(VI)–C angle is a tendency toward higher coordination as demonstrated in $(C_6H_5)_3Te(NCS)$. Selenium in $(C_6H_5)_3Se(NCS)$ is four-coordinate with the compounds being neither isomorphous nor isostructural.[14]

Bond distances and angles within the nine crystallographically independent phenyl rings appear normal and range from 1.35 (1) to 1.40 (1) Å for the C–C distances and from 118.3 (7) to 122.3 (6)° for the C–C–C angles. The mean values of the 54 independent phenyl C–C distances and C–C–C angles are 1.38 (8) Å and 120 (5)°, respectively. The least-squares planes of the nine phenyl rings are given in Table III, planes 6 through 14. The rings are planar with no carbon atom deviating more than 0.020 (8) Å from the least-squares plane of its respective phenyl ring. The average deviation of the carbon atoms from the least-squares planes is 0.005 Å.

The thiocyanate group in the dimer has an N–C–S angle of 175.4 (6)°, while those in the tetramer have angles of 179.1 (6) and 179.2 (6)°. The N–C and C–S distances have respective mean values of 1.15 (2) and 1.64 (1) Å. The NCS groups compare structurally to those in $((C_6H_5)_2TeNCS)_2O$[28] and $(C_6H_5)_3Se(NCS)$.[14] For reference, the N–C distance in KNCS is 1.149 (14) Å and the distance C–S is 1.689 (13) Å.[29] The Te(1,2,3)–N(1,3,2)–C(1,3,2) angles are 93.8 (4), 148.7 (5), and 167.8 (5)°, respectively. For comparison , the Te–N–C angle in $((C_6H_5)_2TeNCS)_2O$ (Te–N = 2.400 (10) Å) is 145.3 (9)°; the thiocyanate group, however, is nonbridging.[28] The Te(1,2,3)–S(1′,2′,3′)–C(1′,2′,3′) angles are 84.1 (2), 97.3 (2), and 105.7 (2)°, respectively. Although Te(1)–S(1)′–C(1)′ is acute, the Te(1)–C(1)′ (3.485 (7) Å) and Te(1)–C(1) (3.426 (7) Å) distances are nearly equal. The three crystallographically independent NCS groups in $(C_6H_5)_3TeNCS$ give rise to three C–N stretching vibrations at 2068, 2061, and 2056 cm^{-1} (± 3 cm^{-1}) in the infrared (KBr and mineral oil mull) and Raman spectra of the compound. In solution, the nature of $(C_6H_5)_3Te(NCS)$ is very solvent dependent.[30]

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Registry No. $(C_6H_5)_3Te(NCS)$, 60965-33-5; $[(C_6H_5)_3Te]^+NCS^-$, 61042-63-5.

Supplementary Material Available: The observed and calculated structure factors (35 pages). Ordering information is given on any current masthead page.

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