The Crystal Structures of Tetramethylammonium Phenyldithiocyanatotellurate(II) and Tetramethylammonium Phenyldiselenocyanatotellurate(II)

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The crystal structures of tetramethylammonium phenyldithiocyanatotellurate(II), [(CH$_3$)$_4$N]-[C$_6$H$_5$Te(SCN)$_2$], I, and tetramethylammonium phenyldiselenocyanatotellurate(II), [(CH$_3$)$_4$N]-[C$_6$H$_5$Te(SeCN)$_2$], II, have been determined by three-dimensional X-ray diffraction methods. The crystals of the two compounds are isomorphous, monoclinic, with space group $C2/c$ (No. 15). There are eight formula units per unit cell, and the unit cell dimensions are: $a = 15.747(6)$ Å, $b = 9.219(3)$ Å, $c = 23.153(8)$ Å, $\beta = 100.58(5)°$ for I, and $a = 15.840(4)$ Å, $b = 9.341(2)$ Å, $c = 23.384(4)$ Å, $\beta = 100.67(2)°$ for II. Intensity data were collected by means of an automatic single-crystal diffractometer, using Nb-filtered MoKα radiation. Least squares refinement, based on 3464 independent, non-zero reflections for I and 2425 for II, resulted in a conventional R value of 0.064 for I and 0.045 for II.

The structure of the phenyldithiocyanatotellurate(II) ion and the phenyldiselenocyanatotellurate(II) ion may be regarded as based on square-planar coordination with one position, *trans* to the phenyl group, vacant. Each tellurium atom is bonded to a phenyl carbon atom and, in directions approximately perpendicular to the Te−C bond, to two thiocyanate sulfur atoms in I and to two selenocyanate selenium atoms in II. The three-centre systems, S−Te−S and Se−Te−Se, are nearly linear. In the thiocyanato compound the bond lengths and angles involving tellurium are: Te−S(1) = 2.665(2) Å, Te−S(2) = 2.702(2) Å, Te−C(3) = 2.104(5) Å, ∠S(1)−Te−S(2) = 174.94(6)°, ∠S(1)−Te−C(3) = 89.34(17)°, and ∠S(2)−Te−C(3) = 87.35(17)°, In the selenocyanato compound the corresponding bond lengths and angles are: Te−Se(1) = 2.7636(11) Å, Te−Se(2) = 2.8233(12) Å, Te−C(3) = 2.100(6) Å, ∠Se(1)−Te−Se(2) = 175.40(3)°, ∠Se(1)−Te−C(3) = 89.5(2)°, ∠Se(2)−Te−C(3) = 87.9(2)°.

The tetramethylammonium ions are subjected to disorder or extreme thermal motions, with the central nitrogen in a fixed position.

Three-coordinated complexes of divalent tellurium have previously been studied by Foss and co-workers.[1,2] The crystal structures of phenylbis(thiourea)tellurium(II) chloride,[1] and of chloro- and bromo(phenyl)thioureatellurium-(II) [2] have been determined. The structures of these compounds can be regarded as based on square-planar coordination with one position, *trans* to the phenyl group, vacant.[1,2]

The present crystal structures of tetramethylammonium phenyldithiocyanatotellurate(II), I, and tetramethylammonium phenyldiselenocyanatotellurate(II), II, are the first structures of anionic complexes of divalent tellurium. They are three-coordinated, as are the compounds referred to above. The syntheses of the two compounds are described in a previous paper.[3]

EXPERIMENTAL

The X-ray data were collected with Nb-filtered MoKα radiation ($\lambda_{\alpha_1} = 0.70926$ Å), by use of a Siemens automatic, off-line, single-crystal diffractometer AED 1, operated as a three-circle instrument. For the thiocyanato compound, I, the measurements were performed on a crystal with the following dimensions, given as distances from the point of intersection of the crystal faces ($\overline{1}1\overline{2}$), ($\overline{1}10$), and ($\overline{1}00$): to ($\overline{1}10$), 0.128 mm; to (001), 0.073 mm; to (00$\overline{1}$), 0.067 mm; to (110), 0.330 mm. For the selenocyanato compound, II, the crystal used had the following dimensions, given as distances from the point of

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Table 1. Atomic coordinates for tetramethylammonium phenyldithiocyanatotellurate(II), in fractions of monoclinic cell edges. Origin at a centre of symmetry. Isotropic thermal parameters (Å²) in the form exp $-[8\pi^2 U(\sin^2 \theta/\lambda^2)]$. Standard deviations from least squares are given in parentheses.

	x	y	z	U
Te	0.14619(2)	0.16977(5)	0.45062(2)	
S(1)	0.15468(13)	−0.1142(2)	0.43041(9)	
S(2)	0.13147(15)	0.4605(3)	0.46097(10)	
C(1)	0.1579(4)	−0.0999(8)	0.3593(3)	
N(1)	0.1601(5)	−0.0899(8)	0.3110(3)	
C(2)	0.1327(5)	0.4917(9)	0.3934(5)	
N(2)	0.1323(6)	0.5106(9)	0.3431(4)	
C(3)	0.0167(4)	0.1692(7)	0.4069(3)	
C(4)	−0.0037(5)	0.1739(9)	0.3458(3)	
C(5)	−0.0882(6)	0.1717(9)	0.3176(4)	
C(6)	−0.1545(5)	0.1653(7)	0.3495(4)	
C(7)	−0.1344(5)	0.1624(9)	0.4100(4)	
C(8)	−0.0504(5)	0.1627(9)	0.4377(4)	
N(3)	0.3783(3)	0.1792(6)	0.3368(2)	0.0503(12)
C(9)	0.3763(7)	0.0750(15)	0.2864(6)	0.139 (4)
C(10)	0.3869(7)	0.0884(14)	0.3910(5)	0.122(4)
C(11)	0.2944(7)	0.2573(12)	0.3242(5)	0.106(3)
C(12)	0.4526(9)	0.2763(12)	0.3327(6)	0.143(4)
H(4)	0.032(4)	0.167(7)	0.322(3)	0.058(19)
H(5)	−0.109(5)	0.146(8)	0.280(4)	0.09(3)
H(6)	−0.219(7)	0.163(9)	0.341(4)	0.12(3)
H(7)	−0.185(6)	0.160(9)	0.430(4)	0.12(3)
H(8)	−0.030(6)	0.179(8)	0.481(4)	0.11(3)

Table 2. Atomic coordinates for tetramethylammonium phenyldiselenocyanatotellurate(II), in fractions of monoclinic cell edges. Origin at a centre of symmetry. Isotropic thermal parameters (Å²) in the form exp $-[8\pi^2 U(\sin^2 \theta/\lambda^2)]$. Standard deviations from least squares are given in parentheses. Of the disordered carbon atoms of the tetramethylammonium ion, C(9) to C(12) are assigned an occupancy factor of 0.6, and C(9') to C(12') are assigned an occupancy factor of 0.4.

	x	y	z	U
Te	0.14761(3)	0.16531(6)	0.44920(2)	
Se(1)	0.15855(6)	−0.12681(10)	0.43357(4)	
Se(2)	0.13252(7)	0.46574(11)	0.45537(5)	
C(1)	0.1577(6)	−0.1129(9)	0.3593(4)	
N(1)	0.1570(6)	−0.1025(9)	0.3106(4)	
C(2)	0.1357(6)	0.4829(11)	0.3856(7)	
N(2)	0.1398(8)	0.4902(12)	0.3349(5)	
C(3)	0.0194(4)	0.1603(8)	0.4052(3)	
C(4)	0.0010(5)	0.1683(11)	0.3454(3)	
C(5)	−0.0858(7)	0.1637(12)	0.3170(4)	
C(6)	−0.1513(6)	0.1574(11)	0.3486(4)	
C(7)	−0.1318(5)	0.1533(12)	0.4068(4)	
C(8)	−0.0462(5)	0.1552(11)	0.4352(4)	
N(3)	0.3782(4)	0.1713(7)	0.3392(3)	0.0566(15)
C(9)	0.3811(14)	0.072(2)	0.2923(9)	0.146(8)
C(10)	0.3873(11)	0.097(2)	0.3952(7)	0.097(5)
C(11)	0.2946(11)	0.2486(19)	0.3259(7)	0.089(5)
C(12)	0.4518(14)	0.272(2)	0.3382(9)	0.137(7)
C(9')	0.381(2)	0.019(3)	0.3634(14)	0.131(11)
C(10')	0.3977(18)	0.247(3)	0.3947(12)	0.118(9)
C11')	0.2931(15)	0.182(3)	0.3016(10)	0.080(7)
C(12')	0.4513(13)	0.204(2)	0.3035(9)	0.067(6)

Table 3. Anisotropic thermal parameters (Å^2) for the phenyldithiocyanatotellurate(II) ion, in the form of exp $-[2\pi^2(h^2a^{-2}U_{11}+\cdots+2hka^{-1}b^{-1}U_{12}+\cdots)]$. All values have been multiplied by 10^3. Standard deviation are given in parentheses.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Te	45.2(2)	69.9(3)	47.3(2)	−1.0(2)	−5.2(2)	6.7(2)
S(1)	75.5(11)	66.4(13)	63.0(10)	7.9(10)	20.0(9)	15.5(9)
S(2)	87.5(14)	76.0(16)	80.7(15)	0.9(12)	−15.0(11)	3.6(11)
C(1)	48(3)	61(5)	70(5)	−2(3)	−9(4)	13(3)
N(1)	102(5)	89(5)	73(4)	1(4)	−15(4)	27(4)
C(2)	59(4)	61(5)	123(8)	1(4)	17(5)	16(5)
N(2)	131(7)	115(7)	115(7)	−2(6)	31(6)	6(6)
C(3)	46(3)	48(4)	48(3)	0(3)	−2(3)	10(2)
C(4)	58(4)	87(6)	53(4)	6(4)	−1(4)	10(3)
C(5)	79(5)	100(7)	62(5)	9(5)	−12(5)	−15(4)
C(6)	52(4)	83(6)	103(7)	5(4)	6(5)	−5(4)
C(7)	48(4)	94(6)	92(6)	8(4)	16(5)	15(4)
C(8)	60(6)	94(6)	64(4)	1(4)	6(5)	24(4)

intersection of the crystal faces (001), ($\bar{1}$01), and (11$\bar{1}$): to (100), 0.113 mm; to ($\bar{1}$00), 0.016 mm; to (10$\bar{1}$), 0.151 mm; to (00$\bar{1}$), 0.141 mm; to (0$\bar{1}$0), 0.244 mm. In each case the crystal was mounted with the b axis approximately along the ψ axis of the diffractometer. Intensity data were collected using a "five value" measuring procedure, as described by Åse.[4] Six reference reflections were measured at intervals of 50 reflections. The net intensities were later brought to a common scale by using the intensity variations of the reference reflections.[4] The scale factors varied from 1.00 to 1.08 for I, and from 1.00 to 1.06 for II. The lower limit for observed reflections was set equal to three times the standard deviation in net intensity. The standard deviation was taken as $(I_t+I_b)^{\frac{1}{2}}$, where I_t is the total intensity, and I_b is the

background intensity.[4] 3464 of 4983 independent reflections within $\theta=30°$ were found to be stronger than the lower limit for I. The corresponding numbers for II were 2425 of 5135.

The data were corrected for Lorentz and polarization effects according to standard procedures, and for absorption,[5] and secondary extinction.[6]

Least squares refinements were carried out with a full-matrix program which minimizes the function $r=(\sum W(|F_o|-K|F_c|)^2$ where K is a scale factor, and the weight, W, is the inverse of the variance in F_o. The variance in F_o was taken to be

$\sigma^2(F_o)=F_o^2[I_t+I_b+k^2(I_t-I_b)^2]/4(I_t-I_b)^2$

where k may be interpreted as the relative standard deviation in the scaling curve. Non-observed reflections for which $K|F_c|$ is greater

Table 4. Anisotropic thermal parameters (Å^2) for the phenyldiselenocyanatotellurate(II) ion, in the form of exp $-[2\pi^2(h^2a^{-2}U_{11}+\cdots+2hka^{-1}b^{-1}U_{12}+\cdots)]$. All values have been multiplied by 10^3. Standard deviations are given in parentheses.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Te	48.5(3)	69.5(4)	58.1(3)	0.8(3)	−6.0(3)	4.8(2)
Se(1)	82.8(7)	58.8(6)	70.3(6)	8.5(5)	2.2(5)	16.0(5)
Se(2)	91.7(8)	61.4(8)	109.4(9)	4.9(6)	−16.5(6)	−14.2(7)
C(1)	75(6)	66(6)	76(6)	−4(5)	−14(5)	26(5)
N(1)	110(7)	101(7)	109(6)	2(5)	−22(6)	29(6)
C(2)	52(6)	52(6)	127(10)	−6(5)	6(9)	21(9)
N(2)	129(9)	123(9)	140(11)	6(7)	15(8)	49(9)
C(3)	49(4)	56(5)	48(4)	2(4)	0(4)	6(3)
C(4)	54(5)	112(8)	59(5)	−5(6)	−6(5)	−1(4)
C(5)	92(7)	132(10)	66(6)	−6(8)	−12(7)	−17(5)
C(6)	55(5)	109(8)	95(7)	4(6)	8(7)	2(5)
C(7)	57(6)	141(10)	90(7)	1(7)	21(7)	16(5)
C(8)	49(5)	116(8)	65(5)	6(6)	0(6)	14(4)

Table 5. Bond lengths (Å) and angles (°) in tetramethylammonium phenyldithiocyanatotellurate(II). Standard deviations are given in parentheses.

Te−S(1)	2.665(2)	S(1)−Te−S(2)	174.94(6)
Te−S(2)	2.702(2)	S(1)−Te−C(3)	89.34(17)
Te−C(3)	2.104(5)	S(2)−Te−C(3)	87.35(17)
S(1)−C(1)	1.663(8)	Te−S(1)−C(1)	96.2(3)
S(2)−C(2)	1.594(11)	Te−S(2)−C(2)	94.3(3)
C(1)−N(1)	1.128(11)	S(1)−C(1)−N(1)	179.8(6)
C(2)−N(2)	1.179(14)	S(2)−C(2)−N(2)	177.8(7)
C(3)−C(4)	1.393(9)	Te−C(3)−C(4)	120.7(4)
C(4)−C(5)	1.370(11)	Te−C(3)−C(8)	121.2(4)
C(5)−C(6)	1.386(14)	C(3)−C(4)−C(5)	120.5(6)
C(6)−C(7)	1.380(13)	C(4)−C(5)−C(6)	120.4(7)
C(7)−C(8)	1.361(10)	C(5)−C(6)−C(7)	119.2(7)
C(8)−C(3)	1.379(10)	C(6)−C(7)−C(8)	120.0(7)
		C(7)−C(8)−C(3)	121.8(7)
		C(8)−C(3)−C(4)	119.0(5)
N(3)−C(9)	1.506(14)	C(9)−N(3)−C(10)	106.2(12)
N(3)−C(10)	1.495(13)	C(9)−N(3)−C(11)	105.4(11)
N(3)−C(11)	1.486(12)	C(9)−N(3)−C(12)	103.8(14)
N(3)−C(12)	1.488(15)	C(10)−N(3)−C(11)	112.1(12)
		C(10)−N(3)−C(12)	115.9(15)
		C(11)−N(3)−C(12)	112.2(13)
C(4)−H(4)	0.86(7)	C(3)−C(4)−H(4)	126(4)
C(5)−H(5)	0.91(8)	C(5)−C(4)−H(4)	122(4)
C(6)−H(6)	1.00(9)	C(4)−C(5)−H(5)	117(5)
C(7)−H(7)	1.00(9)	C(6)−C(5)−H(5)	119(6)
C(8)−H(8)	1.01(9)	C(5)−C(6)−H(6)	117(5)
		C(7)−C(6)−H(6)	123(6)
		C(6)−C(7)−H(7)	115(5)
		C(8)−C(7)−H(7)	124(5)
		C(7)−C(8)−H(8)	123(5)
		C(3)−C(8)−H(8)	118(5)

than the measurement limit were included in the refinement, with $|F_o|$ equal to the limit.

The calculated structure factors were based on the scattering curve of Stewart *et al.*[7] for hydrogen, and the curves listed in *International Tables* (Ref. 8, Table 3.3.1 A and B) for all other atoms. Using the $\Delta f'$ and $\Delta f''$ values given in *International Tables* (Ref. 8, Table 3.3.2 A), the tellurium, selenium, and sulfur scattering curves were corrected for anomalous dispersion by taking the amplitude of f as the corrected value.[4]

The calculations were carried out on a UNIVAC 1110 computer. The programs used in the calculations are described elsewhere.[4] The drawings were made by use of ORTEP.[9]

CRYSTAL DATA

The crystals of I and II are orange red, isomorphous, monoclinic prisms and plates. Systematic absences are: *hkl* for $h+k$ odd, *h0l* for *l* odd. The space group is either *Cc* (No. 9) or *C2/c* (No. 15). Subsequent structure analyses showed the space group to be *C2/c*.

The unit cell dimensions, as refined by least squares from diffractometer-measured θ-values (all about 20°) of 18 reflections for I, and 20 reflections for II, are: $[(CH_3)_4N][C_6H_5Te(SCN)_2]$, I, $a = 15.747(6)$ Å, $b = 9.219(3)$ Å, $c = 23.153(8)$ Å, $\beta = 100.58(5)°$, $Z = 8$, $D_x = 1.59$ g/cm³, $D_m = 1.58$ g/cm³, $\mu_{MoK\alpha} = 21.0$ cm⁻¹. $[(CH_3)_4N]$-$[C_6H_5Te(SeCN)_2]$, II, $a = 15.840(4)$ Å, $b = 9.341(2)$ Å, $c = 23.384(4)$ Å, $\beta = 100.67(2)°$, $Z = 8$, $D_x = 1.87$ g/cm³, $D_m = 1.86$ g/cm³, $\mu_{MoK\alpha} = 64.1$ cm⁻¹.

STRUCTURE DETERMINATION

The structures were solved by Patterson and Fourier methods, and refined by full-matrix least squares. The Fourier maps of I and II show only one distinct peak from the tetramethylammonium cation. This peak was later shown to be at the position of the nitrogen atom. The maps of II show eight small peaks in the neighbourhood of the position of the nitro-

Table 6. Bond lengths (Å) and angles (°) in tetramethylammonium phenylidselenocyanato-tellurate(II). Standard deviations are given in parentheses. Of the disordered carbon atoms of the tetramethylammonium ion, C(9) to C(12) are assigned an occupancy factor of 0.6, and C(9′) to C(12′) are assigned an occupancy factor of 0.4.

Te − Se(1)	2.7636(11)	Se(1) − Te − Se(2)	175.40(3)
Te − Se(2)	2.8233(12)	Se(1) − Te − C(3)	89.5(2)
Te − C(3)	2.100(6)	Se(2) − Te − C(3)	87.9(2)
Se(1) − C(1)	1.735(9)	Te − Se(1) − C(1)	93.9(3)
Se(2) − C(2)	1.749(16)	Te − Se(2) − C(2)	91.7(4)
C(1) − N(1)	1.139(13)	Se(1) − C(1) − N(1)	179.5(7)
C(2) − N(2)	1.181(19)	Se(2) − C(2) − N(2)	177.3(9)
C(3) − C(4)	1.377(10)	Te − C(3) − C(4)	120.0(5)
C(4) − C(5)	1.412(12)	Te − C(3) − C(8)	120.7(4)
C(5) − C(6)	1.387(15)	C(3) − C(4) − C(5)	118.7(7)
C(6) − C(7)	1.351(12)	C(4) − C(5) − C(6)	120.7(7)
C(7) − C(8)	1.396(11)	C(5) − C(6) − C(7)	119.8(8)
C(8) − C(3)	1.365(12)	C(6) − C(7) − C(8)	120.1(8)
		C(7) − C(8) − C(3)	121.0(7)
		C(8) − C(3) − C(4)	120.2(6)
N(3) − C(9)	1.44(2)	C(9) − N(3) − C(10)	111.3(12)
N(3) − C(10)	1.465(19)	C(9) − N(3) − C(11)	107.8(11)
N(3) − C(11)	1.488(18)	C(9) − N(3) − C(12)	104.9(13)
N(3) − C(12)	1.50(2)	C(10) − N(3) − C(11)	110.7(11)
		C(10) − N(3) − C(12)	111.2(11)
		C(11) − N(3) − C(12)	110.8(11)
N(3) − C(9′)	1.53(3)	C(9′) − N(3) − C(10′)	107.9(17)
N(3) − C(10)′	1.48(3)	C(9′) − N(3) − C(11′)	104.1(15)
N(3) − C(11′)	1.47(2)	C(9′) − N(3) − C(12′)	113.5(15)
N(3) − C(12′)	1.51(3)	C(10′) − N(3) − C(11′)	115.2(15)
		C(10′) − N(3) − C(12′)	108.8(14)
		C(11′) − N(3) − C(12′)	110.7(12)

gen atom. Four of these positions were given an occupancy factor 0.6, and the other four an occupancy factor of 0.4. Later refinement of the occupancy factors did not change these values. The Fourier maps of I also show disorder in the positions of the carbon atoms of the tetramethylammonium ion, but not more than four positions for carbon atoms could be picked out with any certainty. These carbon atoms were given unity occupancy factors.

A three-dimensional Fourier difference map, based on all the non-hydrogen atoms, indicated the positions of the phenyl hydrogen atoms in each structure. For I, refinement including the five phenyl hydrogen atoms resulted in reasonable C − H bond lengths and angles. For II, however, refinement including the five phenyl hydrogen atoms did not succeed.

The final refinement converged at an *R*-value of 0.064 for I, and 0.045 for II. The final Fourier difference maps showed no peaks higher than 0.46 e/Å³ for I, and 0.34 e/Å³ for II. The peaks of highest electron density were located in the neighbourhood of the positions of the

disordered methyl carbon atoms of the tetramethylammonium ion.

Observed and calculated structure factors are available from the authors.

The final atomic coordinates and thermal parameters are listed in Tables 1 − 4.

THE PHENYLDITHIOCYANATO- AND PHENYLDISELENOCYANATOTELLU-RATE(II) IONS

Bond lengths and angles in the phenyldithiocyanatotellurate(II) and phenyldiselenocyanatotellurate(II) ions, based on the atomic coordinates in Tables 1 and 2, are listed in Tables 5 and 6. The uncertainties in the cell dimensions are taken into account in the given standard deviations. Views of the structures, as seen normal to the plane through the coordination group, are reproduced in Figs. 1 and 2. A stereoscopic view of the content of the unit cell of the two compounds is shown in Figs. 3 and 4.
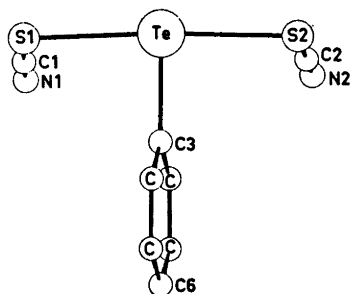
Fig. 1. The phenyldithiocyanatotellurate(II) ion, as seen normal to the plane through the coordination group.
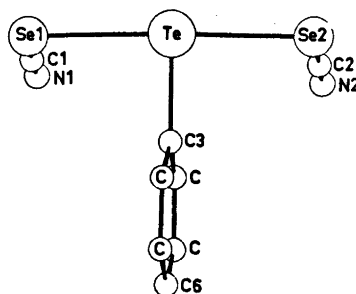

Fig. 2. The phenyldiselenocyanatotellurate(II) ion, as seen normal to the plane through the coordination group.

In the two compounds, each tellurium atom is bonded to a phenyl carbon atom and, in directions approximately perpendicular to the Te – C bond, to two thiocyanate sulfur atoms or to two selenocyanate selenium atoms. The coordination around the tellurium atom is nearly planar in both compounds; the largest deviation from a least-squares plane through Te, S(1), S(2), and C(3) in I is 0.050 Å, and from a least-squares plane through Te, Se(1), Se(2), and C(3) in II, 0.056 Å. These least-squares planes pass 0.036 Å from C(6) in I and 0.030 Å from C(6) in II.

The three-centre systems, S – Te – S and Se – Te – Se, are nearly linear. The S – Te – S bond angle is 174.94(6)° and the Se – Te – Se bond angle is 175.40(3)°. A similar deviation from linearity is found in the crystal structure of phenylbis(thiourea)tellurium(II) chloride where the S – Te – S bond angle is 172.0(4)°.[1]

The Te – C bond nearly bisects the angle of the three-centre system. In I the S – Te – C angles are 89.34(17) and 87.35(17)°, and in II

the Se – Te – C angles are 89.5(2) and 87.9(2)°.

In I the S – Te – S bonding system is slightly asymmetric, with Te – S bond lengths of 2.665(2) and 2.702(2) Å. The mean value of the two Te – S bond lengths is 2.684 Å, which is, within the error, equal to the mean Te – S bond length found in the crystals of phenylbis(thiourea)-tellurium(II) chloride,[1] and in the crystals of centrosymmetric square-planar complexes of divalent tellurium.[10] In II the Se – Te – Se bonding system is a little more asymmetric than the S – Te – S bonding system in I. The Te – Se bond lengths are 2.7636(11) and 2.8233(12) Å, and the mean value is 2.794 Å, which is about 0.02 Å shorter than the average Te – Se bond length, 2.816 Å, found in the crystals of centrosymmetric square-planar complexes of divalent tellurium.[11-13]

The Te – C bond lengths found in the two structures, 2.104(5) Å in I and 2.100(6) Å in II, are equal within the accuracy of the structure determinations. They are equal to the Te – C(sp^2) single covalent bond length, 2.107 Å,
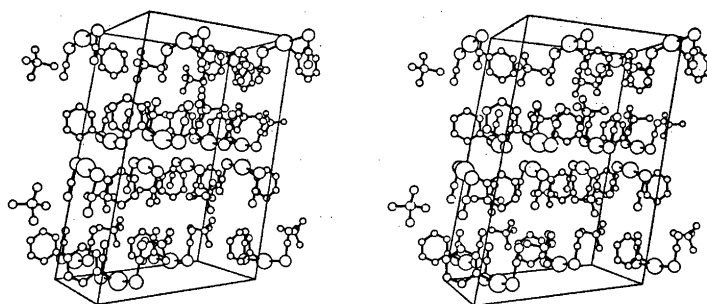

Fig. 3. A stereoscopic view of the cell packing in tetramethylammonium phenyldithiocyanato-tellurate(II), as seen along the *b* crystal axis.
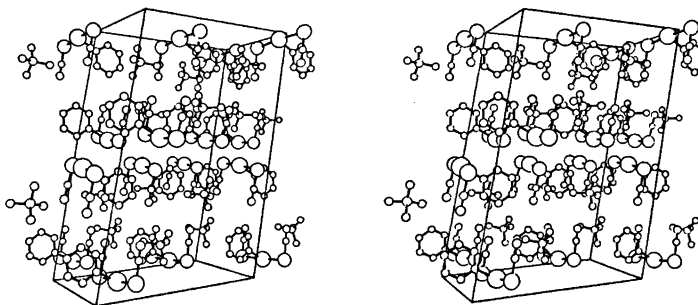
Fig. 4. A stereoscopic view of the cell packing in tetramethylammonium phenyldiselenocyanato-tellurate(II), as seen along the *b* crystal axis.

which is the sum of the covalent radii of tellurium, 1.37 Å,[14] and of sp^2-hybridized carbon, 0.737 Å.[15] The same Te−C bond length has also been found in the crystals of phenylbis(thiourea)tellurium(II) chloride,[1] chloro- and bromo(phenyl)thioureatellurium(II),[2] and o-formylphenyltellurenyl bromide.[16]

The two thiocyanate groups in I and the two selenocyanate groups in II are linear within the accuracy of the structure determinations. The two S−C bond lengths in I are 1.663(8) and 1.594(11) Å, and the Te−S−C angles are 96.2(3) and 94.3(3)°. The two Se−C bond lengths in II are 1.735(9) and 1.794(16) Å, and the Te−Se−C angles are 93.9(3) and 91.7(4)°. The C−N bond lengths in the two thiocyanate groups in I and the two selenocyanate groups in II are equal within the error. The mean value of the four C−N bond lengths is 1.155 Å. The two thiocyanate groups in I are approximately co-planar, and so are the two selenocyanate groups in II. A least-squares plane through the two groups passes 0.021 Å from tellurium in I and 0.017 Å from tellurium in II. In each compound the plane makes an angle of 73.6° with the least-squares plane through the coordination group.

The tellurium atom and the carbon atoms of the phenyltellurium group are nearly co-planar in both structures, the largest deviation from a least-squares plane being 0.01 Å. The angle between this plane and the least-squares plane through the coordination group is 83.2° in I and 85.7° in II.

Divalent tellurium most often forms four-coordinated square-planar complexes, but when a phenyl group is one of the ligands, the position opposite to the phenyl group is vacant.[1,2,10] In

terms of a bonding scheme for divalent tellurium based on *p*-orbitals,[1,2,10,17] the phenyl group engages a tellurium 5*p*-orbital in bonding so effectively that little if any bonding power of this 5*p*-orbital is left for bonding in a direction *trans* to the C−Te bond.

In phenylbis(thiourea)tellurium(II) chloride there is a chloride ion in a direction which makes an angle of 163° with the direction of the Te−C bond, at a distance of 3.61 Å from tellurium.[1] This may be regarded as a fourth, "missing" ligand of a square-planar arrangement. In the two present structures there is no certain approach of a fourth ligand. In II, however, the Se(2) atom of an adjacent molecule located at $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$, where x, y, z are the coordinates of the Se(2) atom in Table 2, lies 3.965(2) Å from tellurium, in a direction which makes an angle of 159.6(2)° with the direction of the Te−C bond. In I the corresponding Te···S distance is larger than 4 Å.

THE TETRAMETHYLAMMONIUM ION

The bond lengths and angles in the tetramethylammonium ions are listed in Tables 5 and 6, and the shapes of the ions appear from Figs. 3 and 4.

The four methyl carbon atoms of the tetramethylammonium ion are disordered in both compounds. The large thermal parameters might indicate that the disorder is due to extreme thermal motions, with the ion rotating more or less about the central nitrogen atom. It appears more plausible, however, that there is a statistical distribution of ions in two or more distinct orientations.

The tetramethylammonium ion is nearly tetrahedral. Due to the disorder, the derived bond lengths and angles are rather inaccurate, but the values are within the normal range.

CRYSTAL PACKING

A stereoscopic drawing of the content of the unit cell of the two compounds is shown in Figs. 3 and 4. There are no particular short non-bonding distances in any of the structures with exception of the Te···Se(2) approach mentioned above. Thus, the two structures consist of well separated tetramethylammonium ions and phenyldithiocyanatotellurate(II) ions in I, and tetramethylammonium ions and phenyldiselenocyanatotellurate(II) ions in II.

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