The Crystal Structures of Chloro(ethylenethiourea)phenyl-tellurium(II) and Bromo(ethyleneselenourea)phenyltellurium(II)

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Chloro(ethylenethiourea)phenyltelluriun(II), $C_6H_5Te(etu)Cl$, I, and bromo(ethyleneselenourea)phenyltellurium(II), $C_6H_5Te(esu)Br$, II, form isomorphous monoclinic crystals with space group $P2_1/c$. The unit cell dimensions for I are: $a = 7.0342(6)$ Å, $b = 12.3808(10)$ Å, $c = 14.3923(11)$ Å, $\beta = 102.252(7)°$, and for II: $a = 7.1968(8)$, $b = 12.8766(10)$ Å, $c = 14.3374(12)$ Å, $\beta = 101.460(9)°$.

In I and II each tellurium atom is primarily three-coordinated, being bonded to one phenyl carbon atom and, in directions nearly perpendicular to the $Te - C$ bond, to one ethylenethiourea sulfur atom and one chlorine atom in I, and to one ethyleneselenourea selenium atom and one bromine atom in II. The three-centre systems $S - Te - Cl$ and $Se - Te - Br$ are nearly linear, and the $Te - C$ bond nearly bisects the angle of the three-centre system. The bond lengths and angles involving tellurium are: $Te - S = 2.5211(10)$ Å, $Te - Cl = 2.8486(10)$ Å, $Te - C = 2.120(2)$ Å, $\angle S - Te - Cl = 176.03(2)°$, $\angle S - Te - C = 89.22(7)°$, $\angle Cl - Te - C = 87.29(7)°$ in I, and $Te - Se = 2.6160(16)$ Å, $Te - Br = 3.0537(16)$ Å, $Te - C = 2.118(7)$ Å, $\angle Se - Te - Br = 175.62(3)°$, $\angle Se - Te - C = 89.94(19)°$, $\angle Br - Te - C = 86.67(19)°$ in II. The fourth position of a square-planar arrangement around tellurium is approached by a chlorine or bromine atom of an adjacent molecule, at $Te \cdots Cl = 3.7401(10)$ Å in I and at $Te \cdots Br = 3.8490(16)$ Å in II, in directions which make an angle of $162.51(7)°$ and $163.31(19)°$ with the direction of the $Te - C$ bond, respectively, for I and II.

Divalent tellurium most often forms four-coordinated square-planar complexes,[1,2] but when a phenyl group is one of the ligands, the position opposite to the phenyl group is vacant.[3-6] The first three-coordinated complexes of divalent tellurium are described by Foss and coworkers, and the crystal structures of chloro- and bromo(phenyl)thioureatellurium(II) have

been determined.[3,4] Later, in a recent paper the crystal structures of two different crystalline forms of bromo(ethylenethiourea)phenyltellurium(II) were reported.[6] The syntheses and crystal data of the two present compounds, chloro(ethylenethiourea)phenyltellurium(II), I, and bromo(ethyleneselenourea)phenyltellurium-(II), II, are reported earlier.[7,8] They are found to be isomorphous with the $P2_1/c$ form of bromo(ethylenethiourea)phenyltellurium(II).

The scope of the present work is to gain further information about the relative *trans* bond-lengthening effects of ligands in tellurium-(II) complexes.

EXPERIMENTAL

Methods used for data collection and reductions, and computational procedures are as described previously.[5,9] For 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 $(01\bar{1})$, $(0\bar{1}\bar{1})$, $(1\bar{1}\bar{1})$, and $(11\bar{1})$: to $(\bar{1}00)$, 0.227 mm; to $(0\bar{1}1)$, 0.141 mm; to(011), 0.125 mm. For compound II, the crystal used had the following dimensions, given as distances from the point of intersection of the crystal faces $(0\bar{1}\bar{1})$, $(01\bar{1})$, and (100): to $(0\bar{1}1)$, 0.078 mm; to (011), 0.047 mm; to $(\bar{1}00)$, 0.180 mm.

The scale factors, based on the reference reflections, varied within 5 % for I, and 4 % for II. 3050 of 3835 independent reflections within $\theta = 30°$ were found to be stronger than the lower limit for I. The corresponding numbers for II are 1842 of 4078.

Table 1. Atomic coordinates in fractions of monoclinic cell edges for chloro(ethylenethiourea)-phenyltellurium(II). Origin at a centre of symmetry. Isotropic thermal parameters ($\mathring{A}^2$) 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	0.20099(2)	0.391455(13)	0.469660(12)	
Cl	0.26387(10)	0.48019(5)	0.65631(5)	
S	0.16956(10)	0.30863(6)	0.30708(5)	
C(1)	0.4176(4)	0.27560(19)	0.52475(17)	
C(2)	0.6097(4)	0.2944(2)	0.5213(2)	
C(3)	0.7502(5)	0.2198(3)	0.5560(2)	
C(4)	0.7029(6)	0.1251(3)	0.5942(3)	
C(5)	0.5153(6)	0.1050(3)	0.5978(4)	
C(6)	0.3708(5)	0.1802(3)	0.5636(3)	
C(7)	− 0.0363(4)	0.2295(2)	0.29672(16)	
C(8)	− 0.2443(5)	0.0862(3)	0.2548(3)	
C(9)	− 0.3504(5)	0.1766(3)	0.2949(3)	
N(1)	− 0.0511(4)	0.13223(19)	0.25949(19)	
N(2)	− 0.1977(3)	0.25823(19)	0.32176(17)	
H(2)	0.640(4)	0.355(3)	0.491(2)	0.052(9)
H(3)	0.886(5)	0.237(3)	0.547(2)	0.078(11)
H(4)	0.801(5)	0.070(3)	0.617(3)	0.081(11)
H(5)	0.479(7)	0.042(4)	0.621(3)	0.116(16)
H(6)	0.254(5)	0.170(3)	0.567(2)	0.074(11)
H(N1)	0.038(5)	0.104(2)	0.238(2)	0.051(9)
H(N2)	− 0.219(5)	0.331(3)	0.343(2)	0.069(10)
H(8A)	− 0.289(6)	0.063(3)	0.195(3)	0.093(13)
H(8B)	− 0.225(5)	0.022(3)	0.298(2)	0.076(11)
H(9A)	− 0.444(5)	0.206(3)	0.251(2)	0.071(11)
H(9B)	− 0.403(5)	0.159(3)	0.352(3)	0.083(12)

CRYSTAL DATA

The crystals of I and II are orange red, isomorphous, monoclinic prisms, extended along the a axis. Systematic absences are: $h0l$ for l odd, $0k0$ for k odd. The space group is $P2_1/c$ (No. 14).

The unit cell dimensions were determined as described elsewhere.[5,6] The θ-values (all abouth 20°) of 29 reflections for I and 31 reflections for II, were measured as described by Maartmann-Moe[10] The unit cell dimensions are: $a = 7.0342(6)$ Å, $b = 12.3808(10)$ Å, $c = 14.3923(11)$ Å, $\beta = 102.252(7)°$, $z = 4$, $D_x = 1.87$ g/cm³, $D_m = 1.87$ g/cm³, $\mu_{MoKa} = 28.7$ cm⁻¹, for I, and: $a = 7.1968(8)$ Å, $b = 12.8766(10)$ Å, $c = 14.3374(12)$ Å, $\beta = 101.460(9)°$, $z = 4$, $D_x = 2.23$ g/cm³, $D_m = 2.23$ g/cm³, $\mu_{MoKa} = 86.2$ cm⁻¹, for II.

STRUCTURE DETERMINATION

The structures were solved by Patterson and Fourier methods, and refined to R-values of 0.024 for I and 0.040 for II. Altogether 171 parameters were refined in each structure. The three-dimensional Fourier difference maps, based on the data of the final refinements, showed no peaks higher than 0.2 e/Å³ for I, and 0.3 e/Å³ for II.

Observed and calculated structure factors for the two structures are available from the author.

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

RESULTS

Bond lengths and angles in chloro(ethylenethiourea)phenyltellurium(II) and bromo(ethyleneselenourea)phenyltellurium(II), based on the atomic coordinates in Tables 1 and 2, are listed in Tables 5 and 6. The uncertainties in the unit cell dimensions are taken into account in the given standard deviations. Views of the structure of I and II, as seen normal to the plane through the coordination group, are shown in Figs. 1 and 2. Stereoscopic

Table 2. Atomic coordinates in fractions of monoclinic cell edges for bromo(ethyleneselenourea)-phenyltellurium(II). Origin at a centre of symmetry. Isotropic thermal parameters ($Å^2$) 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	0.20107(8)	0.39012(4)	0.46453(4)	
Br	0.26934(12)	0.48751(6)	0.66261(5)	
Se	0.17065(12)	0.30477(7)	0.29660(5)	
C(1)	0.4167(11)	0.2825(6)	0.5212(5)	
C(2)	0.6045(13)	0.3054(7)	0.5247(6)	
C(3)	0.7484(14)	0.2341(8)	0.5601(6)	
C(4)	0.6964(16)	0.1400(9)	0.5909(6)	
C(5)	0.5111(18)	0.1157(9)	0.5896(8)	
C(6)	0.3686(15)	0.1870(8)	0.5539(7)	
C(7)	− 0.0442(11)	0.2220(6)	0.2954(5)	
C(8)	− 0.2440(16)	0.0822(8)	0.2660(9)	
C(9)	− 0.3463(14)	0.1714(8)	0.3049(9)	
N(1)	− 0.0580(10)	0.1264(5)	0.2626(5)	
N(2)	− 0.1966(10)	0.2516(5)	0.3228(5)	
H(2)	0.621(12)	0.348(6)	0.486(5)	0.07(3)
H(3)	0.886(16)	0.251(8)	0.562(7)	0.18(4)
H(4)	0.819(10)	0.094(6)	0.620(5)	0.07(2)
H(5)	0.454(15)	0.050(8)	0.596(7)	0.13(4)
H(6)	0.225(11)	0.178(8)	0.547(5)	0.07(2)
H(N1)	0.056(12)	0.093(6)	0.240(6)	0.10(3)
H(N2)	− 0.224(11)	0.333(6)	0.338(5)	0.08(3)
H(8A)	− 0.289(11)	0.067(6)	0.206(5)	0.06(3)
H(8B)	− 0.228(14)	0.028(7)	0.316(6)	0.10(4)
H(9A)	− 0.420(11)	0.198(6)	0.260(5)	0.05(3)
H(9B)	− 0.432(18)	0.201(10)	0.363(9)	0.14(5)

Table 3. Anisotropic thermal parameters ($Å^2$) in the form $\exp - [2\pi^2(h^2a^{-2}U_{11} + \cdots + 2hka^{-1}b^{-1}U_{12} + \cdots]$, for chloro(ethylenethiourea)phenyltellurium(II). The values for Te, Cl, and S have been multiplied by 10^4 and the values for C and N by 10^3. Standard deviations in parentheses.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Te	389.4(9)	342.9(8)	417.6(9)	− 14.1(8)	14.1(8)	81.1(6)
Cl	441(3)	384(3)	439(3)	25(3)	− 12(3)	120(3)
S	435(4)	566(4)	423(3)	− 86(3)	− 62(3)	136(3)
C(1)	38.2(13)	32.9(12)	38.3(13)	− 0.7(11)	3.8(10)	10.3(11)
C(2)	43.9(15)	46.5(16)	49.7(16)	− 2.3(13)	5.1(13)	12.6(13)
C(3)	40.2(16)	69(2)	65.1(19)	5.9(16)	3.7(17)	15.9(16)
C(4)	64(2)	70(2)	69(2)	25.4(19)	15.1(18)	15.1(18)
C(5)	77(3)	64(2)	127(4)	10(2)	49(3)	31(3)
C(6)	48.7(19)	56.4(19)	110(3)	2.4(17)	37(2)	29(2)
C(7)	40.0(14)	37.1(13)	32.1(12)	2.8(11)	− 1.0(10)	6.6(10)
C(8)	53.6(18)	42.9(17)	65(2)	− 5.0(14)	− 12.5(15)	18.1(17)
C(9)	44.2(17)	48.4(17)	68(2)	− 6.4(15)	− 16.7(16)	18.6(16)
N(1)	45.2(14)	41.4(13)	63.6(16)	4.6(11)	− 12.9(11)	19.5(12)
N(2)	40.7(12)	38.8(12)	59.6(14)	− 3.4(10)	− 14.8(11)	19.2(11)

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

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Te	48.2(3)	40.6(3)	48.2(3)	−1.9(3)	0.7(3)	7.2(2)
Br	47.8(5)	40.0(5)	46.7(5)	3.4(4)	−1.0(4)	11.6(4)
Se	43.9(5)	60.3(6)	41.7(5)	−8.0(5)	−5.6(4)	11.0(4)
C(1)	48(5)	36(4)	39(4)	−6(4)	−1(4)	9(4)
C(2)	57(6)	54(6)	45(5)	−3(5)	5(5)	14(5)
C(3)	75(7)	75(7)	54(6)	2(6)	5(5)	9(5)
C(4)	70(8)	84(8)	60(6)	34(7)	7(6)	3(6)
C(5)	90(9)	59(7)	104(8)	1(8)	32(7)	23(7)
C(6)	56(6)	62(6)	85(7)	5(6)	19(5)	15(6)
C(7)	48(5)	43(5)	36(4)	3(4)	−2(4)	3(4)
C(8)	73(8)	46(6)	79(8)	−3(6)	−12(6)	17(7)
C(9)	49(6)	56(6)	94(8)	2(6)	−28(6)	15(6)
N(1)	41(4)	51(5)	78(5)	3(4)	−16(4)	17(4)
N(2)	45(4)	44(4)	67(5)	−5(4)	−14(4)	24(4)

Table 5. Bond lengths (Å) and angles (°) in chloro(ethylenethiourea)phenyltellurium(II). A prime denotes an atom in the position $\bar{x}, 1-y, 1-z$, where x,y,z are the coordinates in Table 1. Standard deviations are given in parentheses.

Te−Cl	2.8486(10)	S−Te−Cl	176.03(2)
Te−S	2.5211(10)	S−Te−C(1)	89.22(7)
Te−C(1)	2.120(2)	Cl−Te−C(1)	87.29(7)
Te−Cl′	3.7401(10)	C(1)−Te−Cl′	162.51(7)
C(1)−C(2)	1.383(4)	Te−C(1)−C(2)	120.19(17)
C(1)−C(6)	1.376(5)	Te−C(1)−C(6)	121.2(2)
C(2)−C(3)	1.368(4)	C(2)−C(1)−C(6)	118.6(2)
C(3)−C(4)	1.365(5)	C(1)−C(2)−C(3)	120.6(3)
C(4)−C(5)	1.355(6)	C(2)−C(3)−C(4)	120.6(3)
C(5)−C(6)	1.389(6)	C(3)−C(4)−C(5)	119.7(3)
		C(4)−C(5)−C(6)	120.6(3)
		C(5)−C(6)−C(1)	119.9(3)
S−C(7)	1.728(3)	Te−S−C(7)	102.57(9)
C(7)−N(1)	1.313(3)	S−C(7)−N(1)	123.20(19)
C(7)−N(2)	1.311(4)	S−C(7)−N(2)	125.49(17)
N(1)−C(8)	1.462(4)	N(1)−C(7)−N(2)	111.3(2)
N(2)−C(9)	1.466(4)	N(1)−C(8)−C(9)	102.8(2)
C(8)−C(9)	1.525(5)	N(2)−C(9)−C(8)	102.4(2)
		C(7)−N(1)−C(8)	111.6(2)
		C(7)−N(2)−C(9)	111.7(2)
C(2)−H(2)	0.91(3)	C(1)−C(2)−H(2)	119.1(19)
C(3)−H(3)	1.01(4)	C(3)−C(2)−H(2)	129.2(19)
C(4)−H(4)	0.98(4)	C(2)−C(3)−H(3)	116.8(19)
C(5)−H(5)	0.90(5)	C(4)−C(3)−H(3)	123.5(19)
C(6)−H(6)	0.84(4)	C(3)−C(4)−H(4)	121(2)
		C(5)−C(4)−H(4)	119(2)
		C(4)−C(5)−H(5)	122(3)
		C(6)−C(5)−H(5)	118(3)
		C(5)−C(6)−H(6)	122(2)
		C(1)−C(6)−H(6)	118(2)
C(8)−H(8A)	0.89(4)	N(1)−C(8)−H(8A)	108(3)
C(8)−H(8B)	1.00(3)	N(1)−C(8)−H(8B)	106(2)
C(9)−H(9A)	0.88(3)	H(8A)−C(8)−H(8B)	108(4)
C(9)−H(9B)	0.99(3)	C(9)−C(8)−H(8A)	120(3)

Table 5. Continued.

N(1) – H(N1)	0.83(3)	C(9) – C(8) – H(8B)	112(2)
N(2) – H(N2)	0.97(3)	N(2) – C(9) – H(9A)	107(2)
		N(2) – C(9) – H(9B)	108(2)
		C(8) – C(9) – H(9A)	112(2)
		C(8) – C(9) – H(9B)	117(2)
		H(9A) – C(9) – H(9B)	109(4)
		C(7) – N(1) – H(N1)	122(2)
		C(8) – N(1) – H(N1)	126(3)
		C(7) – N(2) – H(N2)	122(2)
		C(9) – N(2) – H(N2)	125(3)

Table 6. Bond lengths (Å) and angles (°) in bromo(ethyleneselenourea)phenyltellurium(II). A prime denotes an atom in the position, $\bar{x}, 1$-$y1$-z, where x,y,z are the coordinates given in Table 2. Standard deviations are given in parentheses.

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Te – Br	3.0537(16)	Se – Te – Br	175.62(3)
Te – Se	2.6160(16)	Se – Te – C(1)	89.94(19)
Te – C(1)	2.118(7)	Br – Te – C(1)	86.67(19)
Te – Br′	3.8490(16)	C(1) – Te – Br′	163.31(19)
C(1) – C(2)	1.374(13)	Te – C(1) – C(2)	121.0(5)
C(1) – C(6)	1.385(13)	Te – C(1) – C(6)	119.8(6)
C(2) – C(3)	1.400(13)	C(1) – C(2) – C(3)	121.6(8)
C(3) – C(4)	1.368(15)	C(2) – C(3) – C(4)	117.9(9)
C(4) – C(5)	1.367(18)	C(3) – C(4) – C(5)	121.8(9)
C(5) – C(6)	1.396(15)	C(4) – C(5) – C(6)	119.9(9)
		C(1) – C(6) – C(5)	119.6(9)
		C(2) – C(1) – C(6)	119.2(7)
Se – C(7)	1.875(8)	Te – Se – C(7)	99.5(2)
C(7) – N(1)	1.315(10)	Se – C(7) – N(1)	122.6(5)
C(7) – N(2)	1.294(11)	Se – C(7) – N(2)	125.3(5)
N(1) – C(8)	1.464(13)	N(1) – C(7) – N(2)	112.1(7)
N(2) – C(9)	1.478(12)	N(1) – C(8) – C(9)	103.3(8)
C(8) – C(9)	1.528(16)	N(2) – C(9) – C(8)	101.6(8)
		C(7) – N(1) – C(8)	110.9(7)
		C(7) – N(2) – C(9)	112.0(7)
C(2) – H(2)	0.81(8)	C(1) – C(2) – H(2)	116(4)
C(3) – H(3)	1.00(11)	C(3) – C(2) – H(2)	119(4)
C(4) – H(4)	1.07(7)	C(2) – C(3) – H(3)	123(4)
C(5) – H(5)	0.96(10)	C(4) – C(3) – H(3)	116(4)
C(6) – H(6)	1.03(8)	C(3) – C(4) – H(4)	118(4)
		C(5) – C(4) – H(4)	123(4)
		C(4) – C(5) – H(5)	119(5)
		C(6) – C(5) – H(5)	118(5)
		C(5) – C(6) – H(6)	117(4)
		C(1) – C(6) – H(6)	122(4)
C(8) – H(8A)	0.87(7)	N(1) – C(8) – H(8A)	103(5)
C(8) – H(8B)	0.94(9)	N(1) – C(8) – H(8B)	109(4)
C(9) – H(9A)	0.92(7)	H(8A) – C(8) – H(8B)	108(6)
C(9) – H(9B)	1.09(12)	C(9) – C(8) – H(8A)	114(4)
N(1) – H(N1)	1.03(9)	C(9) – C(8) – H(8B)	108(4)
N(2) – H(N2)	1.09(8)	N(2) – C(9) – H(9A)	101(4)
		N(2) – C(9) – H(9B)	106(4)
		C(8) – C(9) – H(9A)	108(4)
		C(8) – C(9) – H(9B)	107(4)
		H(9A) – C(9) – H(9B)	110(6)
		C(7) – N(1) – H(N1)	119(4)
		C(8) – N(1) – H(N1)	120(4)
		C(7) – N(2) – H(N2)	122(4)
		C(9) – N(2) – H(N2)	123(4)
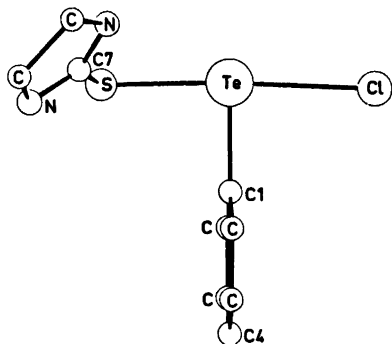
Fig. 1. Chloro(ethylenethiourea)phenyltel-
lurium(II), as seen normal to the plane through
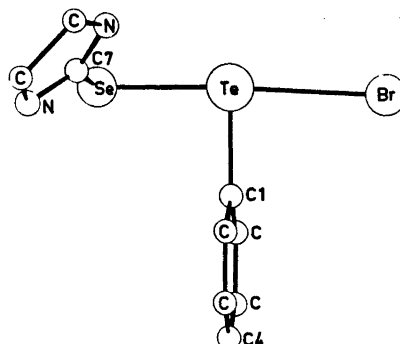the coordination group.

Fig. 2. Bromo(ethyleneselenourea)phenyl-
tellurium(II), as seen normal to the plane
through the coordination group.

views of the content of the unit cell of I and
II are shown in Figs. 3 and 4.

In each of the structures the tellurium atom
is primarily three-coordinated, being bonded
to one phenyl carbon atom and, in directions
nearly perpendicular to the Te − C bond, to one
ethylenethiourea sulfur atom and one chlorine
atom in I, and to one ethyleneselenourea sele-
nium atom and one bromine atom in II.
Thus, the coordination around the tellurium
atoms in I and II are similar to that of the
isomorphous form of bromo(ethylenethiourea)-
phenyltellurium(II).[6] The coordination around
the tellurium atom is nearly planar in both
structures. The largest deviation from a least-
squares plane through Te, S, Cl, and C(1) is
0.024 Å in I. The largest deviation from the
corresponding least-squares plane through Te,
Se, Br, and C(1) is 0.041 Å in II. The least-
squares plane through the coordination group
pass 0.057 Å from C(4) in I and 0.046 Å from
C(4) in II.

The three-centre systems, S − Te − Cl, and
Se − Te − Br are both nearly linear. The S − Te −
Cl bond angle is 176.03(2)° and the Se − Te − Br
bond angle is 175.62(3)°. A similar deviation
from linearity is also found in the crystals of
the isomorphous form of bromo(ethylene-
thiourea)phenyltellurium(II), where the S −
Te − Br bond angle is 175.96(3)°.[6]

The Te − C bond nearly bisects the angle of
the three-centre system in both I and II. The
S − Te − C bond angle is 89.22(7)° and the
Cl − Te − C bond angle is 87.29(7)° in I. In
the structure of II the Se − Te − C bond angle

is 89.94(19)° and the Br − Te − C bond angle
is 86 67(19)°. In the structure of the isomor-
phous form of bromo(ethylenethiourea)phen-
yltellurium(II) the corresponding S − Te − C
and Br − Te − C bond angles are 89.45 and
87.02°, respectively. [6]

The Te − S bond length, 2.5211(10) Å in
I is, within the error, equal to the Te − S
bond length 2.5231(15) Å, found in the crystals
of the isomorphous form of bromo(ethylene-
thiourea)phenyltellurium(II).[6] This is nearly
0.11 Å longer than the sum of the single bond
radii, 2.41 Å,[14] and about 0.02 Å longer than
the Te − S bond length, 2.50 Å, found in the
crystals of chloro- and bromo(phenyl)thio-
ureatellurium(II).[3] In chloro- and bromo-
(ethylenethiourea)phenyltellurium(II)   as   in
chloro-   and   bromo(phenyl)thioureatellurium
(II), substitution of bromine for chlorine has,
within the error, no effect on the length of
the Te − S bond *trans* to chlorine or bromine.

The Te − Cl bond length, 2.8486(10) Å in
I, is about 0.49 Å longer than the sum of
the single bond radii, 2.36 Å, but considerably
shorter than the van der Waals contacts.[11]
In the crystals of chloro(phenyl)thioureatel-
lurium(II) the Te − Cl bond length, 3.00 Å, is
0.64 Å longer than the sum of the single bond
radii.[3] The Te − Cl bond in chloro(ethylene-
thiourea)phenyltellurium(II) shorter than in
chloro(phenyl)thioureatellurium(II),   together
with the Te − Br bond in bromo(ethylene-
thiourea)phenyltellurium(II)   shorter   than
in   bromo(phenyl)thioureatellurium(II),[3,6]   in-
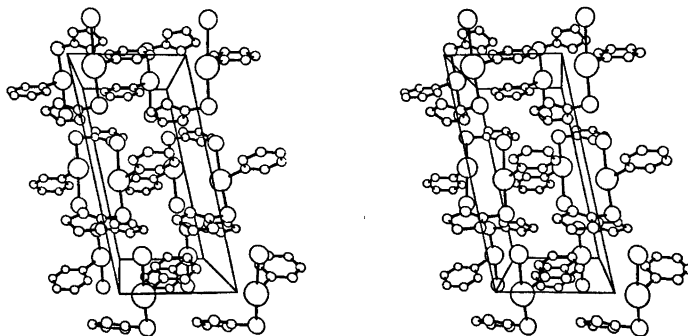dicate a more pronounced *trans* bond-lengthen-

Fig. 3. A stereoscopic view of the cell packing in chloro(ethylenethiourea)phenyltellurium(II), as seen along the *b* crystal axis.

ing effect of thiourea than ethylenethiourea on a Te-halogen bond.

The Te − Se bond length, 2.6160(16) Å, in II, is 0.076 Å longer than the sum of the single bond radii, 2.51 Å.[14] The Te − Br bond length in II, 3.0537(16) Å, is intermediate between the Te − Br bond length, 2.9694 Å, found in the structure of the isomorphous form of bromo-(ethylenethiourea)phenyltellurium(II) [6] and the Te − Br bond length 3.11 Å found in the structure of bromo(phenyl)thioureatellurium (II).[3] This indicates a relative *trans* bond lengthening order: thiourea ≥ ethyleneselenourea > ethylenethiourea when *trans* to a Te − Br bond.

The Te − C bond lengths, 2.120(2) Å in I and 2.118(7) Å in II, are equal, within the accuracy of the structure determination. The same Te − C bond length has also been found in the structures of bromo(ethylenethiourea)-phenyltellurium(II),[6] chloro- and bromo(phen-yl)thioureatellurium(II),[3] chloro(phenyl)bis-thioureatellurium(II),[4] and in the structures of the phenyldithiocyanato- and phenyldi-selenocyanatotellurate(II) anions,[5] indicating that the Te − C bond is nearly a single covalent bond.[5]

As pointed out by Foss *et al.* the coordination around the tellurium atom may be regarded as based on square-planar arrangement.[1-4] In the two present structures, as in the structure of the isomorphous form of bromo(ethylene-thiourea)phenyltellurium(II),[6] the fourth coordination site of a square-planar structure, *trans* to the phenyl group is approached by a halogen atom of an adjacent molecule, over a symmetry centre. In I a chlorine atom of an adjacent molecule, in the position $\bar{x},1-y$, $1-z$, where x,y,z are the chlorine coordinates in Table 1, lies 3.7401(10) Å from tellurium, in a direction which makes an angle of 162.51 (7)° with the direction of the Te − C bond. In II the corresponding bromine atom lies
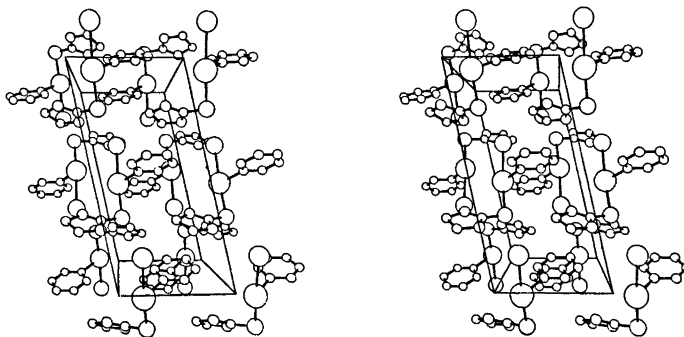

Fig. 4. A stereoscopic view of the cell packing in bromo(ethyleneselenourea)phenyltellurium(II), as seen along the *b* crystal axis.

3.8490(16) Å from tellurium, in a direction which makes an angle of 163.31(19)° with the direction of the Te−C bond.

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 in I and 0.02 Å in II. The angle between this plane and the least-squares plane through the coordination group is 87.24° in I and 86.25° in II.

The sulfur atom, the two nitrogen atoms, and the three carbon atoms of the ethylene-thiourea group are nearly co-planar. So are the selenium atom, the two nitrogen atoms, and the three carbon atoms in the ethylene-selenourea group. The largest deviation from least-squares plane is 0.048 Å in I and 0.045 Å in II. The angle between this plane and the least-squares plane through Te, S, Cl, and C(7) in I or Te, Se, Br, and C(7) in II, is 44.9 and 45.5°, respectively.

The S−C bond length, 1.728(3) Å, and the Te−S−C bond angle of 102.57(9)° in I are, within the error, equal to the S − C bond length, 1.723 Å and Te−S−C bond angle, 102.49° found in the isomorphous form of bromo-(ethylenethiourea)phenyltellurium(II).[6] The corresponding Se−C bond length in II is 1.875 (8) Å, and the Te − Se − C bond angle is 99.5 (2)°.

HYDROGEN BONDING

In both structures the closest nitrogen-halogen approaches occur between N(2) and the halogen atom at $\bar{x},1\text{-}y,1\text{-}z$, where x, y, z are the halogen coordinates in Tables 1 and 2. In I the N(2)···Cl distance is 3.297(2) Å, and the H(N2)···Cl distance is 2.36(3) Å. The N(2)−H(N2)···Cl angle is 162(2)°, the C(7)−N(2)···Cl angle is 116.19(16)°, the C(9)−N(2)···Cl angle is 126.29(16)°, the C(7)−N(2)−H(N2) angle is 122(2)°, and the C(9)−N(2)−H(N2) angle is 125(2)°. In II the N(2) ···Br distance is 3.413(7 Å, and the H(N2)···Br distance is 2.33(8) Å. The N(2)−H(N2)···Br angle is 168(4)°, the C(7)−N(2)···Br angle is 117.3(5)°, the C(9)−N(2)···Br angle is 125.7(5)°, the C(7)−N(2)−H(N2) angle is 122(4)°, and the C(9)−N(2)−H(N2) angle is 123(4)°. This probably represent N−H···Cl and N−H···Br hydrogen bonds in I and II.

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