

# The Structures of Two Crystalline Forms of Bromo-(ethylenethiourea)phenyltellurium(II)

OLAV VIKANE

Department of Chemistry, University of Bergen, N-5014 Bergen-Univ., Norway

The 1:1 complex of benzenetellurenyl bromide with ethylenethiourea,  $C_6H_5Te(etu)Br$ , crystallizes in two different space groups. One form, I, occurs as yellow monoclinic plates with space group  $C2/c$  and  $Z=8$ ; the other form, II, occurs as orange red monoclinic prisms with space group  $P2_1/c$  and  $Z=4$ . The unit cell dimensions for I are:  $a=15.5394(11)$  Å,  $b=9.0893(9)$  Å,  $c=19.0269(18)$  Å,  $\beta=114.774(6)^\circ$ , and for II:  $a=7.0513(6)$  Å,  $b=12.7786(11)$  Å,  $c=14.4676(12)$  Å,  $\beta=102.309(7)^\circ$ .

In both structures, the tellurium atom is bonded to one phenyl carbon atom and, in directions nearly perpendicular to the Te—C bond, to one ethylenethiourea sulfur atom and one bromine atom. The three-centre system S—Te—Br is nearly linear, and the Te—C bond nearly bisects the S—Te—Br angle. The bond lengths and angles involving tellurium are: Te—S = 2.5560(15) Å, Te—Br = 2.8348(10) Å, Te—C = 2.116(3) Å,  $\angle S—Te—Br = 177.22(3)^\circ$ ,  $\angle S—Te—C = 89.05(10)^\circ$ ,  $\angle Br—Te—C = 86.46(10)^\circ$  in I, and Te—S = 2.5231(15) Å, Te—Br = 2.9694(10) Å, Te—C = 2.123(4) Å,  $\angle S—Te—Br = 175.96(3)^\circ$ ,  $\angle S—Te—C = 89.45(12)^\circ$ ,  $\angle Br—Te—C = 87.02(11)^\circ$  in II.

In the structure of II the fourth position of a square-planar tellurium(II) coordination is approached by a bromine atom of an adjacent molecule, at  $Te \cdots Br = 3.8313(10)$  Å, in a direction which makes an angle of  $162.29(11)^\circ$  with the Te—C bond. In the structure of I, this approach of a "fourth ligand" is missing.

The crystal structures of 1:1 complexes between benzenetellurenyl chloride or bromide and thiourea have been determined by Foss and Husebye.<sup>1</sup> The coordination around tellurium was described as based on square-planar four-coordination with one position, *trans* to the phenyl group, vacant.<sup>1,2</sup>

In a recent paper the syntheses of an 1:1 complex between benzenetellurenyl bromide and

ethylenethiourea was reported.<sup>3</sup> The complex was found to crystallize in two different space groups. This article reports the structures of the two different crystalline forms of bromo(ethylenethiourea)phenyltellurium(II). As in the structures of chloro- and bromo(phenyl)thioureatellurium(II), the tellurium atoms are three-coordinated, and the coordinations around tellurium are nearly planar. A comparison of the structures in the two different space groups has been made, and the differences are discussed.

## EXPERIMENTAL

Methods used for data collection and reductions, and computational procedures are as described previously.<sup>4,5</sup> For the  $C2/c$  form, I, the measurements were performed on a crystal with the following dimensions, given as distances from the point of intersection of the crystal faces (001), (110), and (110): to (00 $\bar{1}$ ), 0.109 mm; to (1 $\bar{1}$ 0), 0.187 mm; and to (1 $\bar{1}$ 0), 0.187 mm. For the  $P2_1/c$  form, 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 $\bar{1}$ ), (1 $\bar{1}\bar{1}$ ), and (11 $\bar{1}$ ): to (0 $\bar{1}\bar{1}$ ), 0.155 mm; to (011), 0.148 mm; and to (100), 0.187 mm.

The scale factors, based on the reference reflections, varied within 6 % for I, and 8 % for II. 2624 of 3664 independent reflections within  $\theta=30^\circ$  were found to be stronger than the lower limit for I. The corresponding numbers for II are 2662 of 3982.

## CRYSTAL DATA

The crystals of I are yellow monoclinic 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  $C2/c$ .

Table 1. Atomic coordinates in fractions of monoclinic cell edges for bromo(ethylenethiourea)phenyltellurium(II) with space group *C2/c*. Origin at a centre of symmetry. Isotropic thermal parameters (Å<sup>2</sup>) in the form  $\exp - [8\pi^2 U(\sin^2\theta/\lambda^2)]$ . Standard deviations from least squares are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
Te	0.069468(17)	0.19402(3)	0.406262(15)	
Br	-0.09558(3)	0.34897(5)	0.39148(3)	
S	0.21436(7)	0.04273(13)	0.42009(6)	
C(1)	-0.0182(2)	0.0057(4)	0.3697(2)	
C(2)	-0.0910(3)	0.0030(5)	0.2951(2)	
C(3)	-0.1513(3)	-0.1180(5)	0.2718(3)	
C(4)	-0.1379(3)	-0.2353(5)	0.3214(3)	
C(5)	-0.0654(3)	-0.2329(4)	0.3946(2)	
C(6)	-0.0065(3)	-0.1118(4)	0.4185(2)	
C(7)	0.2663(2)	-0.0064(4)	0.5157(2)	
C(8)	0.3767(4)	-0.1105(6)	0.6283(3)	
C(9)	0.2991(3)	-0.0374(6)	0.6450(3)	
N(1)	0.3428(2)	-0.0881(4)	0.5444(2)	
N(2)	0.2385(2)	0.0286(4)	0.5703(2)	
H(2)	-0.089(3)	0.094(4)	0.259(2)	0.053(11)
H(3)	-0.200(3)	-0.111(5)	0.228(3)	0.067(15)
H(4)	-0.177(3)	-0.312(5)	0.308(3)	0.069(15)
H(5)	-0.055(3)	-0.322(5)	0.431(3)	0.066(13)
H(6)	0.042(2)	-0.117(4)	0.473(2)	0.035(9)
H(8A)	0.436(3)	-0.067(5)	0.650(3)	0.077(17)
H(8B)	0.375(4)	-0.224(6)	0.635(3)	0.100(19)
H(9A)	0.262(3)	-0.099(6)	0.661(4)	0.087(18)
H(9B)	0.326(3)	0.049(6)	0.682(3)	0.080(16)
H(N1)	0.372(3)	-0.127(5)	0.516(2)	0.067(14)
H(N2)	0.189(3)	0.087(5)	0.556(3)	0.073(16)

The crystals of II are orange red monoclinic prisms extended along the *a* axis. Systematic absences are: *h0l* for *l* odd, *0k0* for *k* odd. The space group is *P2<sub>1</sub>/c* (No. 14).

The unit cell dimensions were determined by measuring, on the diffractometer, the  $\theta$ -values (all about 20°) of 27 reflections for I and 29 reflections for II, by a method described by Maartmann-Moe.<sup>6</sup> The calculations were done by a least squares procedure. The standard deviation in the  $\lambda$  value is taken into account in the calculation of the standard deviation in the unit cell parameters. The unit cell dimensions for I are: *a* = 15.5394(11) Å, *b* = 9.0893(9) Å, *c* = 19.0269(18) Å,  $\beta$  = 114.774(6)°, *Z* = 8, *D<sub>x</sub>* = 2.10 g/cm<sup>3</sup>, *D<sub>m</sub>* = 2.11 g/cm<sup>3</sup>,  $\mu_{(MoK\alpha)}$  = 61.3 cm<sup>-1</sup>.

The unit cell dimensions for II are: *a* = 7.0513(6) Å, *b* = 12.7786(11) Å, *c* = 14.4676(12) Å,  $\beta$  = 102.309(7)°, *Z* = 4, *D<sub>x</sub>* = 2.01 g/cm<sup>3</sup>, *D<sub>m</sub>* = 2.02 g/cm<sup>3</sup>,  $\mu_{(MoK\alpha)}$  = 58.7 cm<sup>-1</sup>.

## STRUCTURE DETERMINATION

The structures were solved by Patterson and Fourier methods and refined to *R*-values of 0.028 for I and 0.033 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/Å<sup>3</sup> in either of the two structures.

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 the two forms of bromo(ethylenethiourea)phenyltellurium(II), based on the atomic coordinates in Tables 1 and 2, are listed in Table 5. Views of the structures, as seen normal to the plane through the

Table 2. Atomic coordinates in fractions of monoclinic cell edges for bromo(ethylenethiourea)-phenyltellurium(II) with space group  $P2_1/c$ . Origin at a centre of symmetry. Isotropic thermal parameters ( $\text{\AA}^2$ ) in the form  $\exp - [8\pi^2 U (\sin^2 \theta / \lambda^2)]$ . Standard deviations from least squares are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
Te	0.20656(4)	0.38999(2)	0.46655(2)	
Br	0.27579(7)	0.48648(3)	0.65752(3)	
S	0.17234(19)	0.30383(10)	0.30692(8)	
C(1)	0.4235(6)	0.2785(3)	0.5247(3)	
C(2)	0.6161(7)	0.3003(4)	0.5272(3)	
C(3)	0.7555(7)	0.2269(5)	0.5635(4)	
C(4)	0.7032(10)	0.1320(5)	0.5974(4)	
C(5)	0.5163(11)	0.1110(5)	0.5950(5)	
C(6)	0.3718(9)	0.1840(4)	0.5580(5)	
C(7)	-0.0277(7)	0.2248(3)	0.3014(3)	
C(8)	-0.2307(9)	0.0832(5)	0.2628(5)	
C(9)	-0.3401(8)	0.1698(4)	0.3035(5)	
N(1)	-0.0420(7)	0.1299(3)	0.2650(3)	
N(2)	-0.1882(6)	0.2503(3)	0.3278(3)	
H(2)	0.635(7)	0.379(4)	0.500(3)	0.071(16)
H(3)	0.897(9)	0.235(5)	0.558(4)	0.094(19)
H(4)	0.805(10)	0.074(5)	0.622(5)	0.13(2)
H(5)	0.464(10)	0.035(5)	0.609(4)	0.12(2)
H(6)	0.239(8)	0.163(4)	0.555(4)	0.087(19)
H(8A)	-0.290(7)	0.055(4)	0.203(4)	0.068(17)
H(8B)	-0.221(7)	0.028(4)	0.300(3)	0.060(17)
H(9A)	-0.465(9)	0.193(5)	0.250(4)	0.10(2)
H(9B)	-0.376(8)	0.137(4)	0.363(4)	0.071(17)
H(N1)	0.063(8)	0.098(4)	0.241(4)	0.078(18)
H(N2)	-0.200(8)	0.323(4)	0.353(4)	0.080(17)

Table 3. Anisotropic thermal parameters ( $\text{\AA}^2$ ) in the form  $\exp - [2\pi^2 (h^2 a^{-2} U_{11} + \dots + 2hka^{-1}b^{-1} U_{12} + \dots)]$ , for bromo(ethylenethiourea)phenyltellurium(II) with space group  $C2/c$ . The values for Te, Br, 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	337.2(11)	356.1(13)	398.2(14)	-20.2(11)	-1.9(12)	140.5(10)
Br	409(2)	425(2)	546(3)	151.3(18)	4(2)	154(2)
S	370(5)	683(7)	441(5)	113(5)	-2(6)	192(5)
C(1)	32.1(18)	32.6(19)	33(2)	2.0(15)	-1.5(16)	13.4(16)
C(2)	44(2)	46(2)	34(2)	-6.3(19)	0.9(19)	12.5(19)
C(3)	46(2)	58(3)	39(3)	-8(2)	-2(2)	8(2)
C(4)	51(3)	44(3)	52(3)	-13(2)	-15(2)	27(2)
C(5)	52(2)	35(2)	43(2)	-0.4(18)	-1.2(18)	23(2)
C(6)	41(2)	36(2)	34(2)	4.2(17)	1.6(17)	14.0(18)
C(7)	31.6(19)	38(2)	45(2)	-1.2(16)	-3.3(18)	17.0(18)
C(8)	55(3)	59(3)	61(3)	16(3)	13(3)	24(3)
C(9)	48(3)	67(3)	51(3)	11(2)	8(3)	22(2)
N(1)	47(2)	69(3)	54(2)	21.9(19)	8(2)	25.9(19)
N(2)	44(2)	57(2)	49(2)	15.5(18)	6.8(19)	22.6(18)

Table 4. Anisotropic thermal parameters ( $\text{\AA}^2$ ) in the form  $\exp[-2\pi^2(h^2\alpha^2U_{11} + \dots + 2hka^{-1}b^{-1}U_{13} + \dots)]$ , for bromo(ethylenethiourea)phenyltellurium(II) with space group  $P2_1/c$ . The values for Te, Br, 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	430.5(17)	364.3(15)	490.7(17)	-13.7(15)	26.8(14)	78.3(12)
Br	472(3)	371(2)	476(3)	34(2)	-1(2)	130(2)
S	504(7)	620(8)	493(7)	-100(7)	-62(6)	142(6)
C(1)	44(3)	35(2)	45(2)	2(2)	7.2(19)	7(2)
C(2)	47(3)	49(3)	57(3)	0(2)	3(2)	11(2)
C(3)	44(3)	77(4)	67(3)	14(3)	1(3)	16(3)
C(4)	73(4)	70(4)	74(4)	23(4)	19(3)	13(3)
C(5)	81(5)	70(4)	141(6)	8(4)	58(5)	26(4)
C(6)	54(3)	57(4)	120(5)	-2(3)	38(3)	22(4)
C(7)	44(3)	43(3)	40(2)	-1(2)	-2(2)	4(2)
C(8)	55(4)	49(3)	87(4)	-7(3)	-18(3)	21(3)
C(9)	51(3)	51(3)	83(4)	-11(3)	-21(3)	18(3)
N(1)	56(3)	43(2)	81(3)	2(2)	-21(2)	21(2)
N(2)	45(2)	46(2)	72(3)	-1(2)	-20(2)	24(2)

coordination group, are shown in Figs. 1 and 2. Stereoscopic views of the contents of the unit cells of the two forms are shown in Figs. 3 and 4.

In each of the structures, the tellurium atom is bonded to one phenyl carbon atom and, in directions nearly perpendicular to the Te-C bond, to one bromine atom and one ethylenethiourea sulfur atom. The coordination around the tellurium atom is nearly planar in both structures. The largest deviation from a least-squares plane through Te, Br, S, and C(1) is 0.015  $\text{\AA}$  in I and 0.031  $\text{\AA}$  in II. The least-squares plane through the coordination group passes 0.010  $\text{\AA}$  from C(4) in I and 0.016  $\text{\AA}$  from C(4) in II.

The three-centre system Br-Te-S is nearly linear in both structures. The Br-Te-S bond angle is 177.22(3) $^\circ$  in I and 175.96(3) $^\circ$  in II. A similar deviation from linearity is found in the structure of bromo(phenyl)thioureatellurium(II) where the Br-Te-S bond angle is 174.1 $^\circ$ .<sup>1</sup>

The Te-C bond nearly bisects the angle of the three-centre system. The S-Te-C bond angle is 89.05(10) $^\circ$  in I and 89.45(12) $^\circ$  in II, and the Br-Te-C bond angle is 86.46(10) $^\circ$  in I and 87.02(11) $^\circ$  in II.

The Te-S bond length, 2.5560(15)  $\text{\AA}$  in I and 2.5231(15)  $\text{\AA}$  in II, are both longer than the sum of the single-bond radii, 2.41  $\text{\AA}$ ,<sup>7</sup> and also longer than the Te-S bond length, 2.50  $\text{\AA}$ ,

found in the structure of chloro- and bromo-(phenyl)thioureatellurium(II).<sup>1</sup> The Te-Br bond length, 2.8348(10)  $\text{\AA}$  in I and 2.9694(10)  $\text{\AA}$  in II, are both shorter than the Te-S bond length, 3.11  $\text{\AA}$ , found in the structure of bromo-(phenyl)thioureatellurium(II).<sup>1</sup> The Te-Br bond in I is about 0.135  $\text{\AA}$  shorter than the Te-Br bond in II, and the Te-S bond in I is about 0.033  $\text{\AA}$  longer than the Te-S bond in II. It is seen that the shortest Te-S bond has the longest Te-Br bond in *trans* position. However, the rather small difference between the Te-S bond lengths in I and II is not expected to have such a pronounced effect on the length of the *trans*-positioned Te-Br bond. It is therefore believed that differences in the crystal packing in the two different space groups are the main reason for the longer Te-Br bond in II than in I. The sum of the lengths of the *trans*-positioned Te-S and Te-Br bonds is 5.391  $\text{\AA}$  in I and 5.493  $\text{\AA}$  in II. The sum of the lengths of the *trans*-positioned Te-S and Te-Br bonds in bromo(phenyl)thioureatellurium(II) is 5.61  $\text{\AA}$ .<sup>1</sup> In the structure of *cis*-dibromodithioureatellurium(II)<sup>8</sup> where likewise bromine and thiourea are *trans*-positioned, the Te-S bond length is 2.47  $\text{\AA}$  and the Te-Br bond length is 3.05  $\text{\AA}$ , and the sum of the lengths of the *trans*-positioned Te-S and Te-Br bonds is 5.52  $\text{\AA}$ . The structures of two crystalline forms of di- $\mu$ -bromobis[diethylenethioureatellurium(II)] di-

Table 5. Bond lengths (Å) and angles (°) in bromo(ethylenethiourea)phenyltellurium(II) with space group  $C2/c$ , I, and with space group  $P2_1/c$ , II. A prime denotes an atom in the position  $\bar{x}, 1-y, 1-z$ , where  $x, y, z$  are the coordinates in Table 2. Standard deviations are given in parentheses.

	I	II		I	II
Te-S	2.5560(15)	2.5231(15)	S-Te-Br	177.22(3)	175.96(3)
Te-Br	2.8348(10)	2.9694(10)	S-Te-C(1)	89.05(10)	89.45(12)
Te-Br'		3.8313(10)	C(1)-Te-Br'		162.29(11)
Te-C(1)	2.116(3)	2.123(4)	Br-Te-C(1)	86.46(10)	87.02(11)
C(1)-C(2)	1.396(5)	1.380(7)	Te-C(1)-C(2)	119.0(3)	119.7(3)
C(1)-C(6)	1.377(5)	1.378(8)	Te-C(1)-C(6)	121.3(2)	120.2(3)
C(2)-C(3)	1.391(6)	1.379(7)	C(2)-C(1)-C(6)	119.6(3)	120.0(4)
C(3)-C(4)	1.380(7)	1.387(9)	C(1)-C(2)-C(3)	119.2(3)	119.3(4)
C(4)-C(5)	1.376(5)	1.348(10)	C(2)-C(3)-C(4)	120.3(3)	120.5(5)
C(5)-C(6)	1.381(5)	1.401(9)	C(3)-C(4)-C(5)	120.2(4)	120.1(5)
			C(4)-C(5)-C(6)	119.7(3)	120.6(6)
			C(1)-C(6)-C(5)	120.9(3)	119.5(5)
S-C(7)	1.712(4)	1.723(5)	Te-S-C(7)	104.60(15)	102.49(16)
C(7)-N(1)	1.311(5)	1.317(16)	S-C(7)-N(1)	122.1(3)	123.4(3)
C(7)-N(2)	1.319(7)	1.311(7)	S-C(7)-N(2)	127.6(3)	126.1(3)
N(1)-C(8)	1.471(7)	1.453(8)	N(1)-C(7)-N(2)	110.3(3)	110.4(4)
N(2)-C(9)	1.464(6)	1.473(7)	C(7)-N(1)-C(8)	112.4(4)	112.2(4)
C(8)-C(9)	1.523(9)	1.536(9)	C(7)-N(2)-C(9)	112.1(4)	112.7(4)
			N(1)-C(8)-C(9)	102.2(4)	103.2(4)
			N(2)-C(9)-C(8)	102.7(4)	101.3(4)
C(2)-H(2)	1.08(4)	1.06(5)	C(1)-C(2)-H(2)	114(2)	118(3)
C(3)-H(3)	0.86(4)	1.03(6)	C(3)-C(2)-H(2)	126(2)	123(3)
C(4)-H(4)	0.89(5)	1.04(6)	C(2)-C(3)-H(3)	117(3)	122(3)
C(5)-H(5)	1.03(5)	1.08(7)	C(4)-C(3)-H(3)	122(3)	117(3)
C(6)-H(6)	0.99(3)	0.97(6)	C(3)-C(4)-H(4)	121(3)	122(4)
			C(5)-C(4)-H(4)	119(3)	118(4)
			C(4)-C(5)-H(5)	120(2)	124(4)
			C(6)-C(5)-H(5)	120(2)	116(4)
			C(1)-C(6)-H(6)	125(2)	123(3)
			C(5)-C(6)-H(6)	115(2)	117(3)
C(8)-H(8A)	0.93(5)	0.95(5)	C(7)-N(1)-H(N1)	124(2)	122(3)
C(8)-H(8B)	1.04(6)	0.88(5)	C(8)-N(1)-H(N1)	124(2)	125(3)
C(9)-H(9A)	0.94(6)	1.08(6)	C(7)-N(2)-H(N2)	116(4)	119(3)
C(9)-H(9B)	1.03(5)	1.04(6)	C(9)-N(2)-H(N2)	123(4)	124(3)
N(1)-H(N1)	0.92(5)	0.97(6)	N(1)-C(8)-H(8A)	105(3)	114(3)
N(2)-H(N2)	0.88(5)	1.01(5)	N(1)-C(8)-H(8B)	105(3)	111(3)
			C(9)-C(8)-H(8A)	107(3)	117(3)
			C(9)-C(8)-H(8B)	111(4)	109(4)
			H(8A)-C(8)-H(8B)	116(4)	103(4)
			N(2)-C(9)-H(9A)	109(2)	115(3)
			N(2)-C(9)-H(9B)	105(3)	112(3)
			C(8)-C(9)-H(9A)	116(3)	109(3)
			C(8)-C(9)-H(9B)	111(3)	106(3)
			H(9A)-C(9)-H(9B)	111(5)	113(5)

bromide<sup>a</sup> have Te-S bond lengths of 2.495, 2.491, and 2.481 Å, and the bond lengths of the corresponding *trans*-positioned Te-Br bonds are 3.048, 3.015, and 3.079 Å. The sums of the bond lengths of *trans*-positioned Te-S and

Te-Br bonds are 5.543, 5.506, and 5.560 Å. In the structure of centrosymmetric *trans*-dibromobis(ethylenethiourea)tellurium(II),<sup>10</sup> the Te-S bond length is 2.69 Å and the Te-Br bond length is 2.78 Å, and the sum of the Te-S and

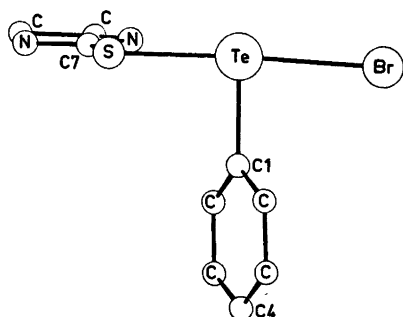


Fig. 1. Bromo(ethylenethiourea)phenyltellurium(II), with space group  $C2/c$ , as seen normal to the plane through the coordination group.

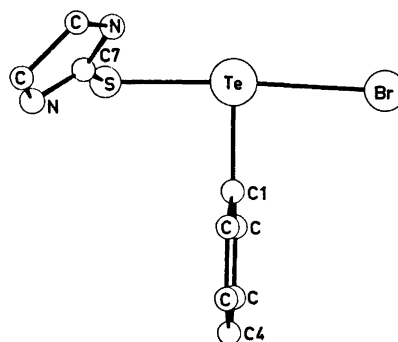


Fig. 2. Bromo(ethylenethiourea)phenyltellurium(II), with space group  $P2_1/c$ , as seen normal to the plane through the coordination group.

the Te-Br bond lengths is 5.47 Å. Thus, although in tellurium(II) complexes with ethylenethiourea in *trans* position to bromine the Te-S bonds are shorter and the Te-Br bonds are longer than the bonds in centrosymmetric complexes of divalent tellurium, the sum of the Te-S and the Te-Br bond lengths varies only slightly, relative to the sum in centrosymmetric complexes.

The Te-C bond lengths found in the present structures, 2.116(3) Å in I and 2.123(4) Å in II, are equal within the accuracies of the structure determinations. The same Te-C bond length has also been found in the crystal structures of chloro- and bromo(phenyl)thioureatellurium(II),<sup>1</sup> phenylbis(thiourea)tellurium(II) chloride,<sup>11</sup> and in the phenyldithiocyanato- and phenyldiselenocyanatotellurate(II) anions,<sup>5</sup> indicating that the Te-C bond is nearly a single covalent bond.<sup>5</sup>

The *trans* bond-lengthening effect of the phenyl group is more pronounced than that of thiourea or ethylenethiourea. In the structure

of II, as in phenylbis(thiourea)tellurium(II) chloride,<sup>11</sup> and in chloro- and bromo(phenyl)thioureatellurium(II),<sup>1</sup> the fourth position of a square-planar coordination is virtually vacant. In II, a bromine atom of an adjacent molecule, at a position  $\bar{x}, 1-y, 1-z$ , where  $x, y, z$  are the bromine coordinates in Table 2, lies 3.8313(10) Å from tellurium, in a direction which makes an angle of 162.29(11)° with the direction of the Te-C bond. In the structure of bromo(phenyl)thioureatellurium(II),<sup>1</sup> a corresponding bromine atom of an adjacent molecule, over a symmetry centre, lies 3.77 Å from tellurium in a direction which makes an angle of 164° with the direction of the Te-C bond. These atoms, although at such a distance as to indicate only very weak bonding interaction with tellurium, approach the fourth coordination site of a square-planar structure. In the structure of I, as in the structures of tetramethylammonium phenyldithiocyanatotellurate(II) and tetramethylammonium phenyldiselenocyanatotellurate(II),<sup>5</sup> there is no

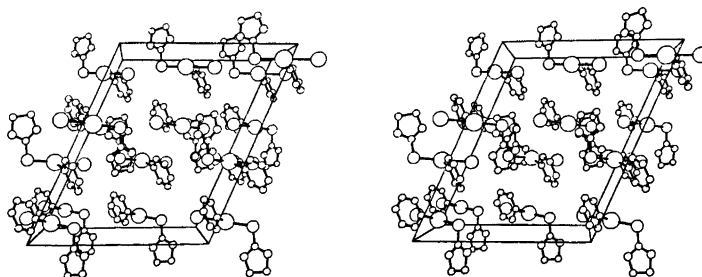


Fig. 3. A stereoscopic view of the cell packing in bromo(ethylenethiourea)phenyltellurium(II), with space group  $C2/c$ , as seen along the  $b$  crystal axis.

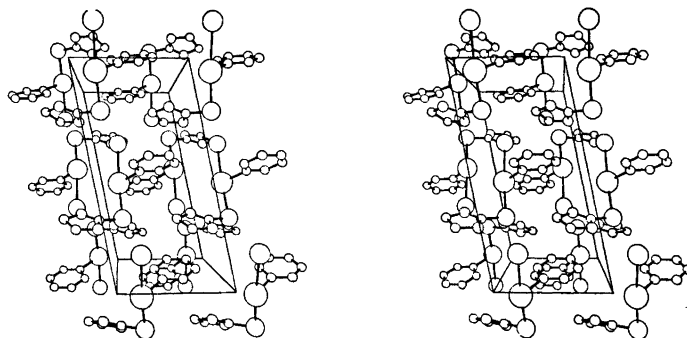


Fig. 4. A stereoscopic view of the cell packing in bromo(ethylenethiourea)phenyltellurium(II), with space group  $P2_1/c$ , as seen along the  $b$  crystal axis.

such approach of a weakly bonded fourth ligand.

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 is 0.025 Å in I and 0.015 Å in II. The angle between this plane and the least-squares plane through the coordination group is 64.6° in I and 87.0° in II.

The sulfur atom, the two nitrogen atoms, and the three carbon atoms of the ethylenethiourea group are nearly planar in both structures. The largest deviation from a least-squares plane is 0.036 Å in I and 0.055 Å in II. In the structure of I the plane of the ethylenethiourea group is nearly co-planar with the least-squares plane through Te, S, Br, and C(7). In II the angle between the two corresponding planes is 44.1°. The S—C bond length in the two structures are equal within the accuracies of the structure determinations, the average bond length is 1.718 Å. The Te—S—C bond angle is 104.60(15)° in I and 102.49(16)° in II.

#### HYDROGEN BONDING

In the structure of I the closest nitrogen-bromine approach occurs between N(1) and the bromine atom at  $x + \frac{1}{2}, y - \frac{1}{2}, z$ , where  $x, y, z$  are the bromine coordinates in Table 1. The N(1)⋯Br distance is 3.471(5) Å and the H(N1)⋯Br distance is 2.62(5) Å. The N(1)—H(N1)⋯Br angle is 154(2)°, the C(7)—N(1)⋯Br angle is 105.4(3)°, the C(8)—N(1)⋯Br angle is 142.0(3)°, the C(7)—N(1)—H(N1) angle is 124(2)°, and the C(8)—N(1)—H(N1) angle is 124(2)°. In the structure of II the closest

nitrogen-bromine approach occurs between N(2) and the bromine atom at  $\bar{x}, 1-y, 1-z$ , where  $x, y, z$  are the bromine coordinates in Table 2. The N(2)⋯Br distance is 3.434(4) Å, and the H(N2)⋯Br distance is 2.49(5) Å. The N(2)—H(N2)⋯Br angle is 156(3)°, the C(7)—N(2)⋯Br angle is 116.1(3)°, the C(9)—N(2)⋯Br angle is 124.6(3)°, the C(7)—N(2)—H(N2) angle is 119(3)°, and the C(9)—N(2)—H(N2) angle is 128(3)°. This probably represents N—H⋯Br hydrogen bonds in the two structures. The apparently stronger hydrogen bond in II than in I, as indicated by the shorter N⋯Br distance, may be one of the effects that cause the longer Te—Br bond in II than in I.

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