## Three-coordinated Divalent Tellurium Complexes. The Crystal and Molecular Structures of Chloro- and Bromo-phenyl(tetramethylthiourea)tellurium(II), and Chloro- and Bromo-phenyl(trimorpholylphosphine-selenide)tellurium(II)

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The crystal and molecular structures of four three-coordinated divalent tellurium complexes have been determined. All four compounds form monoclinic crystals with space group  $P2_1/n$ , Z=4. The unit cell dimensions are: Chlorophenyl(tetramethylthiourea)tellurium(II),  $C_6H_5TeSC(N(CH_3)_2)_2Cl$ , a=7.7301(6), b=12.6097(8), c=15.2179(9) Å,  $\beta=99.011(6)^\circ$ ; bromophenyl(tetramethylthiourea)tellurium(II),  $C_6H_5TeSC(N(CH_3)_2)_2Br$ , a=7.7306(6), b=12.8673(17), c=15.4239(11) Å,  $\beta=99.737(8)^\circ$ ; chlorophenyl(trimorpholylphosphineselenide)tellurium(II),  $C_6H_5TeSeP(NC_4H_8O)_3Cl$ , a=9.1358(7), b=18.6953(16), c=13.4605(10) Å,  $\beta=100.618(6)^\circ$ ; bromophenyl(trimorpholylphosphineselenide)tellurium(II),  $C_6H_5TeSeP(NC_4H_8O)_3Br$ , a=9.2467(12), b=18.9217(16), c=13.3961(12) Å,  $\beta=99.852(9)^\circ$ . The first two compounds, with the tetramethylthiourea group as one of the ligands, are isomorphous, so are also the last two, with the trimorpholylphosphineselenide group.

The four complexes are three-coordinated T-shaped. In a direction nearby perpendicular to the Te-C bond, tellurium is bonded to a halogen atom, and in *trans* position to the halogen atom to a tetramethylthiourea sulfur or a trimorpholylphosphineselenide selenium atom. The three-centre systems Y-Te-X, where Y is chalcogen and X is halogen, are nearly linear. The angles are in the range 174.71(5) to 176.92(6)°. The bond lengths in the three-centre systems are: S-Te-Cl, 2.5954(17) and 2.6684(19) Å; S-Te-Br, 2.5892(24) and 2.8328(12) Å; Se-Te-Cl, 2.7827(9) and 2.6004(20) Å; Se-Te-Br, 2.7689(9) and 2.7607(10) Å. The Te-C bond lengths are found in the range 2.108(6) to 2.150(8) Å and the Y-Te-C and X-Te-C angles are from 87.49(16)° to 93.38(16)°.

Three-coordinated tellurium complexes where phenyl is one of the ligands have been studied at this institute. <sup>1-9</sup> The present paper is a structure report of four such complexes. The ligands are in addition to the phenyl group, tetramethylthiourea, trimorpholylphosphineselenide, chlorine and bromine.

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Table 1. Crystal data and refinement characteristics.

	C <sub>6</sub> H <sub>5</sub> Te(tmtu)Cl	C <sub>6</sub> H <sub>5</sub> Te(tmtu)Br	C <sub>6</sub> H <sub>5</sub> TeSeP(NC <sub>4</sub> H <sub>8</sub> O)CI	C <sub>6</sub> H <sub>5</sub> TeSeP(NC <sub>4</sub> H <sub>8</sub> O)Br
6 (A)	7.7301(6) 12.6097(8)	7.7306(6)	9.1358(7) 18.6953(16)	9.2467(12) 18.9217(16)
(A)		15.4239(11) 99.737(8)	13.4605(10) $100.618(6)$	13.3961(12) 99.852(9)
V (A') M		1512.14 416.84	2259.64	2309.26
•		P2 <sub>1</sub> /n	$P_{21/n}$	$P2_1/n$
		0.71069	0.71069 1.78	0.71069
$D_{\text{obs}}(\mathbf{g/cm}^3)$		1.87	1.77	1.88
		49.32 293	33.12 283	49.61 293
		800	1200	1272
Scan mode No. of reflections		α-2θ 3527	α-2θ 5226	0.039 0-20 5317
	2737	2226	3422	3479
	0.1450.1750.30 0.036 0.040	0.13×0.13×0.28 0.037 0.044	0.08×0.10×0.25 0.037 0.042	0.10×0.10×0.28 0.033 0.037
refined	145	145	253	253
Difference Fourier max value (e $Å^{-3}$ )	6.0	0.8	8.0	0.8
		-		

Table 2. Final fractional atomic coordinates and equivalent temperature factors  $U_{\rm eq}(\mathring{A}^2\times 10^2)$ .  $U_{\rm eq}=\frac{1}{3}\sum_{\rm i}\sum_{\rm j}U_{\rm ij}I_i^*a_j^*\overline{a}_{\rm i}\cdot\overline{a}_{\rm j}$ .

Atom	x	y	z	$U_{ m eq}$
$C_6H_5Te(tm$	tu)Cl			
Te	0.70545(5)	0.06552(3)	0.341300(26)	4.13(2)
S	0.66280(24)	0.10053(13)	0.50460(11)	4.63(9)
Cl	0.73844(28)	0.04490(16)	0.17019(12)	6.13(11)
C(1)	0.4967(ʔ) ´	$0.1708(\hat{5})$	0.3000(3)	3.8(3)
C(2)	0.5318(9)	0.2755(5)	0.2774(4)	5.0(4)
C(3)	0.3935(11)	0.3451(6)	0.2521(5)	6.9(5)
C(4)	0.2197(10)	0.3096(7)	0.2486(5)	7.9(5)
C(5)	0.1873(9)	0.2079(7)	0.2721(5)	6.2(5)
C(6)	0.3229(9)	0.1385(6)	0.2992(4)	5.2(4)
C(7)	0.7583(7)	0.2262(5)	0.5136(3)	3.5(3)
N(1)	0.6618(6)	0.3117(4)	0.5258(3)	4.3(3)
N(2)	0.9280(6)	0.2396(4)	0.5088(3)	4.0(3)
C(11)	0.7348(10)	0.4105(5)	0.5650(5)	5.6(5)
C(12)	0.4664(8)	0.3111(6)	0.5069(5)	6.4(5)
C(21)	1.0577(9)	0.1535(6)	0.5294(5)	6.2(5)
C(22)	0.9946(9)	0.3306(5)	0.4650(4)	5.2(4)
C <sub>6</sub> H <sub>5</sub> Te(tm	tu)Br			
Te	0.69671(8)	0.06615(4)	0.35370(4)	4.92(3)
S	0.6556(3)	0.10542(19)	0.51360(15)	5.71(15)
Br	0.73764(15)	0.03454(8)	0.17654(6)	6.99(7)
C(1)	0.4853(11)	0.1687(6)	0.3082(5)	4.3(5)
C(2)	0.5209(12)	0.2694(6)	0.2845(6)	5.3(5)
C(3)	0.3803(15)	0.3378(8)	0.2583(6)	7.1(7)
C(4)	0.2062(16)	0.3042(9)	0.2541(6)	7.4(8)
C(5)	0.1718(14)	0.2041(9)	0.2775(6)	7.2(7)
C(6)	0.3125(12)	0.1344(7)	0.3059(5)	5.7(6)
C(7)	0.7561(12)	0.2290(6)	0.5214(5)	4.1(5)
N(1)	0.6597(9)	0.3123(6)	0.5310(4)	5.1(5)
N(2)	0.9264(9)	0.2384(5)	0.5171(4)	4.5(5)
C(11)	0.7363(13)	0.4104(6)	0.5690(6)	5.8(6)
C(12)	0.4640(12)	0.3125(9)	0.5102(7)	8.1(8)
C(21)	1.0518(12)	0.1531(7)	0.5404(6)	6.4(6)
C(22)	0.9943(12)	0.3262(7)	0.4728(5)	5.5(6)
C <sub>6</sub> H <sub>5</sub> TeSeF	P(NC <sub>4</sub> H <sub>8</sub> O) <sub>3</sub> Cl			
Te	0.44184(6)	0.069510(27)	0.16366(4)	3.60(5)
Se	0.25799(9)	0.04814(4)	-0.02308(6)	3.66(6)
<u>C</u> l	0.63162(24)	0.08199(11)	0.33229(16)	4.72(13)
P	0.20299(20)	0.15549(9)	-0.08057(13)	2.29(10)
C(1)	0.2632(8)	0.0571(4)	0.2455(\$)	3.3(4)
C(2)	0.2924(10)	0.0253(4)	0.3403(6)	4.7(5)
C(3)	0.1745(11)	0.0154(4)	0.3918(6)	5.8(6)
C(4)	0.0293(10)	0.0346(4)	0.3518(7)	5.2(7)
C(5)	0.0042(9)	0.0656(5)	0.2572(7)	5.2(5)
C(6)	0.1199(9)	0.0771(4)	0.2046(6)	4.2(5)
N(1)	0.0218(6)	0.16916(28)	-0.0884(4)	2.7(3)
C(11)	-0.0388(8)	0.2376(4)	-0.1385(6)	3.2(4)

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Table 2. Continued.

C(12) O(1) C(13) C(14) N(2) C(21) C(22) O(2) C(23) C(24) N(3) C(31)	-0.1886(9) -0.2901(5) -0.2320(9) -0.0847(8) 0.2680(6) 0.2658(9) 0.3927(10) 0.3776(6) 0.3856(9) 0.2539(9) 0.2772(6) 0.2164(8)	0.2543(4) 0.19449(29) 0.1303(5) 0.1091(4) 0.16481(29) 0.1041(4) 0.1156(4) 0.18288(28) 0.2401(4) 0.2346(4) 0.22340(28) 0.2480(4)	-0.1073(6) -0.1356(4) -0.0834(7) -0.1149(6) -0.1861(4) -0.2583(5) -0.3172(6) -0.3692(4) -0.2966(6) -0.2397(5) -0.0126(4) 0.07776(5)	4.4(5) 4.6(3) 5.4(5) 4.0(4) 2.9(3) 3.7(4) 4.8(5) 4.4(4) 4.4(5) 3.5(4) 2.5(3) 3.3(4)
C(32) O(3)	0.2523(9) 0.4112(6)	0.3276(4) 0.33971(26)	0.0931(6) 0.1061(4)	4.2(5) 4.2(3)
C(33)	0.4625(9)	0.3189(4)	0.0156(6)	4.4(5)
C(34)	0.4383(8)	0.2388(4)	-0.0030(6)	3.4(4)
C.H.TeSe	P(NC₄H <sub>8</sub> O)₃Br			
Te	0.43201(5)	0.065600(24)	0.15937(4)	3.68(5)
Se	0.25482(9)	0.04632(3)	-0.02727(5)	3.81(5)
Br	0.62808(9)	0.08091(4)	0.33815(6)	3.69(6)
P	0.20515(19)	0.15398(8)	-0.08060(11)	2.38(9)
C(1)	0.2529(8)	0.0535(3)	0.2414(5)	3.4(4)
C(2)	0.2827(8)	0.0202(4)	0.3369(5)	4.4(4)
C(3)	0.1655(9)	0.0110(4)	0.3902(6)	5.2(5)
C(4)	0.0245(9)	0.0327(4)	0.3496(6)	5.4(5)
C(5)	-0.0038(8)	0.0659(4)	0.2545(6)	4.9(5)
C(6)	0.1119(8)	0.0765(4)	0.1992(6)	4.0(4)
N(1) C(11)	$0.0260(6) \\ -0.0317(7)$	0.16836(26) 0.2362(3)	-0.0878(4) -0.1366(5)	3.0(3)
C(11)	-0.0317(7) -0.1797(8)	0.2537(4)	-0.1366(3) -0.1045(6)	3.4(4) 4.5(4)
O(12)	-0.1797(8) -0.2791(5)	0.19625(26)	-0.1043(0) -0.1321(4)	4.7(3)
C(13)	-0.2245(8)	0.1318(4)	-0.0824(6)	5.3(5)
C(14)	-0.0807(7)	0.1098(3)	-0.1143(5)	4.0(4)
N(2)	0.2687(6)	0.16418(26)	-0.1876(4)	2.7(3)
C(21)	0.2689(8)	0.1059(3)	-0.2613(5)	3.7(4)
C(22)	0.3986(9)	0.1172(4)	-0.3174(5)	4.9(4)
O(2)	0.3880(6)	0.18555(25)	-0.3667(4)	4.9(3)
C(23)	0.3917(8)	0.2411(3)	-0.2929(5)	4.2(4)
C(24)	0.2594(8)	0.2345(3)	-0.2389(5)	3.3(4)
N(3)	0.2814(6)	0.21934(26)	-0.0092(4)	2.8(3)
C(31)	0.2231(8)	0.2435(3)	0.0815(5)	3.4(4)
C(32)	0.2591(8)	0.3227(4)	0.0970(5)	3.9(4)
O(3)	0.4148(5)	0.33401(24)	0.1067(4)	4.3(3)
C(33) C(34)	0.4669(8) 0.4426(7)	0.3132(4) 0.2332(3)	0.0157(5) -0.0015(5)	4.1(4) 3.3(4)
	0.7720( <i>1</i> )	0.2002(0)	0.0015(5)	J.J(¬)

## **EXPERIMENTAL**

Synthesis and preliminary crystal data for the four compounds have been reported previously. 10-11

Intensity data were collected on an Enraf-Nonius CAD 4 computer-controlled diffractometer. The intensities of two reference reflections of medium intensity were

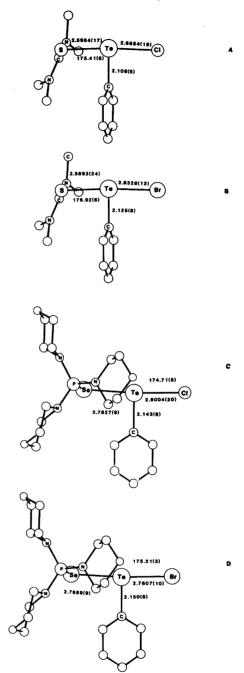


Fig. 1. The coordination of divalent tellurium in A: chlorophenyl(tetramethylthiourea)tellurium(II), B: bromophenyl(tetramethyltiourea)tellurium(II), C: chlorophenyl(trimorpholylphosphineselenide)tellurium(II), and D: bromophenyl(trimorpholylphosphineselenide)tellurium(II).

remeasured at intervals of 10.000 s of exposure time. The variations were within 6.1~% and were used for scaling of the intensity data. The data were corrected for Lorentz and polarization effects and for absorption. The calculated structure factors were based on scattering factors calculated from numerical Hartree-Fock wave functions  $^{12}$  and corrected for anomalous dispersion.

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The structures were solved by Patterson and Fourier methods. Full-matrix least-squares refinements were performed with CRYLSQ of X-Ray 76. The function  $\Sigma W(F_o - KF_c)^2$  where K is a scale factor and  $W=1/\sigma^2(F_o)$ , was minimized. The hydrogen atoms were not included.

Lists of structure factors and anisotropic thermal parameters are available from the authors on request.

## **RESULTS**

Selected bond lengths and angles in chlorophenyl(tetramethylthiourea)tellurium(II), A, bromophenyl(tetramethylthiourea)tellurium(II), B, chlorophenyl(trimorpholylphosphineselenide)tellurium(II), C, and bromophenyl(trimorpholylphosphineselenide)tellurium(II), D, based on the atomic coordinates in Table 2 are listed in Table 3. Views of the structures as seen normal to the tellurium atom and the coordination atoms are shown in Fig. 1. A stereoscopic view of the content in the unit cell of the two chloro compounds are shown in Figs. 2 and 3.

In all four structures, the tellurium atom has a T-shaped coordination, being bonded to a phenyl carbon atom, and in directions nearly perpendicular to the Te-C bond, to a halogen atom and a chalcogen atom. A least-squares plane through the coordination group passes near the phenyl carbon atom in *trans* position to the coordinating carbon atom. Largest distance from the plane, 0.19 Å, is found in the structure of C.

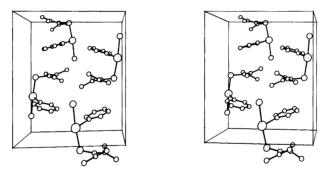


Fig. 2. Packing in the unit cell of chlorophenyl(tetramethylthiourea)tellurium(II).

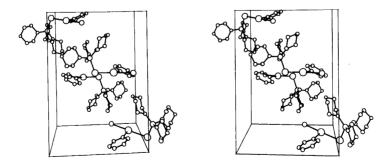


Fig. 3. Packing in the unit cell of chlorophenyl(trimorpholylphosphineselenide)telluri-um(II).

Table 3. Bond lengths (Å) and angles (°). Standard deviations are given in parentheses.

C <sub>6</sub> H <sub>5</sub> TeSC(N(CH <sub>3</sub> ) <sub>2</sub>	) <sub>2</sub> Cl	- <del>-</del>	
Te-S	2.5954(17)	S-Te-Cl	175.41(6)
	2.5554(17)		
Te-Cl	2.6684(19)	S-Te-C(1)	88.40(15)
Te-C(1)	2.108(6)	Cl-Te-C(1)	87.49(16)
C(1)-C(2)	1.401(9)	Te-C(1)-C(2)	119.9(À)
C\1\ C\2\	1.402(0)	To C(1) C(6)	120.5(4)
C(1)-C(6)	1.402(9)	Te-C(1)-C(6)	120.5(4)
		C(2) - C(1) - C(6)	119.6(6)
S-C(7)	1.745(6)	Te-S-C(7)	96.57(19)
C(7) = N(1)	1.340(8)	S-C(7)-N(1)	120.3(4)
C(7) - N(1)		3-C(7)-N(1)	120.3(4)
C(7)-N(2)	1.336(8)	S-C(7)-N(2)	121.1(4)
		N(1)-C(7)-N(2)	118.6(5)
G	\ <b>_</b>		
$C_6H_5TeSC(N(CH_3)_2)$	) <sub>2</sub> Br		
Te-S	2.5892(24)	S-Te-Br	176.92(6)
	2.3072(24)		00 00(22)
Te-Br	2.8328(12)	S-Te-C(1)	88.98(22)
Te-C(1)	2.125(8)	Br-Te-C(1)	88.59(21)
C(1)-C(2)	1.387(12)	Te-C(1)-C(2)	119.4(6)
CYTY CYTY		To COL	110 2(6)
C(1)-C(6)	1.402(13)	Te-C(1)-C(6)	119.3(6)
		C(2) - C(1) - C(6)	121.2(8)
S-C(7)	1.765(8)	Te-S-C(7)	96.74(27)
C(7)-N(1)	1.327(11)	S-C(7)-N(1)	119.1(7)
	1.327(11)	5-C(7)-N(1)	119.1(7)
C(7) - N(2)	1.335(11)	S-C(7)-N(2)	120.3(6)
		N(1) - C(7) - N(2)	120.6(7)
			. ,
C <sub>6</sub> H <sub>5</sub> TeSeP(NC <sub>4</sub> H <sub>8</sub> C	O) <sub>3</sub> Cl		
Te-Se	2.7827(9)	Se-Te-Cl	174.71(5)
Te-Cl	2.6004(20)	Se-Te-C(1)	93.34(18)
Te-C(1)	2.143(8)	Cl-Te-C(1)	90.56(19)
C(1)-C(2)	1.388(10)	Te-C(1)-C(2)	118.9(ô)
C(1) - C(2)	1 275(10)	$T_0 = C(1) = C(6)$	121.6(6)
C(1)-C(6)	1.375(10)	Te-C(1)-C(6)	121.6(6)
		C(2) - C(1) - C(6)	119.5(8)
Se-P	2.1762(18)	Te-Se-P	104.49(5)
P-N(1)	1.659(6)	Se-P-N(1)	109.09(20)
D MY	1.035(0)	C- D N(2)	107.03(20)
P-N(2)	1.646(6)	Se-P-N(2)	107.94(21)
P-N(3)	1.637(5)	Se-P-N(3)	118.15(9)
· /	( )	N(1)-P-N(2)	116.29(28)
		N/1\ D N/2\	
		N(1)-P-N(3)	102.82(28)
		N(2)-P-N(3)	102.82(29)
O 11 TO 0 TO 0 TO 0	~\ <del>~</del>		
$C_6H_5$ TeSeP(NC <sub>4</sub> H <sub>8</sub> C	J)3Br		
Te-Se	2.7689(9)	Se-Te-Br	175.21(3)
	2.7607(10)	So To C(1)	02 20(14)
Te-Br	2.7607(10)	Se-Te-C(1)	93.38(16)
Te-C(1)	2.150(8)	Br-Te-C(1)	90.96(16)
C(1)-C(2)	1.411(9)	Te-C(1)-C(2)	117.5(5)
C(1)-C(6)	1.399(10)	Te-C(1)-C(6)	120.5(5)
C(1)	1.599(10)		121.0(3)
		C(2)-C(1)-C(6)	121.9(7)
Se-P	2.1817(17)	Te-Se-P	103.39(5)
P-N(1)	1.666(6)	Se-P-N(1)	108.84(19)
D NI/2		Co D N/O	
P-N(2)	1.651(7)	Se-P-N(2)	107.89(19)
P-N(3)	1.646(6)	Se-P-N(3)	117.79(19)
• •	• •	N(1)-P-N(2)	115.42(26)
		N(1)-P-N(3)	103.50(26)
		NIZO D NIZO	102 45/27)
		N(2)-P-N(3)	103.65(27)
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The three-centre systems, Y-Te-X, are nearly linear. The deviations from linearity are from 3.08(6) to 5.29(5)°. The Te-C bond nearly bisects the Y-Te-X angles. The S-Te-C bond angles in the structure of A and B are equal within the errors, being 89.0°. The angles Cl-Te-C and Br-Te-C are 87.5 and 88.6°, respectively. In the structure of C and D where the trimorpholylphosphineselenide is one of the ligands, the two Se-Te-C angles are equal within the errors, 93.4°. The X-Te-C angles are also equal, 90.8°. In all former known crystal structures <sup>1-9,14,15</sup> of three-coordinated tellurium complexes with nearly linear three-centre system deviations from linearity are found. The angles X-Te-C and Y-Te-C are less than 90°. The deviation is explained by the electron lone pair repulsion at tellurium. In two of the present structures, C and D, the X-Te-C and Y-Te-C angles are greater than 90°, the bending is in opposite direction. This is probably due to the large steric requirements of the trimorpholylphosphineselenide group.

The length of the Te-S bonds in A and B are equal within the errors. The average value, 2.5923 Å, is 0.18 Å longer than the sum of the single bond radii. 16 The Te-Cl and the Te-Br bonds are 0.31 and 0.32 Å, respectively, longer than single covalent bonds. In the structures of C and D the Te-Se bond lengths are 0.24 and 0.23 Å longer than the single covalent bond length, while the Te-Cl and Te-Br bonds are lengthened with 0.24 and 0.25 Å, respectively. These figures clearly indicate that the ligand tetramethylthiourea has a greater trans bond-lengthening effect on the tellurium-halogen bonds than trimorpholyl-phosphineselenide. From the structures of C and D, the trimorpholylphosphineselenide seems to have about the same bonding force as the halogens chlorine and bromine have towards divalent tellurium in complexes. The total length of the Y-Se-X systems is nearly equal in all the four compounds.

A more detailed discussion of the *trans* bond-lengthening effect of ligands will be given in a following paper.

The weighted mean value of the Te-C bond lengths in the four structures is 2.128(7) Å. None of the four values has a significant deviation from this mean value. The single covalent bond length of Te-Csp<sup>2</sup>, calculated as the sum of the single covalent radii of tellurium, 1.37, and  $5p^2$ -hybridized carbon, 0.737, is 2.107 Å. In complexes of divalent tellurium, the general tendency is towards square-planar four-coordination. However, when one of the ligands is the phenyl group, the tendency is towards T-shaped three-coordination. In some of the complexes, a short contact from tellurium to an atom in *trans* position to the phenyl group is found. The latter complexes can be looked at as intermediates between the two forms. In the present four structures, no short contact is found and the Te-C bond may be described as a strictly 2c-2e covalent bond.

The atoms of the phenyltellurium group are nearly co-planar. The dihedral angle between this plane and the plane of the coordination group is in the structures of A and B 77.9 and 78.9°, respectively. In the structures of C and D the angle is 31.1 and 32.9°, respectively, which is smaller than angles observed in such complexes.

The atoms of the three-center system, Y-Te-X, and the carbon atom of the tetramethylthiourea group in A and B, or the phosphorous atom of the trimorpholylphosphineselenide group in C and D are nearly co-planer. The angle between a least-squares plane and the plane of the coordination group is 75.0 and 76.6° in A and B, and 83.1 and 82.6° in C and D, respectively.

In the former known structures of phenyltellurium complexes, the valence angle at sulfur is found to be larger than the valence angle at selenium. In the present structures the situation is opposite. The valence angle at sulfur is very small being 96.57(19) and 96.74(27)° in A and B, respectively. At selenium the valence angle is very large, 104.49(5) and

103.39(5) in C and D, respectively.

In the structures of A and B, the N-C(S)-N part of the tetramethylthiourea group is planar within errors. The angles at the carbon atom are within errors 120° in accordance with  $sp^2$ -hybridization. The weighted mean value of the bond lengths in the two structures are: S-C=1.752(5) and C-N=1.336(6) Å. Each of the two C-N(C)-C moieties of the tetramethylthiorea group is nearly planar in both structures. The largest deviation from a least-squares plane is 0.04 Å. The weighted mean value of the nitrogen - methyl carbon distances is 1.473(3) Å. The mean value of the angles sulfur-bonded carbon - nitrogen methyl carbon is 122.8(2)° and of methyl carbon – nitrogen –methyl carbon is 113.8(3)°. The tetramethylthiourea groups in A and B are equal within errors, and none of the individual bond lengths or angles which have been averaged, has a significant deviation from the mean values. The dimensions of the group are also in accordance with the results found in the crystal structures trans-dibenzenethiosulfonatobis(tetramethylthiourea)tellurium(II)<sup>18</sup> and dibromo(tetramethylthiourea)selenium(II).<sup>19</sup>

The coordination around the phosphorous atom in the trimorpholylphosphineselenide group in C and D is slightly distorted tetrahedral and the geometry of the group is similar to that found in the structure of the uncomplexed trimorpholylphosphineselenide.<sup>20</sup> The Se-P-N and N-P-N angles are found in the range 102.82(28) to 118.15(19)°. The two Se-P bond lengths are equal within errors, with weighted mean value 2.1791(13) Å which is 0.073 Å longer than the length found in trimorpholylphosphineselenide 20 itself. The lengthening is most probably due to the engagement of the selenium atom in bonding to tellurium in the present structures. The weighted mean value of the P-N bond lengths is 1.644(3) Å, and no individual bond length has a significant deviation from the mean value. In the uncomplexed trimorpholylphosphineselenide where the P-N bond lengths have been determined with better precision, they are different and about 0.02 Å longer than found in the present structures. The slightly shorter P-N bonds in the complexed ligand as compared to the uncomplexed one may reflect a slightly stronger  $p_N$ - $d_P$  backbonding in the complexed ligand. Such an effect is most probably due to the weakening of the Se-P bond when the selenium atom is engaged in bonding to tellurium.

Crystal packing. Stereoscopic views of the content of the unit cell of A and C are shown in Figs. 2 and 3. In all four crystal structures there are no particularly short non-bonding distances between different molecules. The crystals consist of well separated formula units.

## REFERENCES

- 1. Foss, O., Husebye, S. and Marøy, K. Acta Chem. Scand. 17 (1963) 1806.
- 2. Foss, O. and Husebye, S. Acta Chem. Scand. 20 (1966) 132.
- 3. Foss, O. In Andersen, P., Bastiansen, O. and Furberg, S. Selected Topics in Structure Chemistry, Universitetsforlaget, Oslo 1967, p. 145.
  4. Foss, O. Pure Appl. Chem. 24 (1970) 31.
  5. Hauge, S. and Vikane, O. Acta Chem. Scand. A 29 (1975) 755.

- Vikane, O. Acta Chem. Scand. A 29 (1975) 738.
   Vikane, O. Acta Chem. Scand. A 29 (1975) 763.
   Vikane, O. Acta Chem. Scand. A 29 (1975) 787.
- 9. Hauge, S. and Vikane, O. Acta Chem. Scand. A 37 (1983) 723.
- 10. Vikane, O. Acta Chem. Scand. A 29 (1975) 150.
- 11. Hauge, S. and Vikane, O. Acta Chem. Scand. 27 (1973) 3596.
- 12. Cromer, D.T. and Mann, J.B. Acta Crystallogr. A 24 (1968) 321.

Acta Chem. Scand. A 39 (1985) No. 8

- 13. Stewart, J.M., Machin, P.A., Dickinson, C.W., Ammon, H.L., Heck, H. and Flack, H. The X-Ray System, Technical Report TR-445, Computer Science Center, University of Maryland, College Park 1976.
- 14. Foss, O. and Marøy, K. Acta Chem. Scand. 20 (1966) 123.
- 15. Hauge, S., Johannesen, Ø. and Vikane, O. Acta Chem. Scand. A 32 (1978) 901.
- 16. Pauling, L. The Nature of the Chemical Bond, 3rd. Ed., Cornell University Press, Ithaca
- 17. Bastiansen, O. and Tretteberg, M. Tetrahedron 17 (1962) 147.
- 18. Åse, K. and Roti, I. Acta Chem. Scand. A 28 (1974) 104.
- 19. Wynne, K.J., Pearson, P.S., Newton, M.G. and Golen, J. *Inorg. Chem. 11* (1972) 1192. 20. Rømming, C. and Songstad, J. *Acta Chem. Scand. A 33* (1979) 187.

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