Three-Coordinated Divalent Tellurium Complexes: The Crystal and Molecular Structures of Chloro(phenyl)-(trimethyleneselenourea)tellurium(II) and Bromo(phenyl)-(trimethylenethiourea)tellurium(II)

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The title compounds, $C_6H_5Te(trsu)Cl$ (**A**) and $C_6H_5Te(trtu)Br$ (**B**), form monoclinic crystals. Compound **A** crystallizes in the space group $P2_1$ with $Z = 2$, and **B** in the space group $P2_1/n$ with $Z = 4$. The unit cell dimensions for **A** are: a = 7.5560(3), b = 10.7396(10), c = 8.8361(6) Å, β = 115.055(5)°, and for **B**: a = 9.0526(8), b = 15.8748(14), c = 9.8048(9) Å, β = 112.800(7)°.

The compounds belong to the class of T-shaped divalent tellurium complexes. The bonding system can be looked upon as consisting of a 2*c*–2*e* bond and, at right angles to this bond, of a linear 3*c*–4*e* system. In the structure of **A**, the angle of the 3*c*–4*e* system, Se–Te–Cl, is 171.55(9)°. Te–Se = 2.5924(14) and Te–Cl = 2.972(3) Å. The length of the 2*c*–2*e* bond, Te–C, is 2.097(10) Å, Se–Te–C = 93.5(3)° and Cl–Te–C = 83.5(4)°. In the structure of **B**: S–Te–Br = 176.40(7)°, Te–S = 2.5228(25), Te–Br = 2.9041(12), Te–C = 2.128(8) Å, S–Te–C = 92.16(23) and Br–Te–C = 88.77(22)°.

The bonding system, especially the linear 3*c*–4*e* system in the present and in other T-shaped tellurium complexes is discussed.

Dedicated to Professor Olav Foss on his 70th birthday

The syntheses and crystal structures of a number of three-coordinated complexes of divalent tellurium have been reported.[1–14] The present paper discusses the crystal structures of chloro(phenyl)-(trimethyleneselenourea)tellurium(II) and bromo(phenyl)(trimethylenethiourea)tellurium(II). It is part of a study on the relative *trans* influence of ligands in three-coordinated complexes of divalent tellurium. The structures of the three-coordinated complexes have been studied since they can be regarded as model substances for the transition state in nucleophilic displacements at divalent tellurium.

Experimental

Chloro(phenyl)(trimethyleneselenourea)tellurium (II), $C_6H_5Te(trsu)Cl$, was prepared in accordance with the equation:

$$C_6H_5TeTeC_6H_5 + Cl_2 + 2\ trsu \rightarrow 2\ C_6H_5Te(trsu)Cl$$

1.25 mmol (0.5 g) of diphenylditelluride and 2.5 mmol (0.41 g) of trimethyleneselenourea were dissolved in 10 ml of warm methanol. A solution of 1.25 mmol of chlorine in 2.35 ml of tetrachloromethane was added. The resulting warm, orange-red solution was filtered and placed at room temperature for 12 h. The yield was 0.7 g (69 %). The crystals are orange-red, monoclinic prisms; m.p. 157–159 °C. The space group was determined from single-crystal oscillation and

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Weissenberg photographs. The crystals are isomorphous with those of chloro(phenyl)-(trimethylenethiourea)tellurium(II).[6]

The synthesis of, and preliminary crystal data for the yellow compound bromo(phenyl)(trimethylenethiourea)tellurium(II), $C_6H_5Te(trtu)Br$, have been reported previously.[6]

Intensity data were collected on an Enraf-Nonius CAD4 computer-controlled diffractometer. The intensities of two reference reflections of medium intensity were remeasured at intervals of 10000 s of exposure time. The variations were within 2.2% for the chloro and 4.3% for the bromo compound, 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[15] and corrected for anomalous dispersion.

Full-matrix least-squares refinements were performed with CRYLSQ of X-Ray 76.[16] The function $\Sigma w(F_o - KF_c)^2$, where K is a scale factor and $w = 1/\sigma^2(F_o)$, were minimized. The hydrogen atoms were not included. Crystal data and details of refinement are given in Table 1.

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

Results and discussion

Bond lengths and angles in chloro(phenyl)(trimethyleneselenourea)tellurium(II) (**A**) and bromo(phenyl)(trimethylenethiourea)tellurium(II) (**B**), based on the atomic coordinates given in Table 2, are listed in Table 3. Views of the structures, seen normal to the coordination groups, are shown in Fig. 1.

Tellurium is bonded to one phenyl carbon and (normal to the Te–C bond) to selenium of trimethyleneselenourea, and to chlorine in **A** and to sulfur of trimethylenethiourea and bromine in **B**. In the latter, the coordination at tellurium is nearly planar. The largest deviation from a least-squares plane is 0.054 Å. In **A**, the coordination is more distorted, with Te 0.128 above, Se 0.070 below and Cl 0.061 Å below a least-squares co-

Table 1. Crystal data and refinement characteristics.

	$C_6H_5Te(trsu)Cl$	$C_6H_5Te(trtu)Br$
a/Å	7.5560(3)	9.0526(8)
b/Å	10.7396(10)	15.8748(14)
c/Å	8.8361(6)	9.8048(9)
β/°	115.055(5)	112.800(7)
V/Å^3	649.56	1298.93
M	403.24	400.80
Space group	$P2_1$(No. 4)	$P2_1/n$(No. 14)
Z	2	4
λ(Mo$K\alpha$)/Å	0.71073	0.71073
D_x/g cm^{-3}	2.06	2.04
D_{obs}/g cm^{-3}	2.05	2.04
μ/cm^{-1}	55.63	57.60
T/K	293	293
F (000)	366	732
$(\sin\theta/\lambda)$/Å^{-1}	0.6388	0.6388
Scan mode	ω-2θ	ω-2θ
No. of reflections	1595	2999
No. of reflections with $I>2\sigma(I)$	1514	2398
Crystal dimensions/mm	0.25×0.20×0.23	0.13×0.10×0.08
$R(F)$	0.050	0.041
$R_w(F)$	0.048	0.039
No. of parameters refined	135	136
Difference Fourier max. value/e Å^{-3}	1.1	0.9

Table 2. Final fractional atomic coordinates with e.s.d.'s in parentheses.

Atom	*x*	*y*	*z*	B_{eq}/Å^2
$C_6H_5Te(trsu)Cl$				
Te	0.50343(13)	0.25000	0.13502(11)	2.84(3)
Se	0.59667(23)	0.31649(21)	0.44141(19)	3.34(8)
Cl	0.4281(7)	0.1393(4)	−0.1949(5)	3.46(20)
C(1)	0.3129(23)	0.1099(17)	0.1402(17)	2.7(8)
C(2)	0.1341(26)	0.1438(18)	0.1406(20)	3.3(8)
C(3)	−0.0016(23)	0.0481(21)	0.1345(22)	3.7(9)
C(4)	0.0438(27)	−0.0750(20)	0.1261(19)	3.5(9)
C(5)	0.2224(28)	−0.1116(19)	0.1251(19)	3.8(8)
C(6)	0.3576(25)	−0.0169(16)	0.1339(19)	3.0(7)
C(7)	0.3601(22)	0.3800(18)	0.4220(18)	3.2(7)
N(1)	0.2826(22)	0.4870(14)	0.3216(16)	3.4(7)
N(2)	0.2724(19)	0.3325(14)	0.5099(16)	2.9(5)
C(8)	0.1023(25)	0.5421(19)	0.3051(19)	3.6(8)
C(9)	0.0657(29)	0.5173(23)	0.4627(25)	4.7(10)
C(10)	0.0941(27)	0.3786(22)	0.5082(25)	4.3(9)
$C_6H_5Te(trtu)Br$				
Te	0.70091(6)	0.44482(3)	0.33662(6)	2.68(3)
Br	0.54719(13)	0.28697(5)	0.35439(11)	2.89(5)
S	0.83719(28)	0.57823(14)	0.30732(25)	2.99(10)
C(1)	0.4705(9)	0.5021(5)	0.2465(8)	2.3(3)
C(2)	0.3670(11)	0.4818(5)	0.1062(9)	3.1(4)
C(3)	0.2134(11)	0.5195(6)	0.0451(10)	3.6(5)
C(4)	0.1707(11)	0.5801(5)	0.1286(10)	3.2(5)
C(5)	0.2777(11)	0.6000(5)	0.2694(10)	2.9(4)
C(6)	0.4291(10)	0.5613(5)	0.3331(10)	2.8(4)
C(7)	0.8815(9)	0.6373(5)	0.4698(9)	2.6(4)
N(1)	0.9452(9)	0.7129(4)	0.4698(8)	3.4(4)
N(2)	0.8578(9)	0.6083(5)	0.5859(8)	3.4(4)
C(8)	0.9936(14)	0.7698(6)	0.6020(11)	4.4(6)
C(9)	1.0233(12)	0.7220(6)	0.7396(10)	4.0(6)
C(10)	0.8882(12)	0.6606(7)	0.7219(10)	4.3(6)

ordination plane. Both planes pass 0.06 Å from the phenyl carbon atom in *para*-position.

The three-centre systems Se–Te–Cl and S–Te–Br are nearly linear, with a deviation of 8.45(9)° in **A** and 3.60(7)° in **B**. Such deviations are found in all the known structures of three-coordinated tellurium(II) compounds.[3,4,8–12] The Te–C bond nearly bisects the angle of the three-centre system. The Y–Te–C (Y = Se,S) angles are 93.5(3) and 92.2(2)°, and the X–Te–C (X = Cl,Br) angles are 83.5(4) and 88.8(2)°.

The length of the Te–Se bond is about 0.05 Å greater than the sum of the single-bond radii,[17] while the Te–Cl bond is about 0.61 Å longer than the covalent single bond. The figures for Te–S and Te–Br are 0.11 and 0.39 Å, respectively.

The phenyl carbon atoms and the tellurium atom are nearly coplanar. The largest deviation from a least-squares plane through the atoms is 0.040 in **A** and 0.015 Å in **B**. The angle between this plane and a plane through the coordination group is 65.48° in **A** and 71.25° in **B**. The angle between the plane of the atoms of the 3*c*–4*e* system and C(7) of the urea part of the ligand, and the plane of the coordination group is 61.03° in **A** and 87.62° in **B**.

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

$C_6H_5Te(trsu)Cl$			
Te–Se	2.5924(14)	Se–Te–Cl	171.55(9)
Te–Cl	2.972(3)	Se–Te–C(1)	93.5(3)
Te–C(1)	2.097(10)	Cl–Te–C(1)	83.5(4)
C(1)–C(2)	1.401(18)	Te–C(1)–C(2)	119.0(8)
C(1)–C(6)	1.409(15)	Te–C(1)–C(6)	121.0(8)
Se–C(7)	1.852(9)	C(2)–C(1)–C(6)	119.9(9)
C(7)–N(1)	1.418(11)	Te–Se–C(7)	100.4(3)
C(7)–N(2)	1.319(12)	Se–C(7)–N(1)	118.9(8)
		Se–C(7)–N(2)	120.6(7)
		N(1)–C(7)–N(2)	120.3(9)
$C_6H_5Te(trtu)Br$			
Te–Br	2.9041(12)	Br–Te–S	176.40(7)
Te–S	2.5228(25)	Br–Te–C(1)	88.77(22)
Te–C(1)	2.128(8)	S–Te–C(1)	92.16(23)
C(1)–C(2)	1.370(10)	Te–C(1)–C(2)	119.7(7)
C(1)–C(6)	1.411(13)	Te–C(1)–C(6)	118.7(5)
S–C(7)	1.756(9)	C(2)–C(1)–C(6)	121.6(8)
C(7)–N(1)	1.332(11)	Te–S–C(7)	107.1(3)
C(7)–N(2)	1.320(13)	S–C(7)–N(1)	115.3(7)
		S–C(7)–N(2)	122.7(6)
		N(1)–C(7)–N(2)	122.0(8)

The Se–C bond lengths and the Te–Se–C angles are equal to those found in bromo- and iodo-(ethyleneselenourea)phenyltellurium(II).[10,11] The S–C bond and the Te–S–C angles are within the range expected on the basis of comparison with corresponding dimensions in other complexes of divalent tellurium with thiourea or substituted thioureas as ligands.[12,18–21]

The N–C(Se)–N part of the trimethyleneselenourea or the N–C(S)–N part of the trimethylenethiourea is planar. The largest deviation from a least-squares plane is 0.029 Å and is found in **A**. The angle between this plane and the plane of the coordination group is 89.44° in **A**, and 89.25° in **B**. The angles around carbon correspond to sp^2 hybridization. The largest deviation is found for **B**, in which the angle S–C(7)–N(1) is 115.3(7)°.

Hydrogen bonding probably occurs in **A**, between N(2) and Cl (x, y, z + 1). The N(2)···Cl

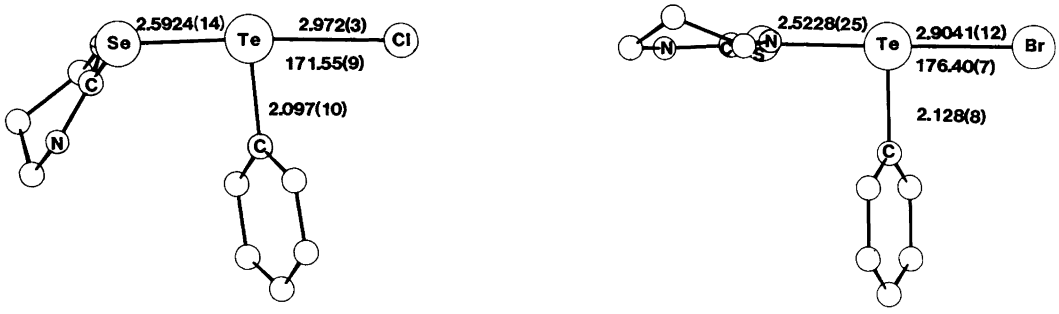

Fig. 1. Left: Chloro(phenyl)(trimethyleneselenourea)tellurium(II). Right: Bromo(phenyl)(trimethylenethiourea)-tellurium(II). Both structures seen normal to the coordination plane.

Table 4. Bond lengths, d_1 and d_2, of 3*c*–4*e* systems in phenyltellurium(II) complexes C_6H_5TeYX and $[C_6H_5TeYX]^-$.

Y[a]	X	Te–Y	Te–X	d_1	d_2	Ref.
tu	Cl	2.500(15)	3.000(15)	1.4600	2.0600	4
trsu	Cl	2.5924(14)	2.972(3)	1.4224	2.0372	This work
etu	Cl	2.5211(10)	2.8486(10)	1.4811	1.9086	10
tmtu	Cl	2.5954(17)	2.6684(19)	1.5554	1.7284	14
trmse	Cl	2.7827(9)	2.6004(20)	1.6127	1.6604	14
tu	Br	2.500(15)	3.11(1)	1.4600	2.00	4
esu	Br	2.6160(16)	3.0537(16)	1.4460	1.9437	10
etu	Br	2.5231(15)	2.9694(10)	1.4831	1.8594	9
etu	Br	2.5560(15)	2.8348(10)	1.5160	1.7248	9
trtu	Br	2.5228(25)	2.9041(12)	1.4828	1.7941	This work
I	Br	2.9033(18)	2.8676(22)	1.5876	1.7576	13
tmtu	Br	2.5892(24)	2.8328(12)	1.5492	1.7228	14
trmse	Br	2.7689(9)	2.7607(10)	1.5989	1.6507	14
esu	I	2.6791(18)	3.0951(14)	1.5091	1.7751	11
etu	I	2.614(2)	3.0033(12)	1.574	1.6833	11
I	I	2.9634(13)	2.9456(14)	1.6434	1.6256	13
SCN	SCN	2.665(2)	2.702(2)	1.625	1.662	8
SeCN	SeCN	2.7636(11)	2.8233(12)	1.5936	1.6533	8

[a]tu = thiourea, etu = ethylenethiourea, tmtu = tetramethylthiourea, trtu = trimethylenethiourea, esu = ethyleneselenourea, trsu = trimethyleneselenoura, trmse = trimorpholylphosphineselenide.

distance is 3.145(10) Å, the C(7)–N(2)···Cl angle is 129.7(5)° and the C(10)–N(2)···Cl angle is 104.9(5)°. In **B**, the closest nitrogen-bromine approach occurs at N(1)···Br ($3/2 - x$, $1/2 + y$, $1/2 - z$) and is 3.415(9) Å. The angle C(7)–N(1)···Br is 118.4(4)° and the angle C(8)–N(1)···Br is 119.5(4)°.

The 3c–4e bonding system in three-coordinated tellurium(II) complexes. As stated by Foss,[18,19] the tellurium(II) complexes may be regarded as models for the transition states in nucleophilic displacements at divalent tellurium:

$$RTeX + Y \rightarrow RTeY + X$$

To a first approximation the model has a linear transition state with 3*c*–4*e* bonds based on a single *p*-orbital of the electrophilic centre to both incoming and outgoing groups, the best nucleophile having the strongest *trans* influence.

The complexes studied, by nature of their stability, are not transition states, but when regarded as models they may provide information about bonding in the transition state. The large amount of data available on the structures, notably for four-coordinated but also for three-coordinated complexes, clearly indicate linear transition states. Table 4 gives bond lengths of phenyl tellurium complexes. The three-centre system of the complexes has varying degrees of asymmetry. The data for the halogen complexes indicate the *trans* influence order: thiourea ~ trimethyleneselenourea ~ ethylenethiourea > trimethylenethiourea > iodine > tetramethylthiourea > trimorpholylphosphineselenide ~ bromide ~ chloride. Each of the three-centre systems may be regarded as a case in which approach of the nucleophile has proceeded to a greater or lesser extent, but has been frozen at a certain stage by the intra- or intermolecular constraints imposed by the crystal environment. The complexes studied are stable intermediates and thus depict the situation at a saddle point of the reaction coordinate for each particular reaction. However, a saddle point relates to the stability of the state and is believed not to reflect on geometry and the nature of the bonding. Each case then provides a sample point on, or close to, the reaction coordinate. A sufficiently large number of points

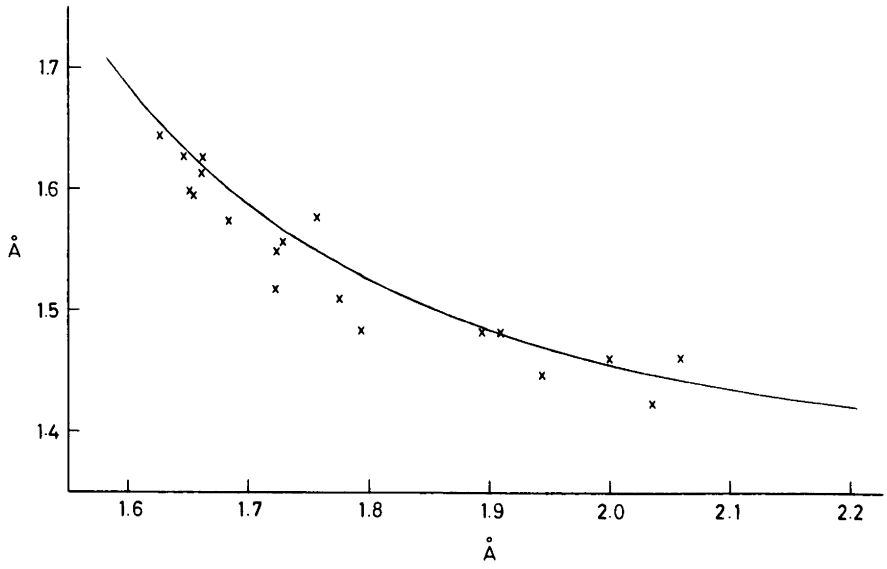

Fig. 2. The relation between d_1 and d_2.

should thus map out the reaction path. Similar arguments have been used to derive the minimum energy pathway for other nucleophilic substitution reactions.[22-24]

The relation between the two bond lengths at divalent tellurium in 3*c*–4*e* systems has been discussed earlier by one of us.[25] The experimental data were fitted by an exponential curve (Fig. 2) given by:

$$(1/2)^{\frac{d_1 - r_{Te}}{r_s - r_{Te}}} + (1/2)^{\frac{d_2 - r_{Te}}{r_s - r_{Te}}} = 1$$

where d_1 and d_2 are the differences between the observed bond lengths and the radii of the complexing atom of the ligands, r_{Te} is the covalent single-bond radius of tellurium(II), and r_s is the effective bonding radius of tellurium(II) in centrosymmetric complexes.

Foss and Maartmann-Moe[26] have recently made a survey of bond lengths in centrosymmetric *trans*-TeL_2X_2 and $[TeL_4]X_2$ complexes. They found the following lengthening of the bonds compared to the sum of the Pauling single-bond radii:[17] Te–Cl 0.22, Te–Br 0.24, Te–I 0.26, Te–S 0.27 and Te–Se 0.27 Å. The variation is, to some degree, caused by electrophilic forces. The values in Table 4 are corrected for this variation. The graph in Fig. 2 is calculated from

$$(1/2)^{\frac{d_1 - 1.37}{0.27}} + (1/2)^{\frac{d_2 - 1.37}{0.27}} = 1$$

A relatively large deviation from the graph is expected for some observations, since the individual observations are influenced by experimental errors, and by differences in structure and crystal environment of the complexes. The crystal structures of the two dimorphs of C_6H_5Te(etu)Br clearly show the latter effect. The relation between the two bond lengths of the 3*c*–4*e* systems in the phenyltellurium(II) complexes seems to be fairly well represented by the equation given above.

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