The Crystal and Molecular Structure of 4-Ethoxyphenyltellurenyl Methylxanthate, $C_2H_5OPhTeSC(S)OCH_3$, 4-Ethoxyphenyltellurenyl Dimethyldithiophosphate, $C_2H_5OPhTeSP(S)(OCH_3)_2$ and Ethylenethiourea[*N,N*-bis(dimethylene)oxide-*N'*-phenylthiourea]-phenyltellurium(II) Bromide, $[PhTe(etu)SC(NHPh)N(CH_2)_4O]Br$

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The crystal and molecular structures of the title compounds, $C_2H_5OPhTeSC(S)OCH_3$ (**1**), $C_2H_5OPhTeSP(S)(OCH_3)_2$ (**2**) and $PhTe(etu)SC(NHPh)N(CH_2)_4O$ (**3**) have been determined by X-ray methods using diffractometer data collected at room temperatures. The crystals of **1** belong to space group $P\bar{1}$ with unit-cell dimensions a = 8.0775(5), b = 9.3474(10), c = 9.9221(10) Å, α = 65.724(8), β = 73.501(7), γ = 78.318(7)°. The structure was refined to a conventional R-factor of 0.034. Compound **1** is built up of essentially L-shaped molecules with a central two-coordinate Te(II) atom. Each Te atom forms two intermolecular weak bonds to sulfur atoms in two neighbouring molecules, and the result is a distorted, square-planar geometry for tellurium. In the L-shaped molecule, the tellurium valency angle, C6–Te–S1, is 96.55(9)°. The crystals of **2** are monoclinic, space group $P2_1/n$, with unit-cell dimensions a = 10.176(2), b = 12.407(1), c = 12.234(1) Å, β = 97.40(1)°. The structure was refined to R = 0.034. Here the structure is also built up of essentially L-shaped molecules with two-coordinate central Te atoms. There is only one intermolecular Te–S contact for each Te atom, resulting in a distorted T-shaped complex. In the L-shaped molecule the tellurium valency angle, S1–Te–C6, is 94.75(8)°.

The crystals of **3** are monoclinic, space group $P2_1$, with unit-cell dimensions a = 8.684(1), b = 14.160(3), c = 10.375(1) Å, β = 108.99(1)°. The final R-factor was 0.048. Tellurium is essentially three-coordinate and bonded to carbon in the phenyl group and to two sulfur atoms (T-shaped). In addition there is a weak bond to the bromine atom, Te–Br = 3.884(1) Å, resulting in a distorted square-planar Te complex.

Divalent tellurium forms square-planar or T-shaped complexes with monodentate and bidentate ligands.[1-10] Very rarely a pentagonal planar structure around tellurium is found.[11,12] The present work is part of a study of the configuration in complexes of divalent tellurium containing an aryl group and a dithiolate group, in some cases also with additional ligands.

Experimental

Preparation of **1**, 4-ethoxyphenyltellurenyl methylxanthate, has been reported earlier.[13] A slightly modified procedure was followed here. 360 g (1 mmol) of 4-ethoxyphenyltellurenylmethylthiosulfonate[2] was dissolved in 10 ml chloroform and added to a 10 ml aqueous solution of 0.310 g (1.25 mmol) sodium thiosulfate pentahydrate. To this solution was added 0.183 g (1.25 mmol) of potassium xanthate dissolved in a minimum amount of water (ca. 1 ml), giving two phases, one red and the other colourless. The red phase was separated by shaking with ether and decanting to another beaker. Then 5 ml n-hexane was added and the volume was halved in vacuum at −5 °C. Yield: 0.160 g (45 %) of stable, orange–red plates and prisms.

Compound **2**, 4-ethoxyphenyltellurenyl dimethyldithiophosphate, was prepared as follows. 0.356 g (ca. 1 mmol) $C_2H_5OPhTeCl_3$ was mixed with 5 ml of CS_2. 0.622 g (ca. 3.75 mmol) $(CH_3O)_2PS_2$ K was dissolved in 5 ml of water. The aqueous solution was slowly mixed with the CS_2 mixture under constant stirring. Two layers formed, a light yellow aqueous layer and a red CS_2 layer which was carefully decanted into another beaker. The red solution was filtered and the volume reduced by 50 % under vacuum.

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0.227 g of orange prisms crystallized out and were washed with 7 ml diethylether. Yield: 56 %.

Preparation of **3**, ethylenethiourea[*N*,*N*-bis(dimethylene)oxide *N*′-phenylthiourea]phenyltellurium(II) bromide was as follows. 0.187 g (0.5 mmol) of PhTe(etu)Br was thoroughly mixed with 0.140 g (0.625 mmol) $O(CH_2)_4NC(S)NHPh$ at room temperature. 8 ml $CHCl_3$ was added stepwise while stirring, giving an orange–red solution. Stirring was continued at the boiling point of chloroform for some minutes. After cooling, the volume was reduced under vacuum to about half the original. On standing a few crystals could be picked out. To the partly oily solution was added 4 ml CS_2. On standing, more crystals separated. Altogether 0.032 g (ca. 12 % yield) of orange plates or prisms were collected. The crystals were washed with CH_2Cl_2 to remove oil.

Structure analysis. All data were measured on an Enraf-Nonius CAD-4 diffractometer. Unit-cell parameters were found from least-squares refinement of the setting angles of 25 reflections. Intensity data were collected using an ω-scan with scan width (1.00 + 0.35tan θ) + 25 % on each side for background, a graphite monochromator and Mo *K*α radiation. The variation of three standard reflections was used for scaling of intensity data, and the data were corrected for Lorentz and polarization effects. The data for **1** and **2** were corrected for absorption. The crystal structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares techniques, the sum minimized being $\Sigma w\Delta^2(F)$, where $w^{-1} = \sigma^2(F)^2 = \sigma^2(I)/4LpI$ and $\sigma^2(I) = \sigma^2(I)\text{count} + (pI)^2$. The attributed weights correspond to the counting statistics $+p$ % of the net intensity. $p = 0.025$ (**1**), 0.030 (**2**) and 0.030 (**3**). Anisotropic temperature factors were applied to all non-hydrogen atoms. The hydrogen atoms were placed geometrically at a fixed C–H distance of 0.95 Å, and refined isotropically using the program HYDRO. Crystal and experimental data and final figures of merit are included in Table 1. All computer programs used belong to the Enraf-Nonius SDP (1987). Tables of observed and calculated structure factors as well as thermal parameters are available from one of the authors (Ø.M.) upon request.

Results and discussion

Interatomic distances and angles of the three complexes based on the atomic coordinates given in Table 2 are listed in Table 3. Table 4 compares the coordination around tellurium for the three complexes in this paper. ORTEP drawings of the three molecules are shown in Fig. 1, and Fig. 2 shows the coordination around tellurium for **1** and **2**.

Coordination around tellurium. For compound **1** the molecules are connected through weak, intermolecular Te···S2 bonds. The bond angle C6–Te–S1 is 96.53(9)°, close to the corresponding angle C6–Te–S2 of 97.24(8)° in the related complex 4-methoxyphenyltellurenyl methylxanthate[1] and the angle C2–Te–S1 of 96.77(9)° found in the strictly monomeric 4-methoxyphenyltellurenyl thiosulfonate.[2] Thus this compound has an angular structure. If the two weak in-

Table 1. Crystal data and structural parameters for the three compounds.

Compound	**1**	**2**	**3**
Diffractometer	Enraf-Nonius CAD-4	Enraf-Nonius CAD-4	Enraf-Nonius CAD-4
Radiation/Scan-mode	Mo *K*α/ω-scan	Mo *K*α/ω-scan	Mo *K*α/ω-scan
Wavelength/nm	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic
a/Å	8.0775(5)	10.176(2)	8.684(1)
b/Å	9.3474(10)	12.407(1)	14.160(3)
c/Å	9.9221(10)	12.234(1)	10.375(1)
α/°	65.724(8)	90.000	90.000
β/°	73.501(7)	97.40(1)	108.99(1)
γ/°	78.318(7)	90.000	90.000
V/Å³	651.6(1)	1531.8(4)	1206.3(3)
Space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1$ (No. 4)
M	355.93	405.93	609.09
Z	2	4	2
F(000)	344	792	600
D_{calc}/g cm^{-3}	1.814	1.760	1.677
Absorption coefficient/cm^{-1}	25.739	23.041	30.596
Crystal dimensions/mm³	0.2×0.2×0.2	0.4×0.2×0.2	0.06×0.1×0.3
Scale factor	0.173	0.273	0.626
No. of independent measurements	3781	4471	2798
No. with $I>2\sigma(I)$	2948	3373	1865
Transmission factor	0.5867–0.7303	0.5868–0.6661	0.8443–1.1763[a]
$R = \Sigma\lvert F_0 - F\rvert/\Sigma F_0$	0.034	0.034	0.049
$R_w = [\Sigma w(F_0 - F)^2/\Sigma w(F_0)^2]^{0.5}$	0.030	0.037	0.049
$S = [\Sigma w(\Delta F)^2/(N-n)]^{0.5}$	1.491	1.479	1.638

[a] For **3** the figures are minimum–maximum absorption correction factors.

Table 2. Fractional atomic coordinates and their estimated standard deviations. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter.

Atom	*x*	*y*	*z*	$B/\text{Å}^2$ [a]
Compound **1**				
Te	0.10779(2)	0.08125(2)	0.14170(2)	4.249(4)
S1	0.3942(1)	0.0429(1)	0.18573(9)	4.45(2)
S2	0.7079(1)	0.2021(1)	0.0491(1)	6.78(3)
O1	−0.2389(3)	0.5525(2)	0.4641(2)	5.18(6)
O2	0.4241(3)	0.2985(3)	−0.0554(2)	4.89(6)
C1	−0.3306(5)	0.7966(4)	0.4934(4)	6.2(1)
C2	−0.2201(5)	0.7185(4)	0.3899(4)	5.22(9)
C3	−0.1536(4)	0.4575(3)	0.3888(3)	3.91(7)
C4	−0.1911(4)	0.3006(4)	0.4597(4)	4.88(8)
C5	−0.1140(4)	0.1947(3)	0.3913(4)	4.58(8)
C6	0.0010(4)	0.2414(3)	0.2513(3)	3.86(7)
C7	0.0397(4)	0.3976(4)	0.1817(3)	4.51(8)
C8	−0.0354(4)	0.5039(4)	0.2500(4)	4.70(8)
C9	0.5091(4)	0.1970(3)	0.0442(3)	4.02(7)
C10	0.5094(6)	0.4299(5)	−0.1796(5)	6.8(1)
Compound **2**				
Te	−0.01291(2)	0.21390(2)	0.14374(2)	4.014(4)
P	−0.28915(8)	0.18506(6)	−0.05913(7)	3.43(1)
S1	−0.12375(8)	0.09776(6)	−0.00049(7)	4.11(2)
S2	−0.3886(1)	0.10288(8)	−0.17530(8)	5.17(2)
O1	0.3667(3)	0.4294(2)	−0.1529(2)	7.26(6)
O2	−0.2485(2)	0.3019(2)	−0.0892(2)	4.37(5)
O3	−0.3649(2)	0.2172(3)	0.0397(2)	4.73(5)
C1	0.4949(7)	0.5716(4)	−0.2077(5)	11.4(2)
C2	0.3865(6)	0.5433(4)	−0.1503(4)	9.9(1)
C3	0.2806(4)	0.3866(3)	−0.0886(3)	4.77(7)
C4	0.2797(4)	0.2755(3)	−0.0796(3)	5.38(8)
C5	0.1963(4)	0.2259(3)	−0.0150(3)	4.77(7)
C6	0.1140(3)	0.2861(2)	0.0414(2)	3.62(6)
C7	0.1172(4)	0.3959(3)	0.0324(3)	4.70(7)
C8	0.2002(4)	0.4469(3)	−0.0320(3)	5.42(8)
C9	−0.1715(4)	0.3204(3)	−0.1775(3)	5.39(8)
C10	−0.4252(4)	0.1353(4)	0.1001(3)	6.8(1)
Compound **3**				
Te	0.16525(9)	0.0000(0)	0.01048(8)	4.18(1)
Br	0.5658(2)	0.0562(1)	0.3034(2)	5.19(3)
S1	−0.0466(4)	0.0551(4)	0.1322(3)	7.0(1)
S2	0.3215(3)	−0.0553(2)	−0.1620(3)	3.63(6)
O	0.516(1)	−0.2896(7)	0.2434(9)	6.5(3)
N1	−0.021(1)	0.0766(8)	0.3893(9)	4.3(2)
N2	0.215(1)	0.0626(9)	0.3591(9)	4.4(2)
N3	0.428(1)	−0.2145(7)	−0.0235(9)	3.9(2)
N4	0.306(1)	−0.2323(7)	−0.2532(9)	3.5(2)
C1	−0.049(1)	−0.058(1)	−0.124(1)	4.4(3)
C2	−0.143(1)	−0.009(2)	−0.235(1)	6.5(4)
C3	−0.287(2)	−0.049(2)	−0.326(2)	11.9(7)
C4	−0.317(2)	−0.143(2)	−0.302(2)	17.3(8)
C5	−0.240(2)	−0.189(2)	−0.195(2)	17.2(5)
C6	−0.090(2)	−0.151(1)	−0.097(2)	7.8(4)
C7	0.054(1)	0.0653(9)	0.298(1)	3.7(3)
C8	0.097(1)	0.083(1)	0.530(1)	4.7(3)
C9	0.258(2)	0.069(1)	0.506(1)	6.1(4)
C10	0.352(1)	−0.1754(9)	−0.146(1)	3.2(2)
C11	0.439(1)	−0.3187(9)	0.000(1)	4.9(3)
C12	0.408(2)	−0.338(1)	0.131(1)	5.7(4)
C13	0.498(2)	−0.191(1)	0.219(1)	5.8(4)
C14	0.537(1)	−0.159(1)	0.096(1)	5.0(3)
C15	0.202(1)	−0.2069(8)	−0.384(1)	3.4(3)
C16	0.048(1)	−0.170(1)	−0.406(1)	4.6(3)
C17	−0.053(2)	−0.154(1)	−0.535(2)	6.0(4)
C18	−0.008(2)	−0.171(1)	−0.645(2)	6.1(4)
C19	0.145(2)	−0.210(1)	−0.627(1)	6.5(4)
C20	0.248(1)	−0.229(1)	−0.497(1)	4.6(3)

[a] $B = 4/3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table 3. Interatomic distances/Å and angles/°. Estimated standard deviations in parentheses.

Compound **1**:			
Symmetry codes: S2′: *x*−1, *y*, *z*; S2″: 1−*x*, −*y*, −*z*			
Te–S1	2.4040(9)	C6–Te–S1	96.53(9)
Te–C6	2.110(3)	Te–S1–C9	107.8(1)
S1–C9	1.744(3)	S1–C9–S2	118.2(2)
S2–C9	1.631(3)	S1–C9–O2	115.4(2)
O1–C2	1.439(4)	C9–O2–C10	119.7(3)
O1–C3	1.351(4)	S2–C9–O2	126.4(2)
O2–C9	1.305(3)	Te–C6–C5	120.7(2)
O2–C10	1.455(4)	Te–C6–C7	120.7(2)
C1–C2	1.489(5)	C4–C3–O1	115.6(2)
Te···O2	3.237(2)	C8–C3–O1	125.4(3)
Te···S2′	3.451(1)	C3–O1–C2	118.2(2)
Te···S2″	3.707(1)	O1–C2–C1	107.5(2)
Phenyl ring (mean)		S2′–Te–S2″	101.36(3)
C3–C8	1.384	S2′–Te–S1	170.43(3)
		S1–Te–S2″	83.81(3)
		C6–Te–S2″	179.49(7)
		C6–Te–S2′	78.35(9)
		Phenyl ring (mean)	
		C–C–C	120.0
Compound **2**: Symmetry codes: S2′: *x*+1/2, −*y*+1/2, *z*+1/2			
Te–S1	2.4391(8)	S1–Te–C6	94.75(8)
Te–C6	2.111(3)	Te–S1–P	102.89(4)
S1–P	2.052(1)	S1–P–S2	107.93(5)
P–S2	1.927(1)	S1–P–O2	110.0(1)
P–O2	1.564(2)	S1–P–O3	109.1(1)
P–O3	1.567(3)	S2–P–O2	116.5(1)
O2–C9	1.433(5)	S2–P–O3	116.1(1)
O3–C10	1.440(5)	O2–P–O3	96.7(1)
C1–C2	1.426(9)	P–O2–C9	120.8(2)
C2–O1	1.427(5)	P–O3–C10	120.0(2)
O1–C3	1.359(5)	Te–C6–C5	121.8(2)
Te···S2′	3.309(1)	Te–C6–C7	119.6(3)
Phenyl ring (mean)		C8–C3–O1	123.7(3)
C3–C8	1.374	C4–C3–O1	116.5(3)
		C3–O1–C2	118.3(3)
		O1–C2–C1	110.4(4)
		S1–Te–S2′	172.41(3)
		Phenyl ring (mean)	
		C–C–C	120.0
Compound **3**			
Te–Br	3.884(1)	C1–Te–S1	80.0(4)
Te–S1	2.664(4)	C1–Te–S2	88.7(4)
Te–S2	2.690(4)	S1–Te–S2	167.41(8)
Te–C1	2.09(1)	Br–Te–S1	98.61(7)
S1–C7	1.66(1)	Br–Te–S2	93.62(6)
C7–N1	1.32(2)	Br–Te–C1	167.5(4)
C7–N2	1.34(1)	Te–S1–C7	107.8(4)
N1–C8	1.49(1)	Te–S2–C10	108.5(4)
N2–C9	1.45(2)	S1–C7–N1	122.6(8)
C8–C9	1.51(2)	S1–C7–N2	127.2(10)
S2–C10	1.72(1)	C7–N1–C8	111.6(9)
C10–N3	1.34(1)	C7–N2–C9	111.5(11)
C10–N4	1.33(1)	N1–C8–C9	102.1(10)
N3–C11	1.49(2)	N2–C9–C8	104.3(9)
N3–C14	1.51(1)	S2–C10–N3	120.8(9)
C11–C12	1.49(2)	C10–N3–C11	123.3(9)
C14–C13	1.49(2)	C10–N3–C14	123.0(10)
O–C12	1.41(2)	N3–C11–C12	107.7(11)
O–C13	1.42(2)	N3–C14–C13	106.8(11)
N4–C15	1.41(1)	C11–C12–O	113.5(12)
Phenyl rings (mean):		C14–C13–O	114.1(13)
C1–C6	1.390	C12–O–C13	108.9(10)
C15–C20	1.374	S2–C10–N4	121.5(8)
		C10–N4–C15	125.2(10)
		Phenyl rings (mean):	
		C–C–C	119.9
		C–C–C	120.0

Table 4. Comparison of the coordination around tellurium for the three complexes. Bond distances are given in Å and angles in °.

	1	2	3
C(Ph)–Te	2.110(3)	2.111(3)	2.09(1)
Te–A	2.4040(9)	2.4391(8)	2.690(4)
Te–B	3.451(1)	3.309(1)	2.664(4)
Te–X	3.707(1)	–	3.884(1)
C(Ph)–Te–A	96.53(9)	94.75(8)	88.7(4)
C(Ph)–Te–B	78.35(9)	83.97(8)	80.0(4)
C(Ph)–Te–X	179.49(7)	–	167.5(4)
A–Te–B	170.43(3)	172.41(3)	167.41(8)
A	S1	S1	S1
B	S2′[a]	S2′[a]	S2
X	S2″[a]	–	Br

[a] Atoms from adjacent molecules.

termolecular Te···S2 bonds are included in the coordination sphere, it may be regarded as a distorted square-planar complex of divalent tellurium, belonging to class II.[14] In Fig. 2 four molecules with one of the coordination groups, $TeCS_3$, shaded, are shown. The Te coordination angles add up to 360.05°, thus roughly demonstrating that S1, C6, Te, S2′ and S2″ are in the same plane. That is, the weakly bonded S2′ and S2″ are also in the coordination plane. The strong *trans* influence of the phenyl group[7,9] is reflected in the fact that the Te···S2″ bond *trans* to it is 3.707(1) Å compared with the other intermolecular Te···S2′ bond of 3.451(1) Å, which is *trans* to the strong Te–S1 bond. Both are shorter than the sum of van der Waals radii of 3.86 Å.[15] They are, as expected, close to the corresponding values found for 4-methoxyphenyltellurenyl methylxanthate,

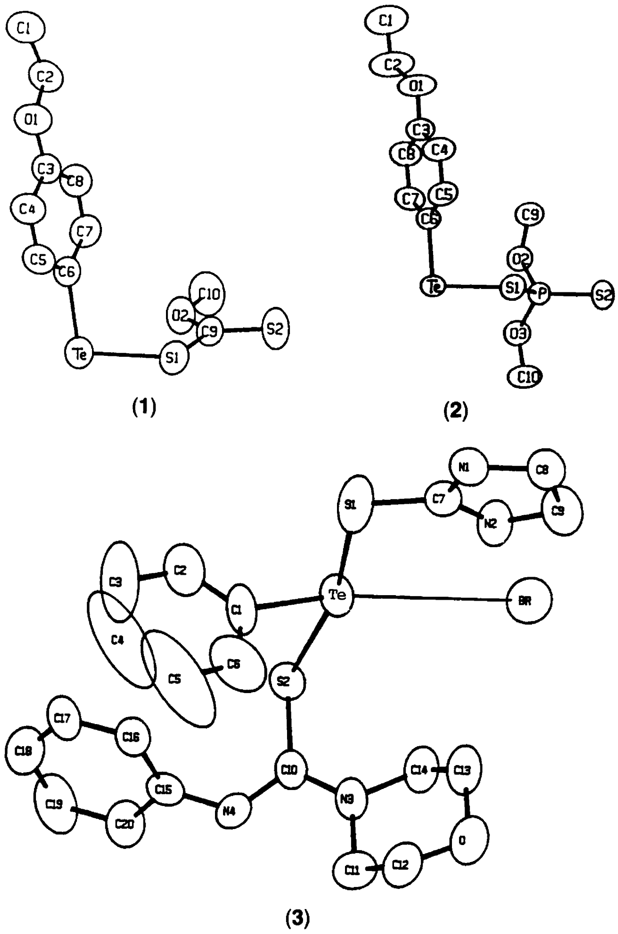

Fig. 1. ORTEP drawings of 4-EtOPhTeSC(OCH$_3$, 4-EtOPhTeSP(S)(OCH$_3$)$_2$ and [PhTe(etu)SC(NHPh)N(CH$_2$)$_4$O]Br.

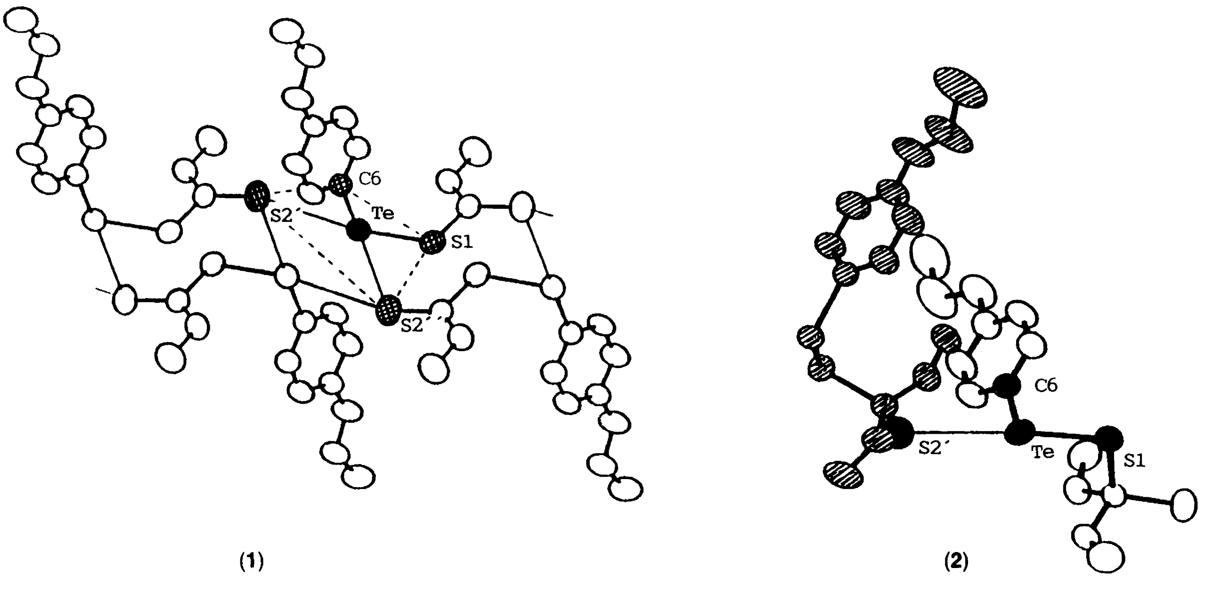

Fig. 2. ORTEP drawings showing (a) the distorted square-planar configuration around tellurium in 4-EtOPhTeSC(S)OCH$_3$, in which the tellurium atom is filled and the atoms bonded to it are shaded; (b) the T-shaped configuration around tellurium (filled) in 4-EtOPhTeSP(S)(OCH$_3$)$_2$, in which the adjacent molecule is shaded.

which are 3.62(1) and 3.467(8) Å, respectively.[1] The Te–C (Ph) bond length is 2.110(3) Å. This is normal,[16,17] as is the Te–S1 bond length of 2.4040(9) Å. [ΣR_{cov} (Te–S) = 2.41 Å.[18]].

In the case of compound **2**, tellurium is bonded to phenyl and, perpendicular to the Te–S(Ph) bond, to a sulfur atom. The L-shaped 4-ethoxyphenyltellurenyl dimethyldithiophosphate molecule has a weak intermolecular contact to a sulfur atom in an adjacent molecule, approximately *trans* to the Te–S1 bond. When the weak Te···S2′ bond is included, **2** may be regarded as a three-coordinate (T-shaped) divalent tellurium complex.

The three-centre system S1–Te–S2′ is nearly linear (172.41°). This is a common feature of all known structures of T-shaped tellurium(II) complexes.[14,19] All bond lengths and angles in the present compound are similar to the corresponding ones in 4-methoxyphenyltellurenyl dimethyldithiophosphate.[3] The intermolecular Te···S2′ contact is weaker in the present structure than in 4-methoxyphenyltellurenyl dimethyldithiophosphate [Te–S2′ = 3.309(1) versus 3.262(1) Å]. On the other hand the Te–S1 distance in the present structure [2.439(1) Å] is shorter than the Te–S1 distance in 4-methoxyphenyltellurenyl dimethyldithiophosphate [2.444(1) Å].[3] In a three-centre four-electron system with two ligands sharing the same p-orbital on the central atom, L_1–Te–L_2, let d_1 = Te–L_1 and d_2 = Te–L_2 be bond lengths minus the covalent radius of L_1 and L_2, respectively. In the present structure the sum $(d_1 + d_2)/2$ is 2.874 Å, which is in excellent agreement with the value 2.853 Å found in 4-methoxyphenyltellurenyl dimethyldithiophosphate.[3] Husebye has found the average of 2.708 Å for 11 T-shaped Te(II) complexes.[14] A least-squares plane through S2′, Te, C6 and S1 shows a rough coplanarity of these atoms; the greatest deviation from planarity is found for tellurium, which is 0.122(0) Å below the plane.

In compound **3** tellurium is bonded to the sulfur atoms of the two thiourea groups, Te–S1(etu) = 2.664(4) Å and Te–S2 = 2.690(4) Å. The mean length, 2.68 Å, of the two Te–S bonds is within the accuracy the same, 2.67 Å, as found for the mean Te–S bond lengths in $PhTe(tu)_2Cl$,[20] and 2.68 Å, as found for Te–S in centrosymmetric square-planar complexes.[5] The rather long Te–S distances indicate a 3c–4e system.[14] The Te–C(Ph) bond length is = 2.09(1) Å, and the angle S1–Te–S2 is 167.41(8)°, compared with the corresponding values of 2.11(4) Å and 172.0(4)° in PhTe $(tu)_2Cl$.[20] The Te–Br distance is 3.884(1) Å, slightly less than the sum of van der Waals distances for Te–Br, 3.91 Å.[15] The angle C–Te–Br is 167.5(4)°, compared with the corresponding angle C–Te–Cl of 163(1)° in $PhTe(tu)_2Cl$.[20] A least-squares plane through Te, S1, S2 and C1 almost shows planarity; the greatest deviation is 0.089 Å for tellurium. The bromine atom is 1.065(2) Å below this plane.

Comparison of the coordination around tellurium for the three complexes. Bond lengths and angles are listed in Table 5 and may be referred to Fig. 3. For divalent tellurium there are two lone, non-bonding pairs in the 5s and $5p_z$ orbitals in the valency shell. These orbitals are probably sp-hybridized.[21] There will therefore be a considerable electron density above and below the coordination plane of $5p_x$ and $5p_y$, which shields the tellurium atom from nucleophilic attack. This explains the square-planar configuration often found for divalent tellurium. It also explains why a fifth ligand will add to tellurium in the coordination plane. In **1** the two lone pairs occupy the octahedral positions above and below the coordination plane (including the two intermolecular Te–S bonds.)

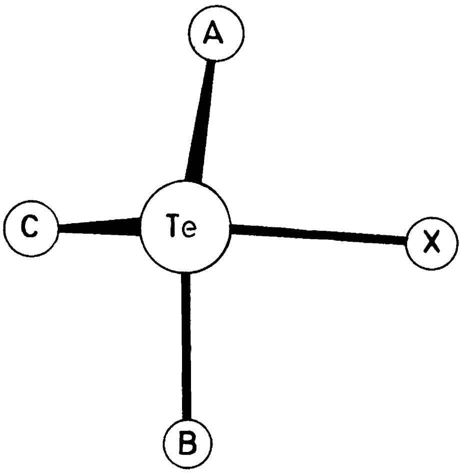

Fig. 3. Diagram showing the coordination around tellurium for the three complexes in this paper.

Compound **2** is T-shaped when the intermolecular Te···S bond is included. The *trans* influence of the phenyl group is so strong that it virtually expels a fourth ligand *trans* to it, making the coordination sphere T-shaped. Mutual repulsion of lone and bonding electron pairs in the valency shell will influence the positions of the lone pairs. In T-shaped complexes of divalent tellurium, the lone pairs will probably take up equatorial positions together with the carbon atom in a trigonal bipyramidal arrangement.

The Te–C(Ph) bond length is 2.111(3) Å and the Te–S1 bond length is 2.439(1) Å, compared with 2.109(3) and 2.4034(9) Å for the corresponding bond lengths in **1**. The bond angle C6–Te–S1 is 94.75(8)°, close to the corresponding angle C6–Te–S1 of 96.55(9)° in **1**. The angle S1–Te–S2′ is 172.41(3)° and the Te–S2′ length is 3.309(1) Å. The corresponding values for **1** are 170.42(3)° and 3.450(1) Å, respectively.

Compound **3** is T-shaped. When one includes the bromine atom *trans* to the phenyl carbon connected to tellurium, one gets the normal four-coordinate arrangement. The distances Te–A and Te–B show that **1** is more distorted than **3**. This is further confirmed when one looks at the valency angles.

The ligands. In compound **1** the methylxanthate group is almost completely planar, and the tellurium atom is only 0.0263(3) Å below this plane. The dihedral angle between the coordination plane and the phenyl group is 100.54(7)°, compared with 101.54(7)° for the corresponding angle of 4-methoxyphenyltellurenyl methylxanthate,[1] and 99.12(7)° for 4-methoxyphenyltellurenyl methanethiosulfonate.[2] Previous investigations have suggested that a dihedral angle of ca. 100° is normal, as it causes maximum separation between tellurium and one of the *ortho* carbon atoms in the phenyl ring.[22] In the methylxanthate group the short C9–S2 distance of 1.631(3) Å compared with the C9–S1 distance of 1.744(3) Å [$\Sigma R_{cov}(Csp^2\text{–}S) = 1.78$ Å[18]] indicates double-bond character in the C9–S2 bond. In the 4-methoxyphenyl end of the molecule there is a normal alkyl–aryl ether linkage.[23] The C–O–C angle is 119.7(3)° and the corresponding bond lengths are C10–O2 = 1.455(4) and O2–C9 = 1.305(3) Å, indicating some double-bond character in the latter.

In compound **2** a least-squares plane through P, O2, O3, C9 and C10 has a maximum deviation from planarity of 0.008(4) Å. The short P–S2 bond length of 1.927(1) Å implies a considerable amount of double-bond character. An average bond length of 1.95 Å is found for the P=S double bond in phosphorus sulfides.[24] The P–S1 bond length of 2.052(1) Å is a normal covalent bond. The short P–O bond lengths of 1.564(2) and 1.567(2) Å are probably due to overlap of p-orbitals of the oxygen atom with d-orbitals on phosphorus atoms as proposed for phosphates.[24]

For compound **3** the morpholyl group has a typical chair form. The phenyl groups connected to tellurium have large anisotropic temperature factors, especially for the C3, C4 and C5 atoms. This may indicate some disorder. The thioureaphenyl group is planar, and the carbon and nitrogen atoms in the etu group are nearly planar.

IR spectrum. For compound **2** the infrared spectrum of the crystals in the 1600–200 cm^{-1} region was obtained with a Perkin Elmer 683 instrument and the CsI disc technique. The P=S frequency in compounds of the type $(RO)_2PS(S)R$, where R and R′ are methyl or ethyl groups (R′ can also be H), has been measured and reported to be 660 cm^{-1}.[25] In this complex one finds a weak intermolecular contact to tellurium, P=S···Te, which is expected to lower the P=S frequency. This is also what is found; ν(P=S) = 623 cm (strong), in excellent agreement with the value (622 cm^{-1}) found for ν(P=S) in $Te[(MeO)_2PS_2]_2$.[25] The ν(P–S) band has a frequency of 495 cm^{-1} (strong), compared with 481 cm^{-1} in $Te[(MeO)_2PS_2]_2$. This is as expected, since the P–S distance is 2.052(1) Å in the present structure, compared with 2.089(7) Å in $Te[(MeO)_2PS_2]_2$.[25]

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