Crystal and Molecular Structures of Three Pairs of Centrosymmetric, Square-Planar Tellurium(II) Complexes

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The crystal structures of *trans*-$Te(etu)_2Br_2$ (*1*) and *trans*-$Te(etu)_2I_2$ (*2*) (etu = ethylenethiourea), determined earlier, have been refined from Mo$K\alpha$ diffractometer data, and the structures of $[Te(etu)_4]Cl_2$ (*3*), $[Te(esu)_4]Cl_2$ (*4*) (esu = ethyleneselenourea), *trans*-$Te(tmtu)_2(SCN)_2$ (*5*) (tmtu = tetramethylthiourea) and *trans*-$Te(tmsu)_2(SeCN)_2$ (*6*) (tmsu = tetramethylselenourea) have been determined and refined, to R = 0.025 (*1*), 0.024 (*2*), 0.021 (*3*), 0.025 (*4*), 0.028 (*5*) and 0.041 (*6*) for 1594, 1730, 3165, 2819, 2306 and 1755 observed reflections, respectively. Complexes *1* and *2* are isomorphous, as are *3* and *4*, and *5* and *6*. The tellurium atoms lie in crystallographic symmetry centres. In the TeS_2X_2 groups of *1* and *2* bond lengths are Te–S 2.656(1) and 2.671(1) Å and Te–X 2.764(1) and 2.955(1) Å for X = Br and I, respectively. In the TeS_4 or $TeSe_4$ groups of complexes *3–6* bond lengths are Te–S 2.666(1)–2.691(1) Å and Te–Se 2.773(1)–2.814(1) Å. The two linear three-centre systems of a group deviate 0.81(2)–2.10(2)° from orthogonality.

The crystal structures of the complexes *trans*-$Te(etu)_2Br_2$ (*1*) and *trans*-$Te(etu)_2I_2$ (*2*) (etu = ethylenethiourea), based on X-ray film data, were reported some time ago.[1] In order to make a survey of bond lengths in centrosymmetric tellurium(II) complexes[2] more accurate data were of interest, and we report here refinements of the above two structures. We also report the structures of two pairs of complexes containing centrosymmetric TeS_4 or $TeSe_4$ coordination groups: $[Te(etu)_4]Cl_2$ (*3*) and $[Te(esu)_4]Cl_2$ (*4*) (esu = ethyleneselenourea), *trans*-$Te(tmtu)_2(SCN)_2$ (*5*) (tmtu = tetramethylthiourea) and *trans*-$Te(tmsu)_2(SeCN)_2$ (*6*) (tmsu = tetramethylselenourea). Complexes *5* and *6* are isomorphous with *trans*-$Te(tmtu)_2(SeCN)_2$.[3]

Experimental

Preparations. The complexes $Te(etu)_2Br_2$, $Te(etu)_2I_2$ and $[Te(etu)_4]Cl_2$ were prepared as described previously.[4,5] Well-developed crystals of the latter were obtained from a saturated, room temp. solution of the dihydrate[5] in dimethylformamide by addition, with swirling, of an equal volume of concentrated HCl.

The complex $[Te(esu)_4]Cl_2$ was prepared by dissolving TeO_2 (0.40 g) in hot concd. HCl (10 cm^3) and adding, with swirling, a warm solution of esu (2.4 g) in water (40 cm^3). The mixture was filtered and allowed to cool, whereupon yellow crystals separated out. They were filtered off and washed with methanol containing a little HCl, and then with diethyl ether; yield 1.4 g of yellow crystals (70 % based on Te) Anal. $C_{12}H_{24}Cl_2N_8Se_4Te$: C, H, N. There was a tendency for the plate-like crystals to grow into composite prisms.

The complex $Te(tmtu)_2(SCN)_2$ was prepared by adding a solution of NH_4SCN (1 g) in methanol (10 cm^3) at room temp. to a mixture of $Te(tmtu)_2Cl_2$[2,6] (0.24 g) and tmtu (0.1 g). On tri-

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Table 1. Crystallographic data.

No.	*1*	*2*	*3*	*4*	*5*	*6*
Complex	$Te(etu)_2Br_2$	$Te(etu)_2I_2$	$[Te(etu)_4]Cl_2$	$[Te(esu)_4]Cl_2$	$Te(tmtu)_2(SCN)_2$	$Te(tmsu)_2(SeCN)_2$
Formula	$C_6H_{12}Br_2N_4S_2Te$	$C_6H_{12}I_2N_4S_2Te$	$C_{12}H_{24}Cl_2N_8S_4Te$	$C_{12}H_{24}Cl_2N_8Se_4Te$	$C_{12}H_{24}N_6S_4Te$	$C_{12}H_{24}N_6Se_4Te$
M	491.74	585.73	607.14	794.72	508.22	695.81
System	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	*C*2/*c* (No. 15)	*C*2/*c* (No. 15)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a/Å	17.196(1)	17.077(2)	7.996(1)	8.152(1)	8.794(1)	8.948(1)
b/Å	5.871(1)	6.226(1)	8.330(1)	8.329(1)	6.261(1)	6.349(1)
c/Å	15.483(1)	15.885(1)	9.662(1)	9.899(1)	19.432(3)	19.655(3)
α/°			98.63(1)	98.19(1)		
β/°	119.84(1)	119.30(1)	109.62(1)	110.93(1)	99.39(1)	99.03(1)
γ/°			103.47(1)	103.86(1)		
V/Å^3	1355.7(4)	1472.8(8)	570.9(3)	590.0(3)	1055.6(4)	1102.8(5)
Z	4	4	1	1	2	2
D_x/g cm^{-3}	2.409	2.641	1.766	2.237	1.599	2.095
F(000)	920	1064	302	374	508	652
μ(Mo*K*α)/cm^{-1}	87.94	65.79	19.50	81.86	18.46	85.08
Crystal volume/mm^3	0.00093	0.0016	0.0047	0.0037	0.0080	0.0017
Transmission factors	0.416–0.702	0.512–0.670	0.701–0.843	0.372–0.474	0.654–0.830	0.267–0.782
Scan rate/° min^{-1}	1.68–0.39	1.68–0.41	3.35–0.39	3.35–0.39	6.71–1.06	3.35–0.50
Unique reflections	1972	2136	3336	3445	3077	3208
Reflections $I > 2\sigma$	1594	1730	3165	2819	2306	1755
No. of variables	90	90	173	162	155	106
Extinction coeff., $g \times 10^7$	2.74	3.69	14.28	9.30	6.46	
R	0.025	0.024	0.021	0.025	0.028	0.041
R_w	0.025	0.028	0.025	0.027	0.030	0.038
S	1.188	1.436	1.306	1.255	1.236	1.387
Max. Δ(ϱ)/e Å^{-3}	0.98	0.96	0.48	0.72	0.35	0.76

Table 2. Fractional atomic coordinates with e.s.d.s in parentheses.

Atom	*x*	*y*	*z*	B_{eq}/Å^2
$Te(etu)_2Br_2$				
Te	¼	¼	0	2.282(5)
Br	0.37769(2)	−0.07730(6)	0.10721(2)	3.689(7)
S	0.22201(5)	0.30139(15)	0.15282(5)	3.05(2)
N(1)	0.12640(15)	−0.0915(5)	0.08450(16)	3.16(5)
N(2)	0.09972(15)	0.1025(5)	0.18545(17)	3.37(6)
C(1)	0.14700(16)	0.0939(5)	0.13914(18)	2.47(6)
C(2)	0.06187(20)	−0.2330(6)	0.09477(24)	3.47(7)
C(3)	0.04393(18)	−0.0987(7)	0.16694(22)	3.64(7)
$Te(etu)_2I_2$				
Te	¼	¼	0	2.458(6)
I	0.38318(2)	−0.08599(5)	0.11114(2)	3.579(5)
S	0.21929(6)	0.30211(17)	0.14823(6)	3.38(2)
N(1)	0.13180(19)	−0.0800(6)	0.08732(20)	3.81(7)
N(2)	0.10051(19)	0.0999(6)	0.18277(21)	3.90(7)
C(1)	0.14844(21)	0.0987(6)	0.13804(21)	2.83(7)
C(2)	0.06915(25)	−0.2206(7)	0.09817(28)	3.99(9)
C(3)	0.04902(23)	−0.0964(7)	0.16803(26)	3.89(8)
$[Te(etu)_4]Cl_2$				
Te	0	0	0	2.305(3)
S(1)	0.10692(6)	−0.24778(5)	0.11892(5)	3.033(8)
S(2)	0.30179(6)	0.08242(6)	−0.0.06650(5)	3.330(9)
Cl	0.12332(6)	0.34882(5)	0.34720(5)	3.619(9)
N(1)	0.20390(24)	−0.00732(18)	0.38023(16)	3.70(4)
N(2)	0.23457(25)	−0.25108(18)	0.41116(18)	3.78(4)
N(3)	0.39806(20)	0.35360(21)	0.17079(17)	3.51(3)
N(4)	0.61278(21)	0.34522(25)	0.08533(21)	4.43(4)
C(1)	0.18430(21)	−0.16294(19)	0.31072(17)	2.51(3)
C(2)	0.44094(21)	0.26625(21)	0.07006(18)	2.71(3)
C(3)	0.26993(29)	0.01988(24)	0.54439(21)	3.72(4)
C(4)	0.28302(29)	−0.15557(24)	0.56590(20)	3.73(4)
C(5)	0.54562(29)	0.51094(27)	0.26123(24)	4.06(5)
C(6)	0.70407(26)	0.49417(26)	0.21357(25)	4.18(5)
$[Te(esu)_4]Cl_2$				
Te	0	0	0	2.288(5)
Se(1)	0.10301(4)	−0.26886(3)	0.11019(3)	2.905(6)
Se(2)	0.29896(4)	0.07897(4)	−0.07801(3)	3.220(6)
Cl	0.11975(10)	0.34258(9)	0.34005(8)	3.69(2)
N(1)	0.2089(4)	−0.01241(28)	0.37813(25)	3.50(6)
N(2)	0.2339(4)	−0.25605(29)	0.41538(27)	3.53(6)
N(3)	0.40302(30)	0.3551(3)	0.17426(27)	3.32(6)
N(4)	0.6190(3)	0.3581(4)	0.0964(3)	4.24(7)
C(1)	0.1873(3)	−0.1697(3)	0.31423(28)	2.43(5)
C(2)	0.4478(3)	0.2751(3)	0.07417(29)	2.68(6)
C(3)	0.2719(4)	0.0181(4)	0.5496(3)	3.58(7)
C(4)	0.2814(5)	−0.1564(4)	0.5657(4)	3.73(7)
C(5)	0.5473(4)	0.5135(4)	0.2685(4)	3.87(8)
C(6)	0.7072(4)	0.5021(4)	0.2280(4)	4.02(8)

contd

Table 2. (contd)

Atom	*x*	*y*	*z*	B_{eq}/Å^2
$Te(tmtu)_2(SCN)_2$				
Te	0	0	0	2.936(4)
S(1)	−0.13019(10)	0.36188(14)	0.03644(5)	4.68(2)
S(2)	0.27506(9)	0.10471(12)	0.07470(4)	3.92(1)
N(1)	−0.2745(4)	0.2199(6)	0.14673(14)	6.66(8)
N(2)	0.2065(3)	−0.1799(4)	0.16860(11)	3.78(5)
N(3)	0.4330(3)	−0.2345(4)	0.12750(12)	4.02(5)
C(1)	−0.2155(4)	0.2770(5)	0.10166(15)	4.57(7)
C(2)	0.3064(3)	−0.1187(5)	0.12714(13)	3.33(5)
C(3)	0.0999(4)	−0.0295(6)	0.19236(16)	5.36(8)
C(4)	0.1741(4)	−0.4028(6)	0.18015(17)	5.26(8)
C(5)	0.5075(4)	−0.3531(7)	0.18895(19)	6.15(9)
C(6)	0.5225(4)	−0.2291(7)	0.06982(19)	5.61(8)
$Te(tmsu)_2(SeCN)_2$				
Te	0	0	0	3.30(1)
Se(1)	−0.13991(9)	0.37482(13)	0.03334(4)	4.85(2)
Se(2)	0.28007(8)	0.13051(12)	0.07311(4)	4.43(2)
N(1)	−0.2794(8)	0.2223(14)	0.1504(3)	7.3(2)
N(2)	0.2069(6)	−0.1642(9)	0.1702(2)	4.3(1)
N(3)	0.4310(6)	−0.2274(9)	0.1320(3)	4.5(1)
C(1)	−0.2248(8)	0.2807(12)	0.1049(3)	4.8(2)
C(2)	0.3076(7)	−0.1081(11)	0.1297(3)	3.9(1)
C(3)	0.1020(9)	−0.0128(15)	0.1929(3)	6.1(2)
C(4)	0.1691(10)	−0.3813(13)	0.1816(3)	5.6(2)
C(5)	0.4979(10)	−0.3522(14)	0.1925(4)	6.4(2)
C(6)	0.5227(8)	−0.2265(15)	0.768(4)	6.2(2)

turation a clear, orange solution was obtained and was placed in a freezer. The solution soon became grey and opaque and was filtered, and crystallization was initiated by seeding with $Te(tmtu)_2(SeCN)_2$.[3] After a few h in a refrigerator the crystals were filtered off and washed rapidly with a little freezer-cold ethanol and then diethyl ether; yield 0.17 g of yellow crystals (65 %). Anal. $C_{12}H_{24}N_6S_4Te$: C, H, N, S.

The complex Te(tmsu)$_2$(SeCN)$_2$ was prepared by triturating a mixture of $Te(tmsu)Cl_2$ (0.37 g) and tmsu (0.4 g) with warm methanol (8 cm^3), and adding KSeCN (0.8 g) and warm methanol (7 cm^3). The mixture was rapidly heated and filtered, and the filtrate was allowed to cool, first to room temperature and then in a refrigerator. The crystals were filtered off and washed as above; yield 0.16 g of brownish-red crystals (23 %). Anal. $C_{12}H_{24}N_6Se_4Te$: C, H, N.

The ligands esu and tmsu, prepared from etu or tmtu by the method of Klayman and co-workers,[7] were a gift from Dr. O. Vikane. $Te(tmsu)Cl_2$ was prepared from TeO_2, HCl and tmsu by a procedure analogous to that for $Te(tmtu)Cl_2$.[8]

X-Ray structure analyses. Data were recorded on a CAD4 diffractometer using graphite-monochromated Mo*K*α radiation (λ = 0.71069 Å). Unit cell dimensions were determined from the diffractometer angles of 23–25 automatically centred reflections. Intensities out to θ = 30° were recorded using the ω-scan mode, with a scan width of 1.00 + 0.35 tan θ, plus 25 % on each side for background. The intensities were corrected for Lorentz and polarization effects, decay and absorption. Maximum decay corrections, based on three reference reflections measured every 2 h of exposure time, were ca. 10, 2, 6, 8, 12 and 19 % for complexes *1–6*, respectively. Reflections

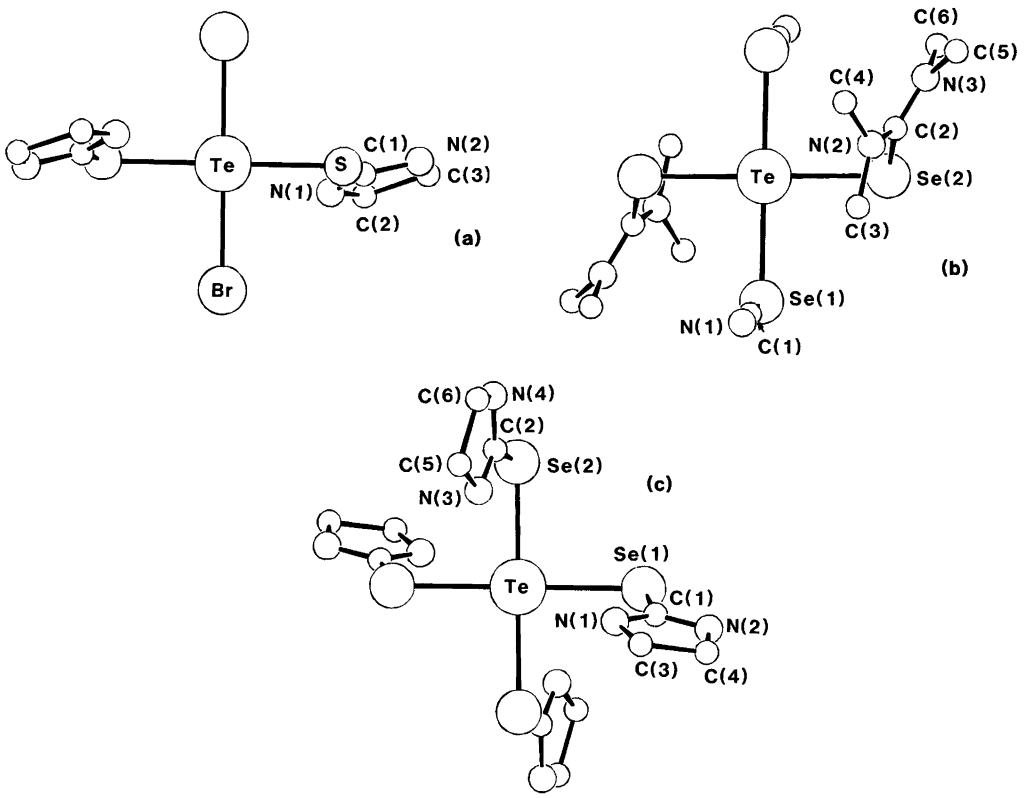

Fig. 1. Views of (a) the *trans*-$Te(etu)_2Br_2$ molecule, (b) the *trans*-$Te(tmsu)_2(SeCN)_2$ molecule and (c) the $[Te(esu)_4]^{2+}$ ion in $[Te(esu)_4]Cl_2$, as seen normal to the coordination planes.

with $I > 2\sigma(I)$ were regarded as observed and were used in the calculations. These were carried out using the Enraf–Nonius SDP programs. Scattering factors, including anomalous dispersion terms, were taken from Ref. 9. Refinements were made by the full matrix least-squares method, the sum minimized being $\Sigma w\Delta^2(F)$ with $w^{-1} = \sigma^2(F) = \sigma^2(I)/4LpI$, and $\sigma^2(I) = \sigma^2(I)_{count} + (0.02I)^2$. Extinction corrections $F_{corr} = F_c(1 + gI_c)^{-1}$ were applied and refined, except for complex *6*. Anisotropic thermal parameters were used for all non-hydrogen atoms. The hydrogens of complexes *1–4* were first placed in calculated positions and those of *5* were located from a Fourier difference map; their positional and thermal parameters [common values of B_{iso} for the hydrogens of *1*, *2* and *4* and individual values for the hydrogens of *3* and *5*] were then refined together with the other parameters. The final fractional hydrogen coordinates for complex *5* were entered for *6* and were held fixed, with a common fixed B_{iso}.

Crystal data are given in Table 1. The structure of complex *4* was solved by Patterson and Fourier difference methods. Starting coordinates for complexes *1* and *2* were those derived previously,[1] for *3* those for *4*, and for *5* and *6* those for the isomorphous $Te(tmtu)_2(SeCN)_2$.[3] The parameter shifts in the last refinement cycles were less than one percent of the associated standard deviations. Atomic coordinates for non-hydrogen atoms are given in Table 2. Thermal parameters, hydrogen coordinates, torsion angles and planes have been deposited with the Cambridge Crystallographic Data Centre.

Results and discussion

Bond lengths and angles are reported in Tables 3–5, and views of one molecule or ion of each isomorphous pair are shown in Fig. 1.

The coordination groups. With the tellurium atoms in crystallographic centres of symmetry, the TeS_2X_2, TeS_4 and $TeSe_4$ coordination groups are exactly planar, and the two three-centre systems of each group are exactly linear. The angles between the two linear systems lie within 90 ± 2.1°.

The refinements confirm the earlier structures[1] of complexes *1* and *2*. The largest revision of any Te–S, Te–Br or Te–I bond length is for Te–S in complex *1*, viz. from 2.686(15) to 2.656(1) Å. The bond lengths in the coordination groups are discussed elsewhere[2] in relation to bond lengths in other centrosymmetric tellurium(II) complexes.

The ethylenethiourea and -selenourea ligands. The SCN_2 or $SeCN_2$ moieties are planar or nearly so. The two ethylene carbon atoms deviate significantly from the plane (see Table 6).

The mean dimensions of the four independent etu ligands, based on the values in Tables 3 and 4, are: S–C 1.713(3), C–N 1.318(2), N–C 1.456(1) and C–C 1.522(4) Å; S–C–N(1) and S–C–N(3) 127.6(1), S–C–N(2) and S–C–N(4) 122.8(2), N–C–N 109.6(2), C–N–C 112.6(1) and N–C–C

Table 3. Distances (Å) and angles (°) in *trans*-$Te(etu)_2X_2$ with e.s.d.s in parentheses.[a]

	X = Br	X = I
Bond lengths		
Te–X	2.764(1)	2.955(1)
Te–S	2.656(1)	2.671(1)
S–C(1)	1.709(3)	1.704(3)
C(1)–N(1)	1.314(4)	1.320(4)
C(1)–N(2)	1.326(3)	1.321(4)
N(1)–C(2)	1.457(4)	1.456(5)
N(2)–C(3)	1.457(5)	1.456(5)
C(2)–C(3)	1.519(5)	1.524(5)
Bond angles		
S–Te–X	89.19(2)	89.15(2)
Te–S–C(1)	105.60(10)	105.23(10)
S–C(1)–N(1)	128.0(2)	128.0(2)
S–C(1)–N(2)	122.3(2)	122.9(3)
N(1)–C(1)–N(2)	109.8(3)	109.2(3)
C(1)–N(1)–C(2)	112.2(3)	112.7(3)
C(1)–N(2)–C(3)	112.6(3)	113.2(3)
N(1)–C(2)–C(3)	103.2(3)	102.8(3)
N(2)–C(3)–C(2)	102.2(3)	102.1(3)

[a]Bond distances: N–H 0.77(4)–0.88(5) Å (mean 0.82 (2) Å), C–H 0.91(5)–1.06(4) Å (mean 0.98(1) Å).

Table 4. Distances (Å) and angles (°) in $[Te(etu)_4]Cl_2$ (Y = S) and $[Te(esu)_4]Cl_2$ (Y = Se) with e.s.d.s in parentheses.[a]

	Y = S	Y = Se
Bond lengths		
Te–Y(1)	2.681(1)	2.802(1)
Te–Y(2)	2.666(1)	2.773(1)
Y(1)–C(1)	1.717(2)	1.870(3)
Y(2)–C(2)	1.714(2)	1.859(3)
C(1)–N(1)	1.315(2)	1.312(3)
C(1)–N(2)	1.316(2)	1.315(3)
C(2)–N(3)	1.312(2)	1.321(3)
C(2)–N(4)	1.325(2)	1.322(4)
N(1)–C(3)	1.456(2)	1.455(4)
N(2)–C(4)	1.459(2)	1.461(4)
N(3)–C(5)	1.455(2)	1.455(4)
N(4)–C(6)	1.455(3)	1.458(5)
C(3)–C(4)	1.529(3)	1.527(4)
C(5)–C(6)	1.514(3)	1.514(5)
Bond angles		
Y(1)–Te–Y(2)	91.06(1)	91.19(1)
Te–Y(1)–C(1)	103.03(5)	98.53(7)
Te–Y(2)–C(2)	103.06(5)	98.77(8)
Y(1)–C(1)–N(1)	127.5(1)	127.6(2)
Y(1)–C(1)–N(2)	122.6(1)	122.0(2)
N(1)–C(1)–N(2)	109.9(2)	110.4(2)
Y(2)–C(2)–N(3)	127.6(1)	127.1(2)
Y(2)–C(2)–N(4)	123.2(1)	123.6(2)
N(3)–C(2)–N(4)	109.3(2)	109.3(2)
C(1)–N(1)–C(3)	112.7(1)	112.3(2)
C(1)–N(2)–C(4)	112.5(1)	112.2(2)
C(2)–N(3)–C(5)	112.6(2)	112.4(3)
C(2)–N(4)–C(6)	112.4(2)	112.2(3)
N(1)–C(3)–C(4)	102.4(1)	102.7(2)
N(2)–C(4)–C(3)	102.3(1)	102.2(2)
N(3)–C(5)–C(6)	102.6(2)	102.4(3)
N(4)–C(6)–C(5)	102.2(2)	102.4(3)

[a]Bond distances: N–H 0.75(2)–0.80(2) Å (mean 0.78 (1) Å), C–H 0.86(2)–1.03(2) Å (mean 0.94(2) Å) for Y = S; N–H 0.69(4)–0.89(4) Å (mean 0.79(5) Å), C–H 0.84(4)–1.01(3) Å (mean 0.92(2) Å) for Y = Se.

102.4(1)°. The two S–C–N angles in each ligand are distinctly different, and in each case the larger angle is associated with the nitrogen atom located closest to tellurium. The Te···N(1) distances are 3.608(3), 3.600(3), and 3.500(2) Å in complexes *1*, *2*, and *3*, respectively and the Te···N(3) distance is 3.489(1) Å in *3*. The hydrogen atoms bonded to these nitrogen atoms are closer: Te···H(1) 3.18(4), 3.17(5), and 3.02(2) Å in complexes *1*, *2* and *3*, respectively, and Te···H(7) 2.97(2) Å in *3*. In the esu ligands of complex *4* the Se–C–N angles are also different (see Table 4): Te···N(1) 3.544(2), Te···N(3) 3.516 (2), Te···H(1) 2.97(4) and Te···H(7) 2.94(4) Å. Repulsions possibly occur, thereby widening the angle.

In uncomplexed etu,[10] the S–C bond length is 1.688(3) Å, which is only slightly different from the mean bond length in the complexes. No structure determination for esu has been reported. In PhTe(esu)Br,[11] the Se–C bond length is 1.875(8) Å, and in PhTe(esu)I,[12] 1.866(7) Å.

The tetramethylthiourea and -selenourea ligands. The structures of four centrosymmetric *trans*-$Te(tmtu)_2X_2$ complexes [X = Cl, Br or I (two forms)] have been reported elsewhere.[2] Including the present complex *5*, the five structures contain eitht independent tmtu ligands, and we discuss these here.

The SCN_2 moieties are planar within estimated error, their mean dimensions being S–C 1.723(3) and C–N 1.334(2) Å, S–C–N 121.9(1) and 119.5 (2)°, and N–C–N 118.6(2)°. For tmtu itself, a gas phase electron diffraction study[13] has yielded S–C 1.676(3) Å, C–N 1.388(5) Å and S–C–N 122.2 (3)°, whilst the values from a single crystal X-ray study[14] are S–C 1.68(1), C–N 1.37(1) Å and S–C–N 119.6°. The S–C bond of tmtu thus lengthens on complexation, as noted earlier,[15] and the C–N bonds become shorter. As in the uncomplexed molecule[13,14] and in other complexes,[3,15,16] the methyl groups, for steric reasons, are rotated out of the SCN_2 plane. The angles between the SCN_2 plane and the $CN(C_{Me})_2$ least-squares planes are 22.4–32.5° (av. 27.6°); this corresponds to angles of 47.5–51.9° (av. 50.5°) between the two $CN(C_{Me})_2$ planes. The environment of the N atoms is not quite planar, the pyramid heights being 0.04–0.10 Å; their average of 0.08 Å may be compared with 0.11 Å in the free molecule.[13]

In tmsu crystals the Se–C bond length is 1.836(4) Å.[17] In complex *6*, at 1.872(6) Å, the bond is longer [$\Delta/\sigma(\Delta) = 5.0$].

The thio- and selenocyanate ligands. These are linear within estimated error. In the SCN^- ion in NaSCN and NH_4SCN[18] the S–C bond length is 1.648(1) Å, whereas for the covalently bonded SCN group in CH_3SCN a value of 1.684(3) Å has been found by microwave spectroscopy.[19] The

Table 5. Distances (Å) and angles (°) with e.s.d.s in parentheses. Y = S or Se: Y(1) in SCN or SeCN ligand, Y(2) in tmtu or tmsu ligand.[a]

	$Te(tmtu)_2(SCN)_2$	$Te(tmsu)_2(SeCN)_2$
Bond lengths		
Te–Y(1)	2.685(1)	2.814(1)
Te–Y(2)	2.691(1)	2.811(1)
Y(1)–C(1)	1.662(4)	1.802(7)
C(1)–N(1)	1.146(4)	1.145(8)
Y(2)–C(2)	1.726(3)	1.872(6)
C(2)–N(2)	1.341(3)	1.341(7)
C(2)–N(3)	1.328(3)	1.334(7)
N(2)–C(3)	1.456(4)	1.462(8)
N(2)–C(4)	1.449(4)	1.445(8)
N(3)–C(5)	1.467(4)	1.475(8)
N(3)–C(6)	1.471(4)	1.459(7)
Bond angles		
Y(1)–Te–Y(2)	92.10(2)	91.45(2)
Te–Y(1)–C(1)	101.32(11)	99.13(21)
Y(1)–C(1)–N(1)	179.6(3)	179.5(6)
Te–Y(2)–C(2)	99.43(9)	95.09(18)
Y(2)–C(2)–N(2)	121.9(2)	122.0(4)
Y(2)–C(2)–N(3)	119.9(2)	120.7(4)
N(2)–C(2)–N(3)	118.2(2)	117.3(6)
C(2)–N(2)–C(3)	121.6(3)	122.0(6)
C(2)–N(2)–C(4)	122.2(3)	122.8(5)
C(3)–N(2)–C(4)	114.9(3)	113.7(6)
C(2)–N(3)–C(5)	122.9(3)	124.2(5)
C(2)–N(3)–C(6)	122.4(3)	122.1(5)
C(5)–N(3)–C(6)	114.1(3)	113.4(5)
Non-bonded contacts		
Y(2)···C(3)	3.075(4)	3.175(6)
Y(2)···C(6)	3.029(4)	3.131(7)
C(4)···C(5)	2.925(7)	2.923(11)
Te···C(3)	3.702(4)	3.758(6)

[a]Bond distances: in complex *5*, C–H 0.89(3)–1.03(4) Å (mean 0.96(2) Å); in *6*, with H coordinates from *5*, C–H 0.85–1.14 Å (av. 0.99 Å).

Table 6. Planes of portions of the molecules.

trans-$Te(etu)_2X_2$

Plane (1): Te, S, X
Plane (2): Te, S, C(1)
Plane (3): S, C(1), N(1), N(2)

	X = Br	X = I
Angles (°) between planes		
(1)–(2)	84.5	80.3
(1)–(3)	80.0	76.2
(2)–(3)	18.0	17.5
Distances (Å) of carbon atoms from thiourea plane (3)[a]		
C(1)	0.000(3)	0.001(3)
C(2)	−0.055(3)	−0.040(4)
C(3)	−0.076(3)	−0.081(4)

$[Te(etu)_4]Cl_2$ and $[Te(esu)_4]Cl_2$[b]

Plane (1): Te, Y(1), Y(2)
Plane (2): Te, Y(1), C(1) or Te, Y(2), C(2)
Plane (3): Y(1), C(1), N(1), N(2) or Y(2), C(2), N(3), N(4)

	Y = S[c]		Y = Se[c]	
Angles (°) between planes				
(1)–(2)	74.7	75.7	72.0	74.7
(1)–(3)	76.2	74.0	73.2	73.6
(2)–(3)	6.3	5.8	7.4	6.4

contd

Table 6. (contd)

Distances (Å) of carbon atoms from thio- or seleno-urea plane (3)[a]

C(1), C(2)	0.002(2)	−0.011(2)	−0.001(3)	−0.005(3)
C(3), C(5)	0,027(2)	0.095(2)	0.042(4)	0.118(3)
C(4), C(6)	0.093(2)	−0.070(2)	0.106(4)	−0.077(3)

$Te(tmtu)_2(SCN)_2$ and $Te(tmtu)_2(SeCN)_2$[b]

Plane (1): Te, Y(1), Y(2)
Plane (2): Te, Y(1), C(1)
Plane (3): Te, Y(2), C(2)
Plane (4): Y(2), C(2), N(2), N(3)

	Y = S	Y = Se
Angles (°) between planes		
(1)–(2)	82.0	81.5
(1)–(3)	55.7	55.4
(1)–(4)	79.0	75.9
(2)–(3)	83.7	84.0
(2)–(4)	30.1	28.9
(3)–(4)	57.1	57.2
Distances (Å) of carbon atoms from thio- or selenourea plane (4)[a]		
C(2)	0.003(3)	0.007(6)
C(3)	−0.499(3)	−0.501(8)
C(4)	0.739(3)	0.742(7)
C(5)	−0.623(4)	−0.580(8)
C(6)	0.445(4)	0.428(8)

[a]Least-squares plane. [b]Y(1) or Y(2) as in Tables 4 and 5. [c]Values for Y(1) ligand on left, for Y(2) ligand on right.

value for complex *5*, 1.662(4) Å, is intermediate between these, in accord with the *3c–4e* mode of bonding in tellurium(II) complexes. For Se–C in the $SeCN^-$ ion, the only reported value appears to be 1.829(25) Å (in KSeCN).[20]

Orientations of the ligands. The positions of the etu and tmtu ligands relative to the coordination plane are defined by the Te–S–C bond angle and by two dihedral angles: the tilt angle[21] (here TeSX/TeSC or TeS_2/TeSC) and the twist angle[21] (here TeSC/SCN_2). Similar parameters apply for the esu and tmsu ligands.

The Te–Se–C bond angles, at 95.1(2)–99.1(2)°, are smaller than the corresponding Te–S–C bond angles by 4.3(2)–4.5(1)° for the esu and tmsu ligands and 2.2(2)° for the SeCN ligands.

For the etu and esu ligands the tilt angles are 72.0–84.5° and the twist angles are 5.8–18.0°. However, for the tmtu and tmsu ligands of complexes *5* and *6* the tilt angles are smaller and the twist angles are larger (see Table 6). The tmtu ligands in the four *trans*-$Te(tmtu)_2X_2$ complexes[2] referred to above are similarly oriented: for the eight tmtu groups, including the present one, the tilt angles are 42.3–61.7 (av. 55.2°) and the twist angles are 52.7–62.8 (av. 57.0°). The arrangement entails a close contact between the Te atom and one of the outer CH_3 groups: Te···C_{Me} 3.640 (5)–3.868(7) Å (mean 3.72(2) Å). In complex *5*, for which hydrogen positions were refined, the Te···C_{Me} distance is 3.702(4) Å and the shortest Te···H distances are 3.25(3) and 3.49(4) Å.

Table 7. Intermolecular contacts (Å) and angles (°) between YCN ligands (Y = S or Se) across symmetry centre at 0, $^1/_2$, 0.

Complex	Y···Y	Y···Y–C
$Te(tmtu)_2(SCN)_2$	3.361(2)	155.4(1)
$Te(tmtu)_2(SeCN)_2$[a]	3.363(4)	151.7(6)
$Te(tmsu)_2(SeCN)_2$	3.398(1)	152.0(2)

[a]Values calculated from atomic coordinates in Ref. 3.

Intermolecular contacts. In complexes *5* and *6*, close approaches occur between S or Se atoms of SCN or SeCN groups of neighbouring molecules. Data for these and for the third isomorph, $Te(tmtu)_2(SeCN)_2$,[3] are summarized in Table 7. The NCS···SCN and NCSe···SeCN systems are almost linear. The Se···Se distances of approach are comparable with the shortest intermolecular contacts in γ-Se_8,[22] viz. 3.346(3) and 3.404(3) Å.

Ionic environment in the salts. The Cl^- ion lies 3.766(1) Å from Te in complex *3* and 3.743(1) Å from Te in *4*; the Te···Cl^- axes make angles of 72.0 and 67.7°, respectively, with the TeS_4 and $TeSe_4$ planes. The N(1)···Cl^- and N(3)···Cl^- distances are 3.218(2) and 3.198(2) Å, respectively, in complex *3* and 3.250(2) and 3.268(3) Å in *4*. These distances indicate N–H···Cl^- hydrogen bonds. The Cl^- ion also partakes in hydrogen bonding to N(2) of the adjacent cation at $x,1+y,z$, the N(2′)···Cl^- distance being 3.148(2) Å in complex *3* and 3.147(2) Å in *4*. The fourth nitrogen atom, N(4), has no Cl^- ion closer than 4.006(2) Å in complex *3* and 3.976(3) Å in *4*.

The structure of $[Te(dmtu)_4]Cl_2$ (dmtu = *N,N′*-dimethylthiourea) has been determined by Barnard *et al.*[23a] In this salt, the shortest Te···Cl^- distance is 4.35 Å and from the reported coordinates,[23a] this Te···Cl^- axis makes an angle of 76.2° with the TeS_4 plane. The authors[23] discuss the state of hybridization of the lone 5*s* and 5*p* electron pairs of tellurium, and take the view that the large Te···Cl^- distance accords with strong repulsion by *sp* hybrid lone pairs. The Te···Cl^- distances in the present salts, 3.766(1) and 3.743(1) Å, are shorter and do not indicate strong repulsions. An ionic radius of 1.81 Å for Cl^- leaves 1.96 and 1.93 Å for Te, both of which are less than the Pauling van der Waals radius[24] of 2.20 Å and also less than Bondi's value[25] of 2.06 Å. Regarding the Te lone pairs, it may be noted that the He(I) photoelectron spectra of $TeBr_2$ and $TeCl_2$ can be satisfactorily interpreted in terms of *p* orbitals alone;[26] the 5*s* orbital of Te lies deeper than the 5*p* orbitals.

Conformations of the $[Te(etu)_4]^{2+}$ ion. The structure of the dihydrate, $[Te(etu)_4]Cl_2 \cdot 2H_2O$, has been reported by Elder *et al.*[27] The tellurium atoms lie on two-fold symmetry axes, and the conformation of the cation, in the authors' notation,[27] is +−+−; the five-membered rings of neighbouring etu ligands lie alternately above and below the TeS_4 plane. The authors[27] suggest that this is the preferred geometry, interactions between neighbouring etu ligands thereby being avoided. However, in $[Te(etu)_4][TeCl_6]$[28] the tellurium atoms also lie on two-fold axes and the geometry of the cation is not +−+− but ++−−. A molecular symmetry centre imposes ++−− geometry, as in the present salt: neighbouring etu ligands lie on the same side of the TeS_4 plane; however, there are no close contacts between the ligands, the shortest distances being H(1)···H(7) 2.95(3), N(3)···H(1) 3.54(2) and N(1)···H(7) 3.64(2) Å. In solution, rapidly established equilibria between conformers probably occur. Methanol dissolves +−+− $[Te(etu)_4]Cl_2 \cdot 2H_2O$, whereupon ++−− $[Te(etu)_4]Cl_2$ crystallizes.[5]

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