Complexes of Tellurium Dithiocyanate and Diselenocyanate with Thioureas and Selenoureas, TeL_2X_2. Crystal and Molecular Structures of *cis* Isomers

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The crystal structures of the complexes *cis*-$Te(tu)_2(SCN)_2$ (**1**) (tu = thiourea), *cis*-$Te(su)_2(SCN)_2$ (**2**) (su = selenourea), *cis*-$Te(trtu)_2(SCN)_2$ (**3**), *cis*-$Te(trtu)_2(SeCN)_2$ (**4**) (trtu = trimethylenethiourea), *cis*-$Te(etu)_2(SCN)_2$ (**5**) (etu = ethylenethiourea), *cis*-$Te(esu)_2(SCN)_2$ (**6**) and *cis*-$Te(esu)_2(SeCN)_2$ (**7**) (esu = ethyleneselenourea) have been determined by X-ray methods. Complexes **1** and **2** are isomorphous, as are **3** and **4**, and **5**–**7**; space groups are: *Fdd*2 (No. 43) with $Z = 8$ for **1** and **2**, *C*2/*c* (No. 15) with $Z = 4$ for **3** and **4**, and $P2_1/c$ (No. 14) with $Z = 4$ for **5**–**7**. The structures were refined to $R = 0.022$ (**1**), 0.037 (**2**), 0.030 (**3**), 0.037 (**4**), 0.026 (**5**), 0.033 (**6**) and 0.037 (**7**) for 1471, 947, 1474, 1845, 3591, 3378 and 3107 observed reflections, respectively. In **1**–**4**, the tellurium atoms lie on two-fold symmetry axes. The TeS_4, TeS_2Se_2 or $TeSe_4$ coordination groups are distorted square-planar. In the approximately linear S–Te–S, S–Te–Se or Se–Te–Se systems, the bonds to the S or Se atoms of the thio- or selenourea ligands [bond lengths Te–S 2.458(1)–2.592(1), Te–Se 2.536(1)–2.657(1) Å] are shorter than the bonds to the *trans*-positioned SCN or SeCN ligands [bond lengths Te–S 2.867(1) –3.163(2), Te–Se 2.872(1)–3.029(1) Å]. The order of *trans*-influence is su > tu ≈ esu > etu ≈ trtu > SeCN > SCN. The relative *trans*-influence of thio and seleno ligands is compared for isomorphous pairs of tellurium(II) complexes in which the *trans*-ligand is the same for both members of each pair, over bond length ranges Te–S 2.425(1)–3.025(1) and Te–Se 2.537(1)–3.029(1) Å. The *trans*-influence of the seleno ligand relative to the thio ligand is largest for bond lengths Te–S 2.63 and Te–Se 2.69 Å. The difference in total lengths of the linear three-centre systems is largest (0.18 Å) for bond lengths Te–S 2.51 and Te–Se 2.60 Å, and is small (0.05 Å) for the longest Te–S and Te–Se distances.

The crystal structures of square-planar *trans*-$TeL_2(SCN)_2$ [L = ethylenethiourea (etu) or tetramethylthiourea (tmtu)] and *trans*–$TeL_2(SeCN)_2$ [L = etu, trimethylenethiourea (trtu), tmtu or tetramethylselenourea (tmsu)] have been reported.[1-3] As part of a study of the relative *trans*-influence of thio and seleno ligands in tellurium(II) complexes, we report here the structures of *cis*-$TeL_2(SCN)_2$ [L = thiourea (tu), selenourea (su), trtu, etu or ethyleneselenourea (esu)] and *cis*-$TeL_2(SeCN)_2$ (L = trtu or esu).

Experimental

Preparations. The complex $Te(su)_2(SCN)_2$. Powdered $Te(su)_2Cl_2$[4] (0.30 g) was treated with NH_4SCN (10 g) in H_2O (15 cm^3). On stirring at room temperature, dissolution and crystallization took place. To obtain larger crystals the mixture was heated, filtered to remove some liberated Te and the filtrate was allowed to cool, giving yellow crystals. Anal. $C_4H_8N_6S_2Se_2Te$: C, H, N.

The complex $Te(esu)_2(SCN)_2$. The compound $Te(esu)_2Br_2$ was treated with an excess of NH_4SCN in hot methanol. The mixture was fil-

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tered and the filtrate allowed to cool, whereupon the product crystallized. Anal. $C_8H_{12}N_6S_2Se_2Te$: C, H, N.

The complex Te(esu)$_2$(SeCN)$_2$ was prepared similarly, using KSeCN instead of NH_4SCN. Found: C 15.86; H 2.02; N 13.25. Calc. for $C_8H_{12}N_6Se_4Te$: C 15.12; H 1.90; N 13.22. The crystals are orange red. The Te(esu)$_2$Br$_2$ used was prepared from TeO_2 and esu (molar ratio 1:4) in HBr/dimethylformamide, and precipitated by adding methanol to the reaction mixture.

The Te(su)$_2$Cl$_2$ used was a gift from Dr. S. Hauge, and the esu, prepared from etu by the method of Klayman and co-workers,[5] was a gift from Dr. O. Vikane. The other complexes were prepared as described previously.[2,6–8]

X-Ray structure analyses. Crystal data, with numbering of complexes, are given in Tables 1 and 2. Crystals of complexes **1** and **2** are isomorphous, as are those of **3** and **4**, and of **5**, **6** and **7**. X-Ray measurements were made on a CAD4 diffractometer using graphite-monochromated Mo*K*α radiation (λ = 0.71069 Å). Unit cell dimensions were derived from the setting angles for 18–25 automatically centred reflections. Intensities were collected using the ω-scan mode and the scan width was 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. The decay corrections, based on three reference reflections measured every 2 h of exposure time, were insignificant except for complex **5**, for which the largest correction factor was 1.139. Reflections 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. Refinements were by full-matrix least-squares, the sum minimized being $\Sigma w\Delta^2(F)$ with $w^{-1} = \sigma^2(F) = \sigma^2(I)/4LpI$ and $\sigma^2(I) = \sigma^2(I)_{\mathrm{count}} + (0.02I)^2$. Atomic scattering factors, with anomalous dispersion terms included, were taken from Ref. 9. Anisotropic thermal parameters were used for all non-hydrogen atoms. Hydrogens were placed geometrically

Table 1. Crystallographic data for tu, su and trtu complexes.

	1	**2**	**3**	**4**
Complex	Te(tu)$_2$(SCN)$_2$	Te(su)$_2$(SCN)$_2$	Te(trtu)$_2$(SCN)$_2$	Te(trtu)$_2$(SeCN)$_2$
Formula	$C_4H_8N_6S_4Te$	$C_4H_8N_6S_2Se_2Te$	$C_{10}H_{16}N_6S_4Te$	$C_{10}H_{16}N_6S_2Se_2Te$
M	396.00	489.80	476.14	569.93
System	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group	*Fdd2* (No. 43)	*Fdd2* (No. 43)	*C2/c* (No. 15)	*C2/c* (No. 15)
a/Å	18.430(2)	18.423(1)	13.275(2)	13.305(1)
b/Å	18.560(2)	18.522(2)	14.418(2)	14.565(2)
c/Å	7.861(1)	8.224(1)	9.731(2)	9.898(2)
β/°			108.70(1)	108.38(1)
V/Å^3	2688.9(9)	2806.3(9)	1764.1(8)	1820.2(9)
Z	8	8	4	4
D_x/g cm^{-3}	1.956	2.318	1.793	2.080
F(000)	1520	1808	936	1080
μ(Mo*K*α)/cm^{-1}	28.67	80.45	22.03	62.19
Crystal volume/mm^3	0.0158	0.0096	0.00074	0.0027
Transmission factors	0.557–0.592	0.194–0.329	0.838–0.882	0.505–0.590
Scan rate/° min^{-1}	3.35–0.74	3.35–0.80	0.84–0.39	2.51–0.47
$\theta_{\max}$/°	36	36	28	30
Unique reflections	1678	1758	2110	2649
Reflections $I > 2\sigma$	1471	947	1474	1845
No. of variables	84	68	96	97
R	0.022	0.037	0.030	0.037
R_w	0.026	0.035	0.029	0.037
S	1.478	1.682	1.206	1.602
Max. Δ(ρ)/e Å^{-3}	0.51	0.93	0.50	1.38

Table 2. Crystallographic data for etu and esu complexes.

	5	6	7
Complex	$Te(etu)_2(SCN)_2$	$Te(esu)_2(SCN)_2$	$Te(esu)_2(SeCN)_2$
Formula	$C_8H_{12}N_6S_4Te$	$C_8H_{12}N_6S_2Se_2Te$	$C_8H_{12}N_6Se_4Te$
M	448.08	541.87	635.67
System	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a/Å	10.642(1)	10.750(1)	10.887(1)
b/Å	12.817(1)	13.043(1)	13.064(1)
c/Å	11.975(1)	12.076(2)	12.325(2)
β/°	102.49(1)	102.96(1)	103.62(1)
V/Å^3	1594.8(6)	1650.2(6)	1703.7(6)
Z	4	4	4
D_x/g cm^{-3}	1.866	2.181	2.478
$F(000)$	872	1016	1160
μ(Mo$K\alpha$)/cm^{-1}	24.30	68.53	110.01
Crystal volume/mm^3	0.0032	0.0052	0.0068
Transmission factors	0.721–0.829	0.304–0.419	0.152–0.370
Scan rate/° min^{-1}	3.35–0.50	3.35–0.50	3.35–0.50
θ_{max}/°	30	30	30
Unique reflections	4638	4780	4953
Reflections $I > 2\sigma$	3591	3378	3107
No. of variables	172	172	172
R	0.026	0.033	0.037
R_w	0.028	0.033	0.035
S	1.139	1.345	1.397
Max. $\Delta(\varrho)$/e Å^{-3}	0.43	1.02	0.86

and were held fixed, at N–H 0.87 and C–H 0.95 Å, with a common, fixed B_{iso}, except for complex **1**, for which positions and individual B_{iso}'s for hydrogens were refined together with the other variables. For complex **4**, an empirical extinction correction, $F_{corr} = F_c(1 + gI_c)^{-1}$ was applied and g refined to 2.94×10^{-7}.

The structure of complex **1** was solved by direct methods (MULTAN) and those of **3** and **5** by Patterson methods, followed by normal Fourier difference procedures. The coordinates for complexes **1**, **3** and **5** were used as starting coordinates for the refinements of **2**, **4**, and **6** and **7**, respectively. The shifts in the final refinement cycle were less than one per cent of the associated standard deviations. Atomic coordinates for non-hydrogen atoms are listed in Tables 3 and 4. Thermal parameters, hydrogen coordinates, torsion angles and planes have been deposited with the Cambridge Crystallographic Data Centre.

Refinements of the inverted structures of complexes **1** and **2**, both of space group $Fdd2$, gave inferior agreement indexes: R, R_w and S 0.023, 0.028 and 1.607, respectively, for **1**, and 0.041, 0.041 and 1.973, respectively, for **2**. In the case of complex **1**, the wrong structure was initially arrived at. Parameter errors in polar space groups caused by wrong polarity or by neglect of anomalous scattering can be large.[10] In the present case, the inverted, wrong structures gave bond lengths Te–S 2.442(1) and 3.055(1) Å for complex **1**, and Te–Se 2.560(1) and Te–S 3.181(2) Å for **2**; the differences between these values and those of Table 5 are 9–24 times the e.s.d.'s.

Complexes **3** and **4** were thought to be *trans* isomers.[2,8] However, the weak *hkl* reflections for l odd which gave rise to that assumption are not caused by Te atoms in symmetry centres but by Te atoms on two-fold axes with y close to zero.

Results and discussion

Dimensional data are given in Tables 5–8, and views of molecules, i.e. one from each isomorphous pair or triad, are shown in Fig. 1.

Table 3. Fractional atomic coordinates with e.s.d.'s in parentheses.

Atom	*x*	*y*	*z*	B_{eq}/Å^2
$Te(tu)_2(SCN)_2$				
S(1)	0	0	0.00000[a]	2.919(3)
S(2)	−0.08935(5)	0.03615(4)	0.21596(14)	4.76(2)
N(1)	−0.10902(4)	0.06875(4)	−0.24044(16)	4.02(1)
N(2)	−0.13867(16)	0.16030(14)	0.3047(5)	4.54(6)
N(3)	−0.02708(16)	0.16692(12)	0.1761(5)	4.37(6)
C(1)	−0.01683(17)	0.18155(17)	−0.3338(6)	5.06(7)
C(2)	−0.08227(15)	0.12992(13)	0.2313(4)	3.21(4)
	−0.05507(13)	0.13580(14)	−0.2947(4)	3.34(5)
$Te(su)_2(SCN)_2$				
Te	0	0	0.00000[a]	3.60(1)
Se	−0.09749(5)	0.03148(4)	0.20587(13)	5.09(2)
S	−0.11133(9)	0.07307(10)	−0.2421(3)	4.73(4)
N(1)	−0.1344(4)	0.1645(3)	0.3191(10)	5.0(1)
N(2)	−0.0285(4)	0.1681(3)	0.1783(10)	4.7(1)
N(3)	−0.0126(4)	0.1799(4)	−0.3303(12)	5.6(2)
C(1)	−0.0833(3)	0.1324(3)	0.2369(11)	3.6(1)
C(2)	−0.0544(3)	0.1366(3)	−0.2935(10)	3.7(1)
$Te(trtu)_2(SCN)_2$				
Te	0	−0.00206(3)	$\frac{1}{4}$	3.250(6)
S(1)	0.10295(8)	0.11759(10)	0.43090(12)	6.04(3)
S(2)	0.12316(8)	−0.14651(9)	0.42898(12)	4.85(3)
N(1)	0.2457(2)	0.1089(3)	0.2890(3)	4.57(8)
N(2)	0.3109(2)	0.1244(3)	0.5352(3)	4.22(8)
N(3)	0.2998(3)	−0.1275(3)	0.3321(4)	6.2(1)
C(1)	0.2303(3)	0.1159(3)	0.4158(4)	3.7(1)
C(2)	0.3512(3)	0.1069(4)	0.2738(4)	5.0(1)
C(3)	0.4270(3)	0.1554(4)	0.3933(5)	5.7(1)
C(4)	0.4207(3)	0.1284(4)	0.5380(5)	5.1(1)
C(5)	0.2277(3)	−0.1342(3)	0.3715(4)	4.0(1)
$Te(trtu)_2(SeCN)_2$				
Te	0	−0.00315(3)	$\frac{1}{4}$	3.526(7)
S	0.10272(10)	0.11957(11)	0.43064(15)	7.42(3)
Se	0.11778(4)	−0.14634(4)	0.43112(5)	5.34(1)
N(1)	0.24264(3)	0.1080(3)	0.2953(4)	5.5(1)
N(2)	0.3093(3)	0.1254(3)	0.5348(4)	5.0(1)
N(3)	0.3058(3)	−0.1285(4)	0.3340(5)	7.0(1)
C(1)	0.2300(3)	0.1168(5)	0.4188(5)	4.2(1)
C(2)	0.3523(4)	0.1040(4)	0.2801(5)	6.1(1)
C(3)	0.4269(4)	0.1494(5)	0.3992(6)	6.9(2)
C(4)	0.4189(4)	0.1272(4)	0.5385(6)	5.9(1)
C(5)	0.2330(4)	−0.1346(3)	0.3721(5)	4.6(1)

[a]Fixed coordinate.

The complexes contain approximately planar TeS_4, TeS_2Se_2 or $TeSe_4$ coordination groups. The groups are slightly tetrahedrally distorted; the plane angles (1)–(2) (Tables 5, 6 and 8) are not zero but range from 5.2° for *cis*-$Te(trtu)_2(SeCN)_2$ to 15.4° for *cis*-$Te(su)_2(SCN)_2$. The *trans*-S–Te–S, S–Te–Se and Se–Te–Se systems deviate 4.1–12.1° from linearity; the largest deviation occurs for *cis*-$Te(su)_2(SCN)_2$.

In the crystals of complexes **1**–**4** the molecules

Table 4. Fractional atomic coordinates with e.s.d.'s in parentheses.

Atom	x	y	z	B_{eq}/Å^2
Te(etu)$_2$(SCN)$_2$				
Te	0.082154(16)	0.151229(13)	0.272722(14)	2.643(3)
S(1)	−0.12642(7)	0.08278(7)	0.31008(6)	4.02(2)
S(2)	0.21021(9)	0.07202(6)	0.45468(6)	4.09(2)
S(3)	−0.05137(9)	0.26981(6)	0.07826(7)	4.53(2)
S(4)	0.31505(8)	0.24958(7)	0.22438(9)	4.94(2)
N(1)	−0.3105(2)	0.0040(2)	0.1465(2)	4.38(6)
N(2)	−0.1220(2)	−0.0474(2)	0.1304(2)	3.90(5)
N(3)	0.2719(2)	−0.0777(2)	0.3143(2)	3.49(5)
N(4)	0.3716(3)	−0.0877(2)	0.4912(2)	4.41(6)
N(5)	−0.1282(3)	0.1146(2)	−0.0857(2)	5.11(7)
N(6)	0.4967(3)	0.0905(3)	0.2597(3)	5.27(7)
C(1)	−0.1869(3)	0.0096(2)	0.1891(2)	3.13(6)
C(2)	0.2861(2)	−0.0363(2)	0.4153(2)	3.19(5)
C(3)	−0.0970(3)	0.1779(2)	−0.0172(2)	3.63(6)
C(4)	0.4207(2)	0.1552(2)	0.2460(2)	3.47(6)
C(5)	−0.3386(3)	−0.0636(3)	0.0466(3)	5.13(8)
C(6)	−0.2065(3)	−0.0974(2)	0.0329(3)	4.12(7)
C(7)	0.3559(3)	−0.1676(3)	0.3143(3)	4.92(8)
C(8)	0.4171(3)	−0.1800(3)	0.4411(3)	5.37(9)
Te(esu)$_2$(SCN)$_2$				
Te	0.87139(26)	0.153397(20)	0.273450(22)	2.755(5)
Se(1)	−0.12489(5)	0.08664(4)	0.31879(4)	4.21(1)
Se(2)	0.22449(5)	0.08000(4)	0.46247(4)	4.27(1)
S(1)	−0.05257(14)	0.26768(10)	0.06968(11)	4.61(3)
S(2)	0.32536(13)	0.24595(11)	0.22073(13)	5.02(3)
N(1)	−0.3117(4)	−0.0036(3)	0.1487(3)	4.6(1)
N(2)	−0.1245(4)	−0.0442(3)	0.1274(3)	4.2(1)
N(3)	0.2725(3)	−0.0813(3)	0.3159(3)	3.6(1)
N(4)	0.3776(3)	−0.0944(3)	0.4904(3)	4.5(1)
N(5)	−0.1249(4)	0.1100(3)	−0.0880(3)	5.1(1)
N(6)	0.5000(4)	0.0857(4)	0.2599(4)	5.3(1)
C(1)	−0.1888(4)	0.0065(3)	0.1880(4)	3.3(1)
C(2)	0.2939(4)	−0.0405(3)	0.4166(3)	3.2(1)
C(3)	−0.0960(4)	0.1743(3)	−0.0216(4)	3.7(1)
C(4)	0.4274(4)	0.1506(4)	0.2447(3)	3.5(1)
C(5)	−0.3382(5)	−0.0694(5)	0.0484(4)	5.5(1)
C(6)	−0.2067(5)	−0.0965(4)	0.0321(4)	4.1(1)
C(7)	0.3492(5)	−0.1719(4)	0.3126(5)	5.2(1)
C(8)	0.4117(5)	−0.1883(4)	0.4390(5)	5.2(1)
Te(esu)$_2$(SeCN)$_2$				
Te	0.088512(35)	0.154642(27)	0.27342(27)	2.778(6)
Se(1)	−0.12359(6)	0.08334(6)	0.31657(6)	4.42(1)
Se(2)	0.22328(7)	0.07793(5)	0.46338(5)	4.34(2)
Se(3)	−0.04846(7)	0.27422(5)	0.07306(5)	4.41(2)
Se(4)	0.32233(7)	0.25180(6)	0.22450(7)	5.15(2)
N(1)	−0.3098(5)	−0.0021(4)	0.1443(4)	4.8(1)
N(2)	−0.1262(5)	−0.0412(4)	0.1244(49)	4.4(1)
N(3)	0.2753(5)	−0.0800(4)	0.3196(4)	3.6(1)
N(4)	0.3771(5)	−0.0952(4)	0.4908(4)	4.6(1)
N(5)	−0.1246(6)	0.1095(5)	−0.0920(4)	5.7(2)
N(6)	0.5018(6)	0.0819(5)	0.2578(5)	5.9(2)
C(1)	−0.1882(5)	0.0087(4)	0.1849(4)	3.5(1)
C(2)	0.2950(5)	−0.0397(4)	0.4185(4)	3.2(1)
C(3)	−0.0954(6)	0.1719(4)	−0.0266(4)	3.8(1)
C(4)	0.4293(5)	0.1476(5)	0.2451(4)	3.4(1)
C(5)	−0.3363(7)	−0.0627(6)	0.0433(5)	5.7(2)
C(6)	−0.2064(6)	−0.0936(5)	0.0311(5)	4.4(2)
C(7)	0.3512(7)	−0.1707(6)	0.3159(6)	5.6(2)
C(8)	0.4107(7)	−0.1870(6)	0.4379(6)	5.6(2)

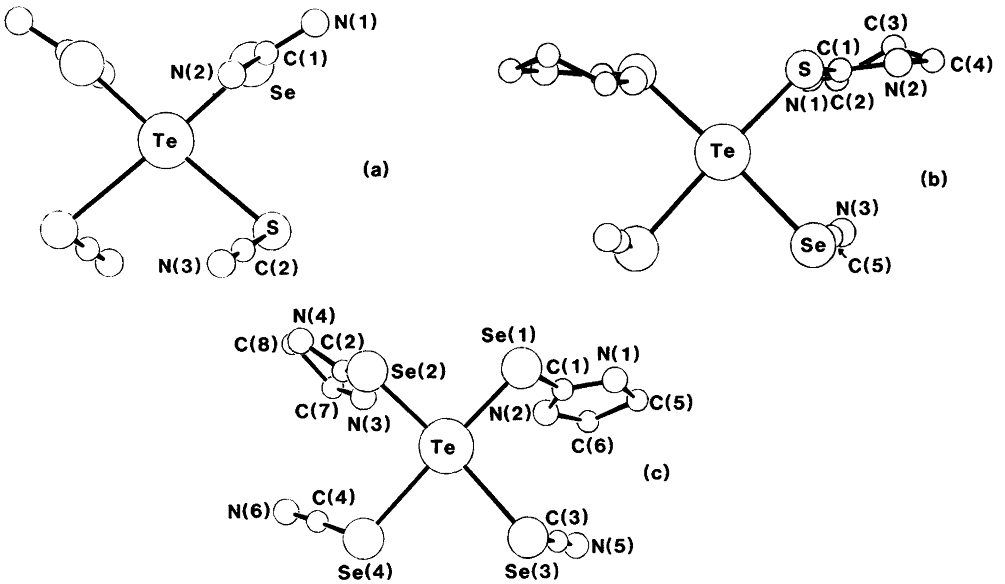

Fig. 1. Views of (a) *cis*-Te(su)$_2$(SCN)$_2$, (b) *cis*-Te(trtu)$_2$(SeCN)$_2$ and (c) *cis*-Te(esu)$_2$(SeCN)$_2$.

possess two-fold axis symmetry, and ligand groups related over the axis lie on different sides of the coordination plane. In complexes **5**–**7** the molecules are asymmetric, and all ligand groups lie on the same side of the coordination plane; this does not entail any close contacts between the groups.

The present structures are the first reported for *cis*-TeL$_2$X$_2$ complexes with X = SCN or SeCN; the thio- or selenourea ligands are *trans* to thio- or selenocyanate ligands. In centrosymmetric *trans*-TeL$_2$X$_2$ and [TeL$_4$]X$_2$ complexes, the mean lengths of twenty Te–S bonds and ten Te–Se bonds are 2.682(3) and 2.806(6) Å, respectively.[11] In the present *cis* complexes, the Te–S$_L$ and Te–Se$_L$ bonds are shorter and the Te–S$_X$ and Te–Se$_X$ bonds are longer, i.e. the *trans*-influence of the thio- or selenourea ligand is greater than that of the thio- or selenocyanate ligand. The data in Tables 5–7 indicate that the *trans*-influence order is su > tu ≥ esu > etu ≈ trtu > SeCN > SCN. The orders tu ≥ esu > etu when *trans* to Br in PhTeLBr, and esu > etu when *trans* to I in PhTeLI, have been noted earlier.[12,13]

The orders su > tu, esu > etu, and SeCN > SCN, i.e. seleno ligand > thio ligand, at the soft tellurium(II) centre are as expected. However, the magnitude of the difference varies with the Te–Se and Te–S distances.

Relative trans-*influence of thio and seleno ligands.* The 3*c*–4*e* bonds are weak and the systems are easily influenced by lattice forces. In order to minimize differences arising from such effects, we compare isomorphous pairs of complexes containing L–Te–L$_{tr}$ systems in which L is a thio ligand for one member of a pair and its seleno analogue for the other member, and the *trans*-ligand L$_{tr}$ is the same for both. Data are listed in Table 9 and differences are plotted against *d*(Te–S) for the thio ligand in Fig. 2. The difference ΔL_{tr} = [*d*(Te–L$_{tr}$) *trans* to Se] – [*d*(Te–L$_{tr}$) *trans* to S] is a measure of the relative *trans*-influence, ΔL = *d*(Te–Se) – *d*(Te–S), and $\Delta D = \Delta L + \Delta L_{tr}$ is the difference in total lengths of the two systems. One of the present pairs, viz. complexes **1** and **2**, is not included. The thiocyanate Te–S bond in complex **2**, at 3.162(2) Å, appears to be anomalously long; this complex, *cis*-Te(su)$_2$(SCN)$_2$, is that in which the coordination group shows the largest distortions.

The data cover bond length ranges Te–S 2.425(1)–3.025(1) and Te–Se 2.537(1)–3.029(1) Å. In Fig. 2, the ΔL_{tr} curve extrapolates to zero for Te–S ca. 2.38 Å, the Te–S single-bond distance. The ΔL and ΔD curves, similarly extrapolated, intersect for Te–S ca. 2.38 Å at ΔL and ΔD ca. 0.12 Å, the difference in the Se and S single-bond radii. For these values, the systems are in a

Table 5. Distances (Å) and angles (°) with e.s.d.'s in parentheses. X = S or Se of thio- or selenourea group; S = sulfur of thiocyanate group. Primed atoms related to unprimed ones over molecular two-fold axis.

	$Te(tu)_2(SeCN)_2$	$Te(su)_2(SCN)_2$
Bond lengths		
Te–X	2.458(1)	2.536(1)
Te–S	3.039(1)	3.163(2)
X–C(1)	1.749(2)	1.904(5)
C(1)–N(1)	1.316(3)	1.304(8)
C(1)–N(2)	1.302(3)	1.299(7)
S–C(2)	1.649(2)	1.632(6)
C(2)–N(3)	1.145(3)	1.152(7)
Bond angles		
X–Te–X′	92.65(5)	96.24(4)
X–Te–S	82.65(3)	82.11(4)
X–Te–S′	170.68(2)	167.93(3)
S–Te–S′	103.10(4)	101.96(7)
Te–X–C(1)	105.62(9)	102.58(19)
X–C(1)–N(1)	113.4(2)	114.8(4)
X–C(1)–N(2)	124.1(2)	123.8(5)
N(1)–C(1)–N(2)	122.5(2)	121.4(5)
Te–S–C(2)	94.54(9)	93.12(22)
S–C(2)–N(3)	178.8(3)	178.0(5)
Angles between planes[a,b]		
(1)–(2)	10.2	15.4
(1)–(3)	80.3	89.1
(2)–(4)	74.4	73.2
(3)–(5)	17.6	9.6

[a] Plane (1): TeXX′; plane (2): TeSS′; plane (3): TeXC(1); plane (4): TeSC(2); plane (5): XC(1)N(1) N(2). [b] The atoms defining least-squares planes (5) lie in the planes within error limits.

state of extreme asymmetry: Se–Te···L_{tr} and S–Te···L_{tr} with Se and S at single-bond distances and L_{tr} at non-bonded distance. The ΔL_{tr} curve reaches a maximum of ca. 0.09 Å for Te–S 2.63 and Te–Se 2.69 Å, i.e. the *trans*-influence of the seleno ligand relative to the thio ligand is largest at these Te–S and Te–Se distances. A maximum of ca. 0.18 Å for the ΔD curve, the difference in total lengths of the systems, occurs at Te–S 2.51 and Te–Se 2.60 Å. At the largest Te–S and Te–Se distances covered by the data, ΔL_{tr} is ca. 0.05 Å and ΔL is small.

Viewed from right to left, the curves of Fig. 2 may be regarded as difference profiles for the last stages of the displacement of a *trans*-ligand, L_{tr}, by a seleno ligand, relative to the displacement of the same *trans*-ligand by the thio analogue, i.e. for L···Te–L_{tr} → L–Te···L_{tr}. The shapes of the curves accord with the properties of linear three-centre systems. For small asymmetries, the total length of the system remains essentially constant; one ligand recedes to the same extent as the other approaches. As the asymmetry increases, the total length increases owing to a larger increase in bonding distance for the leaving, more distant li-

Table 6. Distances (Å) and angles (°) with e.s.d.'s in parentheses. S = sulfur of trimethylenethiourea group; Y = S or Se of thio- or selenocyanate group. Primed atoms as in Table 5.

	$Te(trtu)_2(SCN)_2$	$Te(trtu)_2(SeCN)_2$
Bond lengths		
Te–S	2.530(1)	2.592(1)
Te–Y	2.867(1)	2.872(1)
S–C(1)	1.743(4)	1.734(4)
C(1)–N(1)	1.318(4)	1.315(5)
C(1)–N(2)	1.309(5)	1.297(5)
N(1)–C(2)	1.456(5)	1.464(5)
N(2)–C(4)	1.450(5)	1.447(5)
C(2)–C(3)	1.450(6)	1.440(6)
C(3)–C(4)	1.488(6)	1.452(6)
Y–C(5)	1.664(4)	1.813(4)
C(5)–N(3)	1.144(5)	1.147(5)
Bond angles		
S–Te–S′	94.01(7)	92.80(8)
S–Te–Y	89.83(4)	90.29(4)
S–Te–Y′	173.62(4)	175.29(4)
Y–Te–Y′	86.81(5)	86.86(2)
Te–S–C(1)	104.71(14)	104.54(13)
S–C(1)–N(1)	121.7(3)	121.2(3)
S–C(1)–N(2)	117.6(3)	118.5(3)
N(1)–C(1)–N(2)	120.6(3)	120.3(3)
C(1)–N(1)–C(2)	122.7(3)	123.2(3)
N(1)–C(2)–C(3)	110.6(3)	109.6(4)
C(2)–C(3)–C(4)	113.5(4)	115.9(4)
C(3)–C(4)–N(2)	110.7(3)	110.8(3)
Te–Y–C(5)	95.35(14)	94.63(11)
Y–C(5)–N(3)	178.8(4)	178.9(4)
Angles between planes[a,b]		
(1)–(2)	7.4	5.2
(1)–(3)	74.7	73.7
(2)–(4)	75.2	77.1
(3)–(5)	39.5	39.5

[a] Plane (1): TeSS′; plane (2): TeYY′; plane (3): TeSC(1); plane (4): TeYC(5); plane (5): SC(1)N(1)N(2). [b] As in Table 5.

Table 7. Distances (Å) and angles (°) with e.s.d.'s in parentheses. X = S or Se in an etu or esu group; Y = S or Se in a SCN or SeCN group.[a]

	$\mathrm{Te(etu)_2(SCN)_2}$	$\mathrm{Te(esu)_2(SCN)_2}$	$\mathrm{Te(esu)_2(SeCN)_2}$
Bond lengths			
Te–X(1)	2.515(1)	2.610(1)	2.657(1)
Te–X(2)	2.520(1)	2.607(1)	2.650(1)
Te–Y(1)	2.885(1)	2.979(1)	3.005(1)
Te–Y(2)	2.947(1)	3.025(1)	3.029(1)
X(1)–C(1)	1.728(3)	1.891(4)	1.882(5)
X(2)–C(2)	1.722(3)	1.876(4)	1.866(5)
Y(1)–C(3)	1.641(3)	1.638(4)	1.806(6)
Y(2)–C(4)	1.634(3)	1.640(5)	1.770(6)
C(1)–N(1)	1.306(3)	1.306(5)	1.308(7)
C(1)–N(2)	1.310(3)	1.295(5)	1.293(6)
C(2)–N(3)	1.300(3)	1.300(5)	1.299(6)
C(2)–N(4)	1.316(3)	1.318(5)	1.320(6)
C(3)–N(5)	1.150(4)	1.153(5)	1.138(6)
C(4)–N(6)	1.145(4)	1.139(5)	1.152(7)
N(1)–C(5)	1.455(4)	1.459(6)	1.445(7)
N(2)–C(6)	1.459(4)	1.454(5)	1.442(7)
N(3)–C(7)	1.458(4)	1.447(5)	1.452(7)
N(4)–C(8)	1.456(4)	1.458(6)	1.452(8)
C(5)–C(6)	1.514(5)	1.513(6)	1.512(8)
C(7)–C(8)	1.525(5)	1.538(7)	1.506(9)
Bond angles			
X(1)–Te–X(2)	92.22(3)	92.50(2)	90.98(2)
X(1)–Te–Y(1)	91.59(3)	92.17(3)	93.45(2)
X(1)–Te–Y(2)	174.89(3)	175.95(3)	175.74(2)
X(2)–Te–Y(1)	171.93(3)	171.37(3)	170.84(2)
X(2)–Te–Y(2)	91.24(3)	89.47(3)	91.02(2)
Y(1)–Te–Y(2)	84.52(3)	85.43(4)	84.05(2)
Te–X(1)–C(1)	102.88(9)	100.39(12)	100.08(16)
Te–X(2)–C(2)	106.60(9)	103.54(11)	103.49(15)
Te–Y(1)–C(3)	101.77(10)	101.47(14)	100.40(15)
Te–Y(2)–C(4)	103.37(10)	102.98(14)	101.81(16)
X(1)–C(1)–N(1)	121.3(2)	120.5(3)	121.7(4)
X(1)–C(1)–N(2)	127.5(2)	127.9(3)	128.2(4)
N(1)–C(1)–N(2)	111.2(2)	111.6(4)	110.1(5)
X(2)–C(2)–N(3)	128.1(2)	128.3(3)	128.6(4)
X(2)–C(2)–N(4)	120.6(2)	120.2(3)	121.1(4)
N(3)–C(2)–N(4)	111.2(3)	111.4(4)	110.3(5)
Y(1)–C(3)–N(5)	178.7(3)	178.1(4)	177.8(5)
Y(2)–C(4)–N(6)	178.2(3)	178.4(4)	177.8(5)
C(1)–N(1)–C(5)	111.4(3)	110.8(4)	111.6(5)
C(1)–N(2)–C(6)	111.7(2)	112.3(4)	113.5(5)
C(2)–N(3)–C(7)	112.0(2)	112.2(3)	113.0(5)
C(2)–N(4)–C(8)	111.4(3)	111.0(4)	110.7(5)
N(1)–C(5)–C(6)	103.2(2)	103.4(4)	103.3(5)
N(2)–C(6)–C(5)	102.4(2)	102.0(3)	101.5(4)
N(3)–C(7)–C(8)	102.3(3)	102.2(4)	101.4(5)
N(4)–C(8)–C(7)	102.5(3)	102.2(4)	103.7(5)

[a] For $\mathrm{Te(etu)_2(SCN)_2}$ and $\mathrm{Te(esu)_2(SeCN)_2}$, Y(1) = S(3) or Se(3) of Table 4, Y(2) = S(4) or Se(4).

Table 8. Planes of portions of molecules. X and Y as in Table 7.

Plane (1): TeX(1)X(2) Plane (5): TeY(1)C(3)
(2): TeY(1)Y(2) (6): TeY(2)C(4)
(3): TeX(1)C(1) (7): X(1)C(1)N(1)N(2)
(4): TeX(2)C(2) (8): X(2)C(2)N(3)N(4)

	$Te(etu)_2$–$(SCN)_2$	$Te(esu)_2$–$(SCN)_2$	$Te(esu)_2$–$(SeCN)_2$
Angles (°) between planes			
(1)–(2)	7.8	7.8	8.5
(1)–(3)	57.0	56.0	53.9
(1)–(4)	75.4	78.3	77.5
(2)–(5)	70.5	72.3	71.5
(2)–(6)	40.0	40.7	42.2
(3)–(7)	35.3	31.3	32.3
(4)–(8)	7.1	4.6	5.2
Distances (Å) from least-squares plane TeX_2Y_2			
Te	0.099(1)	0.102(1)	0.113(1)
X(1)	0.014(1)	0.017(1)	0.022(1)
X(2)	−0.068(1)	−0.074(1)	−0.085(1)
Y(1)	−0.061(1)	−0.066(1)	−0.076(1)
Y(2)	0.016(1)	0.021(1)	0.026(1)
Distances (Å) of carbon atoms from thio- or seleno-urea least-squares planes (7) and (8)			
Plane (7)			
C(1)	0.008(3)	0.002(4)	0.015(6)
C(5)	−0.020(4)	−0.010(6)	0.009(7)
C(6)	0.020(3)	0.013(5)	−0.040(6)
Plane (8)			
C(2)	−0.004(3)	−0.006(4)	0.003(6)
C(7)	0.032(4)	0.063(5)	0.041(7)
C(8)	−0.093(4)	−0.106(5)	−0.113(7)

gand relative to the decrease for the incoming ligand. A *trans*-influencing ligand causes a greater lengthening of the *trans*-bond when itself at a smaller distance from Te, and vice versa. When two *trans*-influencing ligands are compared, the same applies for the differences: as the displacement proceeds, the more *trans*-influenced leaving ligand acquires an increasingly larger lead, until the difference reaches a maximum and then vanishes at the non-bonded distance.

The profiles of Fig. 2 viewed from left to right depict the reverse processes, i.e. $L_{tr}\cdots Te–S \rightarrow L_{tr}–Te\cdots S$ relative to $L_{tr}\cdots Te–Se \rightarrow L_{tr}–Te\cdots Se$.

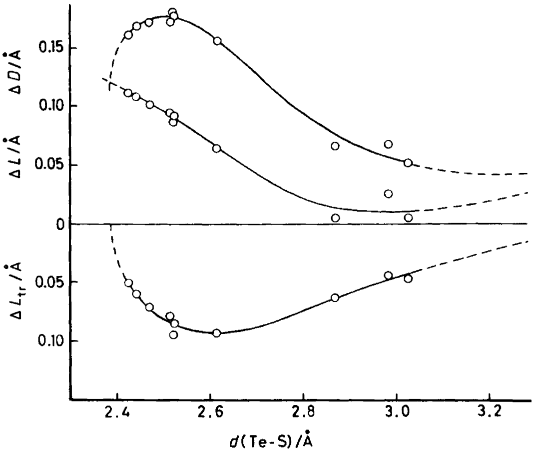

Fig. 2. Difference profiles for the relative *trans*-influence of thio and seleno ligands.

ΔL_{tr} is initially zero but increases: the approach of L_{tr} is easier when *trans* to S than when *trans* to Se. ΔL decreases, i.e. the thio ligand leaves more easily. Thus, in the initial stages, $L_{tr}\cdots Te$ bond making is further advanced for $L_{tr}\cdots Te–S$ than for $L_{tr}\cdots Te–Se$, and Te–S bond breaking is further advanced than Te–Se bond breaking, although to a smaller degree since ΔD increases.

Table 9. Bond lengths (Å) and angles (°) in isomorphous pairs of tellurium(II) complexes.[a]

Pair	Complex	Te–L	Te–L_{tr}	L–Te–L_{tr}	$10^3\Delta L$	$10^3\Delta L_{tr}$	$10^3\Delta D$	Ref.
(1)	$\mathrm{Te_2(tmtu)_2Cl_4}$	2.425(1)	3.217(2)	171.64(4)	112	50	162	14
	$\mathrm{Te_2(tmsu)_2Cl_4}$	2.537(1)	3.267(1)	172.00(1)				
(2)	$\mathrm{Te_2(tmtu)_2Br_4}$	2.441(2)	3.284(1)	173.18(4)	109	59	168	14
	$\mathrm{Te_2(tmsu)_2Br_4}$	2.550(1)	3.343(1)	173.29(2)				
(3)	$\mathrm{Te_2(tmtu)_2I_4}$	2.473(2)	3.360(1)	175.19(4)	102	71	173	14
	$\mathrm{Te_2(tmsu)_2I_4}$	2.575(1)	3.431(1)	174.89(1)				
(4)	*cis*–$\mathrm{Te(etu)_2(SCN)_2}$	2.515(1)	2.947(1)	174.89(3)				This work
		2.520(1)	2.885(1)	171.93(3)	95	78	173	
	cis–$\mathrm{Te(esu)_2(SCN)_2}$	2.610(1)	3.025(1)	175.95(3)	87	94	181	
		2.607(1)	2.979(1)	171.37(3)				
(5)	PhTe(etu)Br	2.523(2)	2.969(1)	175.96(3)	93	85	178	15
	PhTe(esu)Br	2.616(2)	3.054(2)	175.62(3)				12
(6)	PhTe(etu)I	2.614(2)	3.003(1)	175.88(4)	65	92	157	13
	PhTe(esu)I	2.679(2)	3.095(1)	177.31(2)				
(7)	*cis*–$\mathrm{Te(trtu)_2(SCN)_2}$	2.867(1)	2.530(1)	173.62(4)	5	62	67	This work
	cis–$\mathrm{Te(trtu)_2(SeCN)_2}$	2.872(1)	2.592(1)	175.29(4)				
(8)	*cis*–$\mathrm{Te(esu)_2(SCN)_2}$	2.979(1)	2.607(1)	171.37(3)				This work
		3.025(1)	2.610(1)	175.95(3)	26	43	69	
	cis–$\mathrm{Te(esu)_2(SeCN)_2}$	3.005(1)	2.650(1)	170.84(2)	4	47	51	
		3.029(1)	2.657(1)	175.74(2)				

[a] L = thio or seleno ligand, Te–L = Te–S or Te–Se; L_{tr} = *trans*-ligand; ΔL, ΔL_{tr} and ΔD: see text.

References

1. Åse, K., Bøyum, K., Foss, O. and Marøy, K. *Acta Chem. Scand. 25* (1971) 2457.
2. Åse, K., Foss, O. and Roti, I. *Acta Chem. Scand. 25* (1971) 3808.
3. Foss, O., Maartmann-Moe, K. and Marøy, K. *Acta Chem. Scand., Ser. A 40* (1986) 685.
4. Hauge, S. and Tysseland, M. *Acta Chem. Scand. 25* (1971) 3072.
5. Klayman, D.L. and Shine, R.J. *J. Chem. Soc., Chem. Commun.* (1968) 372; *J. Org. Chem. 34* (1969) 3549; Klayman, D.L. and Griffin, T.S. *J. Am. Chem. Soc. 95* (1973) 197.
6. Foss, O. and Hauge, S. *Acta Chem. Scand. 13* (1959) 1252; *15* (1961) 1615.
7. Foss, O. and Fossen, S. *Acta Chem. Scand. 15* (1961) 1618.
8. Foss, O. and Marøy, K. *Acta Chem. Scand. 15* (1961) 1945.
9. Cromer, D.T. and Waber, J.T. *International Tables for X-Ray Crystallography,* Kynoch Press, Birmingham 1974, Vol. 4, Table 2.2B; Cromer, D.T. *Ibid.* Table 2.3.1.
10. Ueki, T., Zalkin, A. and Templeton, D.H. *Acta Crystallogr. 20* (1966) 836; Cruickshank, D.W.J. and McDonald, W.S. *Ibid. 23* (1967) 9.
11. Foss, O. and Maartmann-Moe, K. *Acta Chem. Scand., Ser. A 40* (1986) 675.
12. Vikane, O. *Acta Chem. Scand., Ser. A 29* (1975) 763.
13. Vikane, O. *Acta Chem. Scand., Ser. A 29* (1975) 787.
14. Eide, J., Foss, O., Maartmann-Moe, K., Maberg, O. and Scheie, A. *Acta Chem. Scand., Ser. A 41* (1987) 67.
15. Vikane, O. *Acta Chem. Scand., Ser. A 29* (1975) 738.

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