Crystal Structures of Three Tellurium(II)-Selenourea (su) Complexes: $Te(su)_2Cl_2$, $Te(su)_2Br_2$ and $[Te_2(su)_6](SCN)_4$

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Foss, O. and Maartmann-Moe, K., 1987. Crystal Structures of Three Tellurium(II)-Selenourea (su) Complexes: $Te(su)_2Cl_2$, $Te(su)_2Br_2$ and $[Te_2(su)_6](SCN)_4$. – Acta Chem. Scand., Ser. A 41: 321–327.

The crystal structures of the complexes $(Te(su)_2Cl_2$ (**1**), $Te(su)_2Br_2$ (**2**) and $[Te_2(su)_6](SCN)_4$ (**3**) (su = selenourea) have been determined by X-ray methods and refined to R 0.037 (**1**), 0.031 (**2**) and 0.032 (**3**) for 2155, 2265 and 3425 observed reflections, respectively. The crystals are triclinic, space group $P\bar{1}$ (No. 2), with $Z = 2$ for **1** and **2**, and $Z = 1$ for **3**. Those of **1** and **2** are isomorphous and contain $Te(su)_2^{2+}$ units with Se–Te–Se 97.63(2)° (**1**) and 97.60(2)° (**2**), and Te–Se 2.530(1) – 2.540(1) Å. One X^- coordinates to Te *trans* to Se(2) at Te–Cl 3.196(1), Te–Br 3.289(1) Å, and, more weakly and less linearly, to a symmetry centre-related Te *trans* to Se(1) at Te–Cl 3.476(1), Te–Br 3.617(1) Å. The second X^-, in essentially planar, centrosymmetric $C(Te)Se(\mu\text{–}X)_2$ $Se(Te)C$ arrangements, coordinates to Se(1) *trans* to C and Te at Se–Cl 3.446(1) and 3.360(1), Se–Br 3.534(1) and 3.443(1) Å, respectively. The $[Te_2(su)_6]^{4+}$ cations of **3** contain essentially planar, centrosymmetric $Se_2Te(\mu\text{–}Se)_2TeSe_2$ groups. In the Se–Te–Se systems of the $TeSe_4$ moiety, Te–Se = 2.605(1), 3.141(1) Å with Se–Te–Se 176.33(1)°, and 2.651(1), 3.005(1) Å with Se–Te–Se 175.28(1)°, the longer bonds being the bridging ones. The anions of **3** form nearly linear $[NCS\cdots SCN]^{2-}$ dimers, with $S\cdots S$ 3.368(2) Å.

The complexes $Te(su)_2Cl_2$ (**1**) and $Te(su)_2Br_2$ (**2**) (su = selenourea) were prepared by Hauge and Tysseland.[1] X-ray photographs indicated that the crystals were triclinic[2] and not isomorphous with those of the thiourea (tu) analogues, $Te(tu)_2X_2$ (X = Cl, Br or I). The latter contain square-planar *cis*–TeS_2X_2 coordination groups.[3,4] In the course of studies of the relative *trans*-influence of ligands in tellurium(II) complexes,[4–7] we determined the crystal structures of complexes **1** and **2**. Coordination at selenium(II) as well as tellurium(II) was found to occur.

In samples of yellow $Te(su)_2(SCN)_2$ prepared from $Te(su)_2Cl_2$ and aqueous NH_4SCN,[6] red crystals were sometimes observed. One such crystal was subjected to X-ray analysis, and proved to be dinuclear $[Te_2(su)_6](SCN)_4$ (**3**), the first reported salt of the $[Te_2(su)_6]^{4+}$ ion. The thiourea analogue, $[Te_2(tu)_6](HF_2)_4$, was the first salt of a dinuclear tellurium(II) complex ion to be structurally characterized,[8] and the structures of $[Te_2(etu)_6](ClO_4)_4$ (etu = ethylenethiourea)[9] and $[Te_2(trtu)_6](ClO_4)_4$ (trtu = trimethylenethiourea) (two crystalline forms)[10] have later been determined.[11] The refined structure of $[Te_2(tu)_6](HF_2)_4$ at 133 K was reported recently.[12]

We report here the structures of complexes **1** – **3**.

Experimental

The samples of complexes **1** and **2** were a gift from Dr. S. Hauge. The crystals were brownish-yellow prisms extended along the *a* axis. A red crystal of **3** was picked out from among a majority of yellow $Te(su)_2(SCN)_2$.

X-ray measurements were made on a CAD4 diffractometer using graphite-monochromated Mo$K\alpha$ radiation (λ = 0.70169 Å). Unit cell dimensions were determined from the setting angles of 22–25 automatically centred reflections. Intensities were recorded by $\omega/2\theta$ scan for complexes **1** and **2** and ω scan for **3**. The scan width was 1.00 + 0.35 tan θ, plus 25 % on each side for

background, the scan rate was 1.68–0.39° min^{-1}, and θ_{max} was 28°. The intensities were corrected for Lorentz and polarization effects, decay, and absorption. Max. decay corrections, based on the intensities of three reference reflections measured every 2 h of exposure time, were 3.0–3.8%. 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. Scattering factors, refinements and weights were as in Ref. 13. Anisotropic thermal parameters were used for non-hydrogen atoms. Hydrogens were placed geometrically, at N–H 0.87 Å, and were kept fixed, with a common fixed B_{iso} for each structure.

Crystal data are given in Table 1. The structures of complexes **2** and **3** were solved by direct (MULTAN) and Fourier difference methods, and the refined coordinates of **2** were used as starting coordinates for the refinement of **1**. The cell volume of complex **3** compared to that of $Te(su)_2(SCN)_2$,[6] and its formation along with the latter substance, indicated that the red crystals might be $[Te_2(su)_6](SCN)_4$. This was assumed to be the cell content, and the *E* map gave the positions of Te and the three Se atoms. The shifts in the last refinement cycles were less than one per cent of the associated standard deviations. Atomic coordinates for non-hydrogen atoms are listed in Tables 2 and 3. Thermal parameters, hydrogen coordinates, torsion angles and planes have been deposited with the Cambridge Crystallographic Data Centre.

Results and discussion

Dimensional data are given in Tables 4–6, and views of the $Te(su)_2X_2$ structure and the $[Te_2(su)_6]^{4+}$ ion are shown in Figs. 1 and 2.

Complexes **1** *and* **2**, *Te(su)*$_2$*X*$_2$. The su ligands coordinate to tellurium(II) in *cis* positions, forming $[(H_2N)_2C\text{–}Se\text{–}Te\text{–}Se\text{–}C(NH_2)_2]^{2+}$ units with Se–Te–Se angle 97.6(1)° and Te–Se bond lengths

Table 1. Crystallographic data[a].

	1	**2**	**3**
Complex	$Te(su)_2Cl_2$	$Te(su)_2Br_2$	$[Te_2(su)_6](SCN)_4$
Formula	$C_2H_8Cl_2N_4Se_2Te$	$C_2H_8Br_2N_4Se_2Te$	$C_{10}H_{24}N_{16}S_4Se_6Te_2$
M	444.54	533.45	1225.63
a/Å	6.212(1)	6.406(1)	8.320(1)
b/Å	8.219(1)	8.164(1)	9.499(1)
c/Å	11.615(1)	11.933(1)	11.350(1)
α/°	69.99(1)	71.40(1)	106.81(1)
β/°	75.46(1)	77.12(1)	90.60(1)
γ/°	82.85(1)	83.16(1)	96.89(1)
V/Å^3	538.9(2)	575.9(2)	851.5(3)
Z	2	2	1
D_x/g cm^{-3}	2.739	3.076	2.390
F(000)	404	476	568
μ(Mo*K*α)/cm^{-1}	105.69	167.87	89.44
Crystal volume/mm^3	0.0008	0.0024	0.0056
Transmission factors	0.408–0.752	0.096–0.502	0.202–0.436
Unique reflections	2595	2779	4094
Reflections $I > 2\sigma$	2155	2265	3425
No. of variables	100	101	173
Extinction coefficient, $g \times 10^7$		1.69	7.59
R	0.037	0.031	0.032
R_w	0.048	0.036	0.040
S	2.596	2.077	2.227
Max. Δ(ϱ)/e Å^{-3}	1.38	2.04	1.07

[a]In each case: Crystal system triclinic, space group $P\bar{1}$ (No. 2).

Table 2. Fractional atomic coordinates for $Te(su)_2X_2$ with e.s.d.'s in parentheses.

Atom	*x*	*y*	*z*	B_{eq}/Å^2
$Te(su)_2Cl_2$				
Te	0.19593(7)	−0.09811(5)	0.13597(4)	2.693(9)
Se(1)	−0.03022(10)	0.01760(8)	0.31156(5)	2.28(1)
Se(2)	0.04222(11)	−0.39789(9)	0.22677(6)	2.94(1)
Cl(1)	0.34670(26)	0.29342(22)	0.01331(14)	2.88(3)
Cl(2)	0.33149(26)	−0.22554(23)	0.49328(14)	3.12(3)
N(1)	−0.1846(9)	0.2831(8)	0.1197(5)	3.0(1)
N(2)	−0.4546(9)	0.1046(8)	0.2619(5)	3.2(1)
N(3)	0.4598(9)	−0.4838(8)	0.2906(5)	3.2(1)
N(4)	0.1763(9)	−0.6498(9)	0.4283(6)	3.7(1)
C(1)	−0.2496(10)	0.1496(8)	0.2195(5)	2.3(1)
C(2)	0.2526(10)	−0.5206(8)	0.3258(5)	2.5(1)
$Te(su)_2Br_2$				
Te	0.17817(6)	−0.10796(5)	0.14362(3)	2.636(7)
Br(1)	0.33910(9)	0.28736(7)	0.00763(5)	2.96(1)
Br(2)	0.32680(8)	−0.22126(8)	0.49188(5)	2.99(1)
Se(1)	−0.03515(8)	0.01660(7)	0.30708(4)	2.38(1)
Se(2)	0.03706(9)	−0.40990(7)	0.23096(5)	3.00(1)
N(1)	−0.1947(7)	0.2751(6)	0.1219(4)	3.2(1)
N(2)	−0.4469(7)	0.0986(7)	0.2569(4)	3.3(1)
N(3)	0.4457(7)	−0.4865(6)	0.2919(4)	3.1(1)
N(4)	0.1822(8)	−0.6504(7)	0.4238(5)	3.9(1)
C(1)	−0.2504(8)	0.1439(6)	0.2173(5)	2.3(1)
C(2)	0.2475(8)	−0.5255(7)	0.3265(5)	2.4(1)

Table 3. Fractional atomic coordinates for $[Te_2(su)_6](SCN)_4$ with e.s.d.'s in parentheses.

Atom	*x*	*y*	*z*	B_{eq}/Å^2
Te	0.06860(3)	0.12257(3)	0.19278(2)	2.477(5)
Se(1)	−0.09500(6)	0.23492(6)	0.38426(4)	3.64(1)
Se(2)	0.35849(5)	0.20820(5)	0.30771(4)	3.00(1)
Se(3)	−0.24733(5)	0.02936(5)	0.04388(4)	2.86(1)
S(1)	−0.22079(19)	−0.29022(18)	0.13523(18)	5.87(4)
S(2)	0.31770(23)	0.48720(20)	0.16012(19)	6.31(5)
N(1)	−0.0535(6)	0.4730(5)	0.2836(5)	6.5(1)
N(2)	−0.2527(6)	0.4787(5)	0.4193(5)	5.6(1)
N(3)	0.2953(5)	−0.0250(5)	0.4135(4)	4.7(1)
N(4)	0.5004(5)	−0.0470(5)	0.2838(4)	4.7(1)
N(5)	−0.1604(5)	0.2737(5)	−0.0431(4)	5.0(1)
N(6)	−0.3990(5)	0.2735(5)	0.0463(5)	5.8(1)
N(7)	−0.1330(8)	−0.1573(8)	0.3807(5)	9.0(2)
N(8)	0.4319(5)	0.6625(4)	0.3947(3)	3.0(1)
C(1)	−0.1369(6)	0.4145(5)	0.3569(5)	3.7(1)
C(2)	0.3859(5)	0.0258(5)	0.3398(4)	2.8(1)
C(3)	−0.2693(5)	0.2113(5)	0.0119(4)	3.2(1)
C(4)	−0.1683(7)	−0.2090(6)	0.2808(6)	6.0(1)
C(5)	0.3757(7)	0.6000(6)	0.3021(6)	6.7(1)

Table 4. Distances (Å) and angles (°) in $Te(su)_2X_2$ with e.s.d.'s in parentheses. Primed and double-primed atoms related to unprimed ones over symmetry centre in $\frac{1}{2},0,0$ and $0,0,\frac{1}{2}$, respectively.

	X = Cl	X = Br
Bond lengths		
Te–Se(1)	2.535(1)	2.540(1)
Te–Se(2)	2.530(1)	2.540(1)
Te–X(1)	3.196(1)	3.289(1)
Te–X(1′)	3.476(1)	3.617(1)
Se(1)–X(2)	3.446(1)	3.534(1)
Se(1)–X(2″)	3.360(1)	3.443(1)
Se(1)–C(1)	1.936(4)	1.933(4)
Se(2)–C(2)	1.919(4)	1.925(4)
C(1)–N(1)	1.309(5)	1.305(4)
C(1)–N(2)	1.296(5)	1.296(5)
C(2)–N(3)	1.290(5)	1.289(5)
C(2)–N(4)	1.321(5)	1.301(5)
Bond angles		
Se(1)–Te–Se(2)	97.63(2)	97.60(2)
Se(1)–Te–X(1)	82.39(2)	84.97(1)
Se(1)–Te–X(1′)	156.34(2)	153.53(1)
Se(2)–Te–X(1)	173.70(2)	174.35(2)
Se(2)–Te–X(1′)	84.44(2)	88.77(1)
X(1)–Te–X(1′)	98.09(3)	91.13(1)
Te–Se(1)–X(2)	86.57(2)	87.43(1)
Te–Se(1)–X(2″)	171.81(2)	174.72(2)
Te–Se(1)–C(1)	96.40(12)	96.34(11)
X(2)–Se(1)–X(2″)	99.56(3)	96.52(1)
X(2)–Se(1)–C(1)	176.13(11)	175.51(11)
X(2″)–Se(1)–C(1)	77.74(12)	79.86(11)
Te–Se(2)–C(2)	100.19(12)	100.31(11)
Te–X(1)–Te′	81.91(3)	88.87(1)
Se(1)–X(2)–Se(1″)	80.44(3)	83.48(1)
Se(1)–C(1)–N(1)	118.3(3)	119.2(3)
Se(1)–C(1)–N(2)	118.3(3)	118.3(3)
N(1)–C(1)–N(2)	123.3(4)	122.4(4)
Se(2)–C(2)–N(3)	121.4(3)	121.2(3)
Se(2)–C(2)–N(4)	116.5(3)	116.7(3)
N(3)–C(2)–N(4)	122.0(4)	121.9(4)

2.530(1) – 2.540(1) Å. These are close to single-bond length; the sum of the Pauling single-bond radii is 2.54 Å,[14] but in $Te[Se(S)PEt_2]_2$, Te–Se 2.501(3) Å was observed.[15] The C–Se–Te–Se–C sequences are *trans*-rotameric with torsion angles 100.8 and 91.4° in complex **1** and 101.7 and 91.5° in **2**. The sequences are very similar to that in *cis*-$Te(su)_2(SCN)_2$, which is of C_2 symmetry: Se–Te–Se 96.2(1)°, Te–Se 2.536(1) Å, torsion angles 90.9°.[6]

The thiourea analogues $Te(tu)_2X_2$, referred to earlier,[3,4] contain *cis*-TeS_2X_2 coordination groups of C_2 symmetry; the groups are slightly tetrahedrally distorted but essentially planar. The Te–X bond lengths and S–Te–X angles for *trans*-positioned ligands are 2.936(1) Å and 172.50(2)° for X = Cl, and 3.038(1) Å and 171.73(2)° for X = Br. In $Te(su)_2X_2$, all atoms lie in general positions. Only one X^- coordinates to Te, and only one Se–Te–X system is equally linear: Te–X and Se–Te–X 3.196(1) Å and 173.70(2)° for X = Cl, and 3.289(1) Å and 174.35(2)° for X = Br. The longer Te–X bounds in $Te(su)_2X_2$ illustrate the greater *trans*-influence of su relative to tu.[6] This X^-, labelled X(1), occurs *trans* to Se(2), and Te–Se(2) is slightly longer, by 0.010(1) Å, for X = Br than for X = Cl; at these Te–X distances, the *trans*-influence of Br is slightly greater than that of Cl.[7] The $TeSe_2X(1)$ fragments lie close to a symmetry centre, at $\frac{1}{2},0,0$, and loosely held Se_2Te

Table 5. Planes for the $Te(su)_2X_2$ structures. Primed and double-primed atoms as in Table 4.

Plane (1): TeSe(1)Se(2)
(2): TeX(1)X(1′)
(3): Se(1)X(2)X(2″)
(4): TeSe(1)C(1)
(5): TeSe(2)C(2)
(6): Se(1)C(1)N(1)N(2)[a]
(7): Se(2)C(2)N(3)N(4)[a]

		X = Cl	X = Br
Angles (°) between planes			
(1)–(2)		23.8	26.2
(1)–(4)		79.2	78.3
(1)–(5)		88.6	88.5
(3)–(4)		5.9	4.2
(4)–(6)		65.1	65.7
(5)–(7)		33.3	32.8
Distances (Å) from planes			
Plane	Atom		
(1)	X(1)	0.351(2)	0.289(1)
	X(1′)	−1.392(2)	−1.573(1)
(3)	Te	0.241(1)	0.155(1)
	C(1)	−0.093(6)	−0.089(5)
(6)	C(1)	0.012(6)	0.012(5)
(7)	C(2)	−0.018(7)	−0.019(5)

[a]Least-squares plane.

Table 6. Distances (Å) and angles (°) in $[Te_2(su)_6](SCN)_4$ with e.s.d.'s in parentheses. Primed atoms related to unprimed ones over symmetry centre in 0,0,0.

Bond lengths			
Te–Se(1)	2.605(1)	C(1)–N(1)	1.292(5)
Te–Se(2)	2.651(1)	C(1)–N(2)	1.307(4)
Te–Se(3)	3.005(1)	C(2)–N(3)	1.288(4)
Te–Se(3′)	3.141(1)	C(2)–N(4)	1.307(4)
Se(1)–C(1)	1.891(4)	C(3)–N(5)	1.287(4)
Se(2)–C(2)	1.910(3)	C(3)–N(6)	1.302(4)
Se(3)–C(3)	1.895(3)	C(4)–N(7)	1.118(7)
S(1)–C(4)	1.637(7)	C(5)–N(8)	1.112(7)
S(2)–C(5)	1.685(7)		
Bond angles			
Se(1)–Te–Se(2)	95.87(1)	Se(1)–C(1)–N(1)	122.3(3)
Se(1)–Te–Se(3)	88.05(1)	Se(1)–C(1)–N(2)	116.0(3)
Se(1)–Te–Se(3′)	176.33(1)	N(1)–C(1)–N(2)	121.7(4)
Se(2)–Te–Se(3)	175.28(1)	Se(2)–C(2)–N(3)	121.8(3)
Se(2)–Te–Se(3′)	87.21(1)	Se(2)–C(2)–N(4)	117.5(2)
Se(3)–Te–Se(3′)	88.97(1)	N(3)–C(2)–N(4)	120.7(3)
Te–Se(1)–C(1)	101.36(11)	Se(3)–C(3)–N(5)	121.8(3)
Te–Se(2)–C(2)	97.39(9)	Se(3)–C(3)–N(6)	118.5(3)
Te–Se(3)–Te′	91.03(1)	N(5)–C(3)–N(6)	119.7(3)
Te–Se(3)–C(3)	98.36(10)	S(1)–C(4)–N(7)	178.1(5)
Te′–Se(3)–C(3)	99–08(10)	S(2)–C(5)–N(8)	169.9(4)

Angles between planes[a]

(1)–(2)	3.3				
(1)–(3)	80.9	(3)–(6)	18.3	(6)–(7)	1.3
(1)–(4)	82.5	(4)–(7)	66.3	(6)–(8)	13.9
(2)–(5)	80.7	(5)–(8)	57.5	(7)–(8)	12.9

[a]Plane (1): TeSe(1)Se(2); plane (2): TeSe(3)Se(3′); plane (3): TeSe(1)C(1); plane (4): TeSe(2)C(2); plane (5): TeSe(3)C(3); plane (6): Se(1)C(1)N(1)N(2); plane (7): Se(2)C(2)N(3)N(4); plane (8): Se(3)C(3)N(5)N(6). The atoms defining least-squares planes (6)–(8) lie in the planes within error limits.

$(\mu\text{-X})_2TeSe_2$ dimers result: the symmetry-related X(1), labelled X(1′), coordinates weakly only to Te, at longer Te–X distances and with Se(1)–Te–X(1′) angles which deviate ca. 25° from linearity (see Table 4 and the planes of Table 5).

The X^- labelled X(2), and X(2″) related to X(2) through the symmetry centre at $0,0,\frac{1}{2}$, coordinate not to Te but to Se(1), *trans* to C(1) and Te, respectively. Dimeric, essentially planar C(Te)Se$(\mu\text{-X})_2$Se(Te)C groups result, with C–Se–X and Te–Se–X three-centre systems which are close to linear. The Se–X bridges are rather long: Se–Cl 3.446(1) and 3.360(1) Å, and Se–Br 3.534(1) and 3.443(1) Å, *trans* to C and Te, respectively; the averages are ca. 0.40 Å shorter than the sums of the Se van der Waals radius and the ionic radii of Cl or Br.[14] In *cis*-Se(tu)$_2$X$_2$[16] the Se–X bonds are shorter, by ca. 0.20 Å, but in these complexes the bonds are terminal and not bridging, and the *trans*-influence exerted on Se–X is, presumably, weaker. In complexes of tellurium dihalides with ethyleneselenourea (esu)[7] and tetramethylselenourea (tmsu),[5] similar close approaches of X to Se *trans* to C occur, but not *trans* to Te; the closest approaches are Se–Cl 3.494(1) Å in $[Te_2(esu)_4Cl_2]Cl_2$ and Se–Br 3.501(1) Å in $[Te_2(esu)_2Br_2]Br_2$(mon.).[7]

The Te–Se(1) bond interconnecting the Te and Se(1) coordination groups forms part of a distorted linear four-centre system, X(1′)–Te–Se(1)–X(2″). The dimeric Te– and Se(1)-coordinated groups alternate in the crystals along the

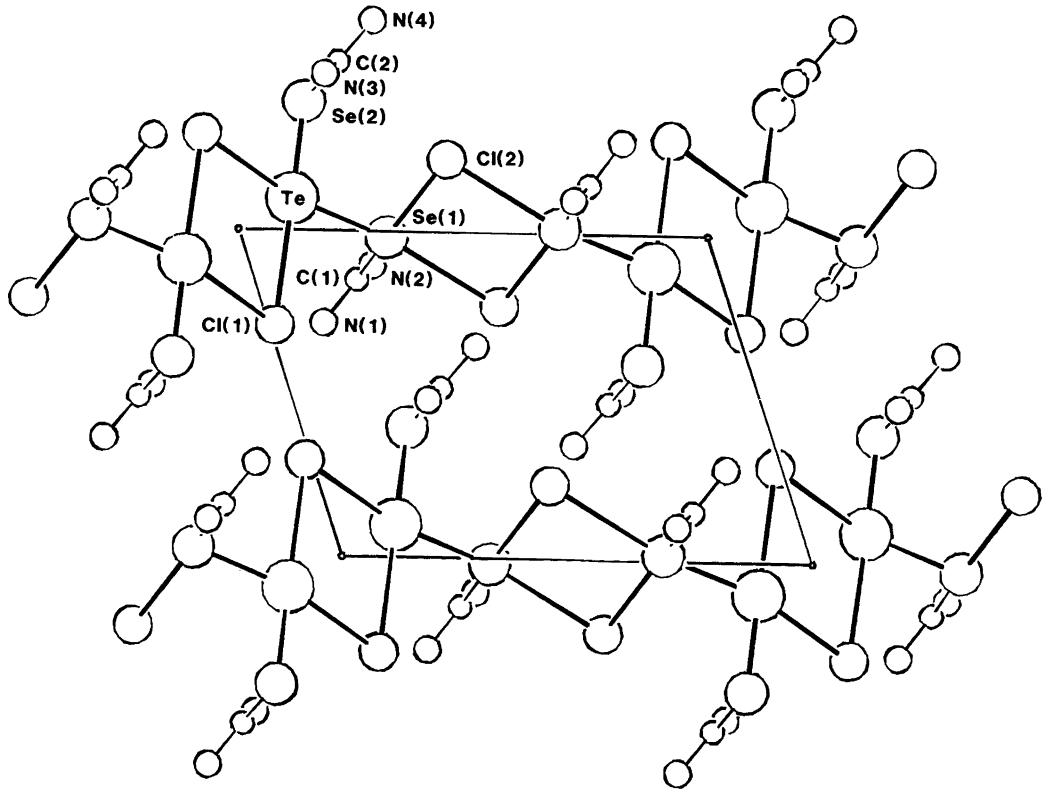

Fig. 1. The $Te(su)_2X_2$ structure for X = Cl, as seen along the *a* axis. Parts of two of the infinite, parallel chains are shown. The unit cell is outlined; origin upper left, *c* horisontal.

line through the symmetry centres at $\frac{1}{2},0,0$ and $0,0,\frac{1}{2}$.

Complex **3**, *$[Te_2(su)_6](SCN)_4$*. The $[Te_2(su)_6]^{4+}$ ion consists of two $Te(su)_2^{2+}$ units bridged by the Se atoms of two su molecules. The centre of symmetry at 0,0,0 relates the two halves. The Se_2Te $(\mu\text{-}Se)_2TeSe_2$ coordination group is essentially planar; the terminal atoms Se(1) and Se(2) lie −0.098(1) and 0.127(1) Å, respectively, from the exact plane of the four central atoms. In the $TeSe_4$ groups, the bridging Te–Se bonds, at 3.005(1) and 3.141(1) Å, are longer than the terminal, *trans*-positioned bonds, which are 2.651(1) and 2.605(1) Å, respectively. In the centrosymmetric $TeSe_4$ group of $[Te(su)_4]Cl_2$, Te–Se = 2.814 (3) and 2.809(4) Å.[1] In the asymmetric Se–Te–Se systems of *cis*-$Te(esu)_2(SeCN)_2$,[6] the bond lengths, 2.657(1) and 3.029(1) Å, and 2.650(1) and 3.005(1) Å, are very similar to those in the present structure.

In the terminal $Te(su)_2^{2+}$ units the C–Se–Te–Se–C sequence is *trans*-rotameric as in $Te(su)_2X_2$; the torsion angles are 99.1 and 97.5°. The $-C(NH_2)_2$ parts of the three su groups on one side of the Te ··· Te line lie above the coordination plane, and the parts of the other three su groups lie below the plane (see Fig. 2). The su groups are nearly parallel, the angles between the $SeCN_2$ planes being 1.3–13.9°. The conformation is the same as for the $[Te_2(tu)_6]^{4+}$ ion in the HF_2^- salt.[8,12]

One of the SCN^- ions is distinctly non-linear: S(2)–C(5)–N(8) = 169.9(4)°. The closest approaches of S to Te or Se atoms are Te ··· S(2) 3.933(1), Se(2) ··· S(2) 3.566(1) and Se(3) ··· S(1) 3.509(1) Å. A short approach occurs between SCN^- ions: S(1) ··· S(2′) = 3.368(2) Å, where

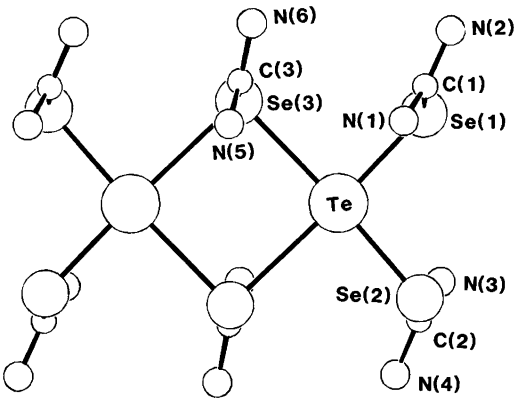

Fig. 2. The $[Te_2(su)_6]^{4+}$ ion in the thiocyanate salt.

S(2′) is related to S(2) over the symmetry centre at 0,0,0. The C(4)–S(1)···S(2′) and S(1)···S(2′)–C(5′) angles are 174.5(2) and 173.6(2)°, respectively, so that the $[NCS\cdots SCN]^{2-}$ units are essentially linear. A similar S···S approach, 3.361(2) Å at C–S···S 155.4(1)°, occurs between Te–bonded SCN groups in *trans*–$Te(tmtu)_2(SCN)_2$ (tmtu = tetramethylthiourea).[17] From a survey of structural data on crystals containing thiocarbonyl groups, Nyburg and Faerman[18] conclude that the van der Waals shape of sulfur is not spherical; the van der Waals radius of sulfur is shorter at the front of the groups, as short as 1.60 Å along the carbon-to-sulfur bond vector. However, the linearity of the approaches for the thiocyanate and thiocarbonyl groups may indicate incipient multi-centre bonding interactions, rather than van der Waals forces.

The S atoms of the SCN^- ions lie rather close to su Se atoms: S(1)···Se(3) 3.509(1) and S(2)···Se(2) 3.566(1) Å, at angles of 173.9(1) and 163.7(1)°, respectively, with the directions of the Se–C bonds.

The selenourea groups. In crystals of selenourea itself, Se–C = 1.86(3) Å.[19] More accurate data are available for the molecule in solvates: Se–C 1.867(4) Å in $[(su)_3]SO_4\cdot su\cdot 2H_2O$,[20] and 1.853(5) Å in $[Co(acac)_3]\cdot 2su$;[21] the mean value is 1.862(5) Å. In the present complexes and in *cis*-$Te(su)_2(SCN)_2$,[6] Se–C = 1.891(4) – 1.936(4) Å, and the bond thus lengthens on complexation, as does the tmsu Se–C bond.[4,5]

For thiourea in tellurium(II) complexes, the Te–S–C bond angle tends to decrease with increasing TeS/SCN_2 dihedral angle (thiourea twist angle). The S–C bond length, besides increasing with decreasing Te–S bond length, tends to increase with increasing twist angle.[13] The data for selenourea, although sparse, indicate qualitatively similar trends.

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Received December 30, 1986.