Dinuclear, Square-Planar Complexes of Tellurium Dichloride, Dibromide and Diiodide with Ethyleneselenourea, $[Te_2L_4X_2]X_2$. Crystal Structures of Di-Se-Bridged (X = Cl or Br) and Di-X-Bridged (X = Br or I) Isomers. Relative *trans*-Influence of Cl, Br and I

Olav Foss,* Randi Hermansen, Kjartan Marøy and Tore Moberg

Department of Chemistry, University of Bergen, N-5000 Bergen, Norway

Foss, O., Hermansen, R., Marøy, K. and Moberg, T., 1987. Dinuclear, Square-Planar Complexes of Tellurium Dichloride, Dibromide and Diiodide with Ethyleneselenourea, $[Te_2L_4X_2]X_2$. Crystal Structures of Di-Se-Bridged (X = Cl or Br) and Di-X-Bridged (X = Br or I) Isomers. Relative *trans*-Influence of Cl, Br and I. – Acta Chem. Scand., Ser. A 41: 130–138.

The complexes $[Te_2(esu)_4Cl_2]Cl_2$ (**1**), $[Te_2(esu)_4Br_2]Br_2$ (three forms: **2**, **3** and **4**) and $[Te_2(esu)_4I_2]I_2$ (**5**) (esu = ethyleneselenourea) have been prepared and their crystal structures determined by X-ray methods. Complexes **1** and **2** form isomorphous triclinic crystals, space group $P\bar{1}$ (No. 2) with $Z = 1$; complex **3** is monoclinic, space group $C2c$ (No. 15) with $Z = 4$; complexes **4** and **5** form isomorphous orthorhombic crystals, space group $Fddd$ (No. 70) with $Z = 8$. The crystals contain dinuclear $[Te_2(esu)_4X_2]^{2+}$ cations with planar coordination groups, which are di-Se-bridged in **1** and **2** and di-X-bridged in **3**–**5**. In the Se–Te–X sequence of the $TeSe_3X$ groups of **1** and **2**, bond lengths and angles are Te–Se 2.664(1) and 2.648(1), Te–X 2.701(1) and 2.855(1) Å, and Se–Te–X 175.57(3) and 174.76(4)°, for X = Cl and Br, respectively. In the *cis*-$TeSe_2X_2$ groups of **4** and **5**, bond lengths and angles are Te–Se 2.582(1) and 2.618(1), Te–X 3.086(1) and 3.251(1) Å, and Se–Te–X 173.99(4) and 173.47(3)°, for X = Br and I, respectively. The relative *trans*-influence of Cl, Br and I in tellurium(II) complexes is compared for isomorphous pairs in which the *trans*-ligand is the same for the two members of each pair, over bond length ranges Te–Cl 2.701(1)–3.267(1), Te–Br 2.855(1)–3.343(1) and Te–I 3.162(1)–3.431(1). Å. Iodide has the largest *trans*-influence. For Cl and Br, a reversal appears to occur at bond lengths Te–Cl 2.75 and Te–Br 2.90 Å, Br having the greater *trans*-influence for longer Te–Cl and Te–Br distances and Cl the greater *trans*-influence for shorter distances.

We report here the preparation and crystal structures of the tellurium(II) complexes $[Te_2(esu)_4X_2]X_2$ (esu = ethyleneselenourea, X = Cl, Br or I). The spontaneously crystallizing form was triclinic for X = Cl, monoclinic for X = Br, and orthorhombic for X = I. The latter two are isomorphous with the monoclinic and orthorhombic forms of di-Br-bridged $[Te_2(etu)_4Br_2]Br_2$ (etu = ethylenethiourea).[1,2] On seeding with crystals of the chloro or iodo complex, the triclinic and orthorhombic forms of $[Te_2(esu)_4Br_2]Br_2$ were also obtained. In the triclinic crystals, the bridging atoms are Se instead of Cl or Br.

*To whom correspondence should be addressed.

Experimental

Preparations. The esu, prepared from etu by the method of Klayman and co-workers,[3] was a gift from Dr. O. Vikane. The HCl, HBr and HI used were ca. 37, 48 and 57 % (*w/w*), respectively.

The complex $[Te_2(esu)_4Cl_2]Cl_2$. To TeO_2 (0.40 g, 2.5 mmol) dissolved with heating in HCl (5 cm^3)

was added, with swirling, a solution of esu (1.49 g, 10 mmol) in dimethylformamide (DMF) (20 cm^3). The clear, orange-red mixture was warmed, and warm methanol (20 cm^3) was added. Crystallization started on scratching the beaker walls. After 1 h, the crystals were filtered off and washed with methanol containing a little HCl, and then with diethyl ether; yield, ca. 1.1 g (89 % based on Te) of brownish-yellow, flat, triclinic prisms. Anal. $C_6H_{12}Cl_2N_4Se_2Te$: C, H, N.

The complex $[Te_2(esu)_4Br_2]Br_2$ was prepared as above, using HBr instead of HCl and washing with methanol and then diethyl ether; yield ca. 1.4 g (96 % based on Te) of brownish-yellow, long, thin, monoclinic prisms. Found: C 12.73; H 2.12; N 9.77. Calc. for $C_6H_{12}Br_2N_4Se_2Te$: C 12.31; H 2.07; N 9.57.

The triclinic and orthorhombic forms of $[Te_2(esu)_4Br_2]Br_2$ were obtained from the same reaction mixture when crystallization was initiated by seeding with crushed crystals of $[Te_2(esu)_4Cl_2]Cl_2$ and $[Te_2(esu)_4I_2]I_2$, respectively. In order to obtain well-developed orthorhombic crystals it was found advantageous to keep the reaction vessel in a warm water bath during crystallization and then filter after ca. 45 min to avoid discolouration of the crystals.

The complex $[Te_2(esu)_4I_2]I_2$. To TeO_2 (0.40 g, 2.5 mmol) dissolved with heating in HCl (5 cm^3) was added, with swirling, a solution of esu (2.24 g, 15 mmol) in DMF (40 cm^3). The mixture was warmed, and a warm mixture of methanol (40 cm^3) and HI (5 cm^3) was added. Crystallization started on scratching the beaker walls. The re-

Table 1. Crystallographic data.

	1	2	3	4	5
Complex	$[Te_2(esu)_4Cl_2]Cl_2$	$[Te_2(esu)_4Br_2]Br_2$	$[Te_2(esu)_4Br_2]Br_2$	$[Te_2(esu)_4Br_2]Br_2$	$[Te_2(esu)_4I_2]I_2$
Formula	$C_{12}H_{24}Cl_4N_8Se_4Te_2$	$C_{12}H_{24}Br_4N_8Se_4Te_2$	$C_{12}H_{24}Br_4N_8Se_4Te_2$	$C_{12}H_{24}Br_4N_8Se_4Te_2$	$C_{12}H_{24}I_4N_8Se_4Te_2$
M	993.23	1171.06	1171.06	1171.06	1359.03
System	Triclinic	Triclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	*C2/c* (No. 15)	*Fddd* (No. 70)	*Fddd* (No. 70)
a/Å	8.242(1)	8.433(1)	26.979(3)	14.374(2)	14.833(1)
b/Å	8.262(1)	8.464(1)	11.542(1)	31.654(3)	32.226(2)
c/Å	11.074(1)	11.171(1)	9.336(1)	12.204(2)	12.646(2)
α/°	106.47(1)	106.98(1)			
β/°	106.96(1)	107.11(1)	101.75(1)		
γ/°	93.96(1)	94.59(1)			
V/Å^3	682.1(2)	716.8(4)	2846.3(9)	5552.9(1.9)	6045.2
Z	1	1	4	8	8
D_x/g cm^{-3}	2.418	2.713	2.733	2.801	2.986
F(000)	460	532	2128	4256	4832
μ(Mo*K*α)/cm^{-1}	83.65	135.01	136.00	139.42	113.30
Crystal volume/ mm^3	0.0023	0.00037	0.00048	0.00044	0.00043
Transmission factors	0.267–0.638	0.407–0.638	0.359–0.526	0.404–0.519	0.520–0.568
Scan rate/° min^{-1}	6.71–1.06	3.35–0.50	3.35–0.50	5.03–0.80	5.03–0.75
θ_{max}/°	30	28	28	32	32
Unique reflections	3972	3446	3425	2410	2619
Reflections $I >$ $2\sigma(I)$	3011	2062	1903	996	1180
No. of variables	136	136	137	70	71
R	0.031	0.043	0.044	0.053	0.041
R_w	0.034	0.044	0.045	0.053	0.040
S	1.246	1.250	1.264	1.415	1.094
Max. Δ(ϱ)/e Å^{-3}	0.72	1.02	1.02	1.03	0.85

Table 2. Fractional atomic coordinates for triclinic $[Te_2(esu)_4X_2]X_2$ with e.s.d.'s in parentheses.

Atom	*x*	*y*	*z*	B_{eq}/Å^2
$[Te_2(esu)_4Cl_2]Cl_2$				
Te	0.26589(3)	0.00813(3)	0.087030(25)	2.446(5)
Se(1)	0.56155(6)	0.19599(6)	0.19734(4)	3.23(1)
Se(2)	0.09603(6)	0.26515(5)	0.05894(4)	2.76(1)
Cl(1)	0.41432(17)	−0.26794(15)	0.10997(13)	4.12(3)
Cl(2)	0.05581(13)	0.26263(14)	0.36388(11)	3.12(2)
N(1)	0.4578(4)	0.2320(6)	0.4281(4)	4.0(1)
N(2)	0.7323(4)	0.2816(5)	0.4696(4)	3.6(1)
N(3)	0.0910(5)	0.1349(4)	−0.2128(3)	3.2(1)
N(4)	0.1790(5)	0.4080(4)	−0.1225(4)	3.1(1)
C(1)	0.5816(5)	0.2377(5)	0.3780(4)	2.5(1)
C(2)	0.1257(5)	0.2674(5)	−0.1043(4)	2.3(1)
C(3)	0.5232(6)	0.2859(8)	0.5731(5)	4.3(1)
C(4)	0.7175(6)	0.3154(8)	0.6039(5)	4.3(1)
C(5)	0.1406(6)	0.1797(5)	−0.3167(4)	3.1(1)
C(6)	0.1920(6)	0.3751(5)	−0.2556(4)	3.3(1)
$[Te_2(esu)_4Br_2]Br_2$				
Te	0.26450(8)	0.02034(8)	0.08445(6)	2.81(1)
Br(1)	0.42135(15)	−0.26093(13)	0.10773(11)	3.91(3)
Br(2)	0.04911(12)	0.27540(12)	0.36404(9)	3.01(2)
Se(1)	0.55150(12)	0.20960(13)	0.19766(9)	3.23(2)
Se(2)	0.09230(13)	0.26325(12)	0.05745(9)	2.90(2)
N(1)	0.4504(11)	0.2554(13)	0.4238(8)	4.6(2)
N(2)	0.7170(10)	0.2829(12)	0.4692(8)	4.2(2)
N(3)	0.0854(12)	0.1344(9)	−0.2132(8)	3.7(2)
N(4)	0.1644(11)	0.4028(9)	−0.1250(8)	3.3(2)
C(1)	0.5732(11)	0.2413(11)	0.3767(8)	2.6(2)
C(2)	0.1165(11)	0.2654(10)	−0.1054(8)	2.3(2)
C(3)	0.5091(14)	0.2719(17)	0.5669(11)	5.0(3)
C(4)	0.7022(14)	0.3083(16)	0.6003(11)	4.6(3)
C(5)	0.1264(13)	0.1778(12)	−0.3190(9)	3.3(2)
C(6)	0.1778(12)	0.3694(12)	−0.2583(9)	3.4(2)

action vessel was kept in a warm water bath during crystallization. After ca. 1 h, the crystals were filtered off and washed with methanol, and then with diethyl ether; yield ca. 1.1 g (65 % based on Te) of light red, orthorhombic prisms or plates. Anal. $C_6H_{12}I_2N_4Se_2Te$: C, H, N. The complex was also obtained by dissolving $[Te_2(esu)_4Cl_2]Cl_2$ (0.20 g) in warm DMF/HI (20:1, 5 cm^3) and adding warm methanol (10 cm^3); yield, after cooling to room temperature and then in a refrigerator, 0.22 g (80 %).

Attempts to obtain the monoclinic or orthorhombic forms of $[Te_2(esu)_4Cl_2]Cl_2$ or the triclinic or monoclinic forms of $[Te_2(esu)_4I_2]I_2$ by seeding were not successful.

X-Ray structure analyses. Data were recorded on a CAD4 diffractometer using graphite-monochromated Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å). Unit cell dimensions were determined from the setting angles for 22–25 automatically centred reflections. The ω mode was used for intensities and the scan width was $1.00 + 0.35 \tan\theta$, plus 25 % on each side for background. Crystal data, with numbering of complexes, are given in Table 1. Intensities were corrected for Lorentz and polarization effects, decay (max. ca. 6 %, in the case of complex **2**) and absorption. Reflections with $I > 2\sigma(I)$ were regarded as observed and were used in the calculations. Except for complex **1**, the crystals in the samples were small and there were relatively many unobserved reflections. Programs, atomic scattering factors, refinements

Table 3. Fractional atomic coordinates for monoclinic $[Te_2(esu)_4Br_2]Br_2$ with e.s.d.'s in parentheses.

Atom	*x*	*y*	*z*	B_{eq}/Å^2
Te	0.068775(27)	0.17018(6)	0.44060(8)	2.71(1)
Br(1)	0	0.35405(14)	¼	3.22(3)
Br(1′)	0	−0.00623(13)	¼	3.84(3)
Br(2)	0.17959(5)	0.32517(11)	0.27647(12)	3.49(2)
Se	0.12983(4)	0.31602(10)	0.59460(12)	2.90(2)
Se′	0.10912(4)	−0.00595(10)	0.58700(12)	2.76(2)
N(1)	0.0711(4)	0.2541(8)	0.8069(10)	3.8(2)
N(2)	0.1050(4)	0.4223(8)	0.8417(10)	3.2(2)
N(1′)	0.1897(3)	0.0581(8)	0.4462(10)	2.9(2)
N(2′)	0.1989(4)	−0.1109(8)	0.5491(11)	3.6(2)
C(1)	0.0994(4)	0.3318(9)	0.7586(11)	3.7(2)
C(2)	0.0542(5)	0.2956(11)	0.9378(13)	4.1(3)
C(3)	0.0779(5)	0.4140(10)	0.9639(12)	3.8(3)
C(1′)	0.1704(4)	−0.0188(9)	0.5179(11)	2.6(2)
C(2′)	0.2384(4)	0.0163(11)	0.4139(13)	3.6(3)
C(3′)	0.2473(5)	−0.0964(12)	0.5023(16)	5.1(3)

Table 4. Fractional atomic coordinates for orthorhombic $[Te_2(esu)_4X_2]X_2$ with e.s.d.'s in parentheses. Origin at centre of symmetry.

Atom	*x*	*y*	*z*	B_{eq}/Å^2
$[Te_2(esu)_4Br_2]Br_2$				
Te	⅛	⅛	0.31191(10)	2.80(2)
Br(1)	⅛	0.05933(6)	⅛	3.26(4)
Br(2)	−⅛	0.06108(6)	⅜	3.42(4)
Se	0.11023(9)	0.06645(4)	0.45817(11)	2.69(2)
N(1)	0.3011(8)	0.0905(3)	0.4914(11)	4.2(3)
N(2)	0.2684(8)	0.0268(4)	0.5482(10)	3.2(2)
C(1)	0.2370(8)	0.0616(4)	0.5017(10)	2.4(2)
C(2)	0.3883(11)	0.0751(6)	0.5373(15)	5.4(4)
C(3)	0.3664(10)	0.0314(4)	0.5738(13)	3.8(3)
$[Te_2(esu)_4I_2]I_2$				
Te	⅛	⅛	0.31838(7)	2.73(2)
I(1)	⅛	0.05855(3)	⅛	3.36(2)
I(2)	−⅛	0.05961(3)	⅜	3.33(2)
Se	0.11436(7)	0.06593(3)	0.45998(8)	3.03(2)
N(1)	0.2975(7)	0.0908(3)	0.4914(9)	5.3(2)
N(2)	0.2708(6)	0.0293(3)	0.5477(7)	3.5(2)
C(1)	0.2376(7)	0.0621(3)	0.5004(8)	2.7(2)
C(2)	0.3859(10)	0.0780(4)	0.5347(12)	7.0(3)
C(3)	0.3679(9)	0.0342(3)	0.5698(9)	4.1(2)

and weights were as described in Ref. 4. Anisotropic thermal parameters were used for non-hydrogen atoms. Hydrogens were placed geometrically, at distances C−H 0.95 and N−H 0.87 Å, and were held fixed, with a common fixed B_{iso} for each structure. For complex **5**, an extinction coefficient *g* was included as a variable, as in Ref. 4, and it refined to a value of 1.79×10^{-8}.

The structures of complexes **1**, **2**, **4** and **5** were solved by Patterson and by Fourier difference

methods. The refinement of the structure of complex **3** began with the coordinates of the monoclinic etu analogue.[2] The shifts in the last cycle of refinements were less than one per cent of the associated standard deviations. Atomic coordinates for non-hydrogen atoms are listed in Tables 2–4. Thermal parameters, complete bond lengths and angles, hydrogen coordinates, torsion angles and planes have been deposited with the Cambridge Crystallographic Data Centre.

Results and discussion

In an earlier study of complexes of tellurium dihalides with etu, three crystalline species of empirical formula $Te(etu)_2Br_2$ were obtained.[1] One was isomorphous with $Te(etu)_2I_2$ and was shown to be square-planar *trans*-$Te(etu)_2X_2$,[5] whereas the other two (one monoclinic and one orthorhombic) were dimorphs of dinuclear, di-Br-bridged $[Te_2(etu)_4Br_2]Br_2$.[2] No $Te(etu)_2X_2$ complex was obtained for X = Cl, and for X = I, only *trans*-$Te(etu)_2I_2$ was formed. In the present study of esu analogues, $Te(esu)_2X_2$ species were obtained for X = Cl, Br or I: triclinic crystals were formed for X = Cl, triclinic, monoclinic and orthorhombic crystals for X = Br, and orthorhombic crystals for X = I. These complexes contain dinuclear $[Te_2(esu)_4X_2]^{2+}$ ions which are di-X-bridged in the monoclinic and orthorhombic forms, and the crystals of these are isomorphous with the monoclinic and orthorhombic forms of $[Te_2(etu)_4Br_2]Br_2$, respectively. In the triclinic crystals, the bridging atoms are Se instead of Cl or Br. Thus, on going from X = Cl to X = I, an isomeric change of bridging ligand takes place. For X = Br, both isomers occur.

Bond lengths and angles in the coordination groups are listed in Tables 5–7. Views of the $[Te_2(esu)_4Br_2]^{2+}$ ion, which is di-Se-bridged in the triclinic form **2** isomorphous with **1**, and di-Br-bridged in the orthorhombic form **4** isomorphous with **5**, are shown in Fig. 1. In the triclinic forms **1** and **2**, the two halves of the dinuclear ions are related by a symmetry centre, and in the monoclinic form **3**, by a two-fold axis passing through the bridging Br atoms. In the orthorhombic forms **4** and **5**, three intersecting two-fold axes are present, one passing through the bridging Br or I atoms and one through the Te atoms. In monoclinic **3**, the ion approaches 222 symmetry. The coordination groups are essentially planar.

Table 5. Distances (Å) and angles (°) in the coordination groups of triclinic $[Te_2(esu)_4X_2]X_2$ with e.s.d.'s in parentheses. Primed atoms related to unprimed ones over symmetry centre in 0,0,0.

	X = Cl	X = Br
Bond lengths		
Te–Se(1)	2.550(1)	2.534(1)
Te–Se(2)	2.664(1)	2.648(1)
Te–Se(2′)	3.285(1)	3.338(1)
Te–X(1)	2.701(1)	2.855(1)
Se(1)–C(1)	1.886(4)	1.890(9)
Se(2)–C(2)	1.898(4)	1.895(7)
Bond angles		
Se(1)–Te–Se(2)	94.91(2)	95.80(4)
Se(1)–Te–Se(2′)	174.59(2)	173.66(4)
Se(1)–Te–X(1)	89.45(3)	89.30(4)
Se(2)–Te–Se(2′)	90.35(1)	90.49(3)
Se(2)–Te–X(1)	175.57(3)	174.76(4)
Se(2′)–Te–X(1)	85.31(3)	84.39(3)
Te–Se(1)–C(1)	99.86(11)	99.63(27)
Te–Se(2)–Te′	89.65(1)	89.51(3)
Te–Se(2)–C(2)	96.79(11)	96.78(24)
Te′–Se(2)–C(2)	93.81(11)	94.65(25)

Table 6. Distances (Å) and angles (°) in the coordination groups of orthorhombic $[Te_2(esu)_4X_2]X_2$ with e.s.d.'s in parentheses. Primed and double-primed atoms related to unprimed ones over two-fold axes through Te and through X(1), respectively.

	X = Br	X = I
Bond lengths		
Te–X(1)	3.086(1)	3.251(1)
Te–Se	2.582(1)	2.618(1)
Se–C(1)	1.904(10)	1.901(10)
Bond angles		
X(1)–Te–X(1′)	84.68(5)	82.42(3)
X(1)–Te–Se	91.58(3)	92.04(3)
X(1)–Te–Se′	173.99(4)	173.47(3)
Se–Te–Se′	92.53(6)	93.70(5)
Te–X(1)–Te″	95.32(5)	97.58(3)
Te–Se–C(1)	99.9(3)	100.0(3)

The plane containing the Te atoms and the bridging atoms is exact by symmetry; the terminal atoms deviate slightly from the plane (see Table 8).

In the triclinic crystals, the Te–X bonds are terminal. With bond lengths Te–Cl 2.701(1) and

Table 7. Distances (Å) and angles (°) in the coordination group of monoclinic $[Te_2(esu)_4Br_2]Br_2$ with e.s.d.'s in parentheses. Primed and double-primed atoms as in Table 6; the axis through Te is a pseudo two-fold axis only.

Bond lengths			
Te–Br(1)	3.126(1)	Te–Br(1′)	3.068(1)
Te–Se	2.579(1)	Te–Se′	2.565(1)
Se–C(1)	1.887(10)	Se′–C(1′)	1.899(10)
Bond angles			
Br(1)–Te–Br(1′)	84.35(3)	Br(1)–Te–Se	96.43(4)
Br(1)–Te–Se′	168.47(4)	Br(1′)–Te–Se	177.38(3)
Br(1′)–Te–Se′	85.64(4)	Se–Te–Se′	93.82(4)
Te–Br(1)–Te″	94.46(5)	Te–Br(1′)–Te″	96.83(5)
Te–Se–C(1)	100.5(3)	Te–Se′–C(1′)	100.7(3)

Table 8. Planes of portions of the molecules. Primed and double-primed atoms as in Tables 5–7.

$[Te_2(esu)_4X_2]X_2$ (tric.)			
Plane (1): Te, Se(1), Se(2)		Plane (4): Se(1), C(1), N(1), N(2)	
(2): Te, Se(1), C(1)		(5): Se(2), C(2), N(3), N(4)	
(3): Te, Se(2), C(2)		(6): Te, Se(2), Te′, Se(2′)	
	X = Cl		X = Br
Angles (°) between planes			
(1)–(2)	85.6		83.7
(1)–(3)	84.9		86.2
(2)–(4)	23.1		23.0
(3)–(5)	50.0		49.5
Distances (Å) from plane (6)			
Se(1)	0.057(1)		−0.036(1)
X(1)	−0.041(1)		−0.058(1)
$[Te_2(esu)_4Br_2]Br_2$ (mon.)			
Plane (1): Te, Se, Se′		Plane (4): Se, C(1), N(1), N(2)	
(2): Te, Se, C(1)		(5): Se′, C(1′), N(1′), N(2′)	
(3): Te, Se′, C(1′)		(6): Te, Br(1), Te″, Br(1′)	
Angles (°) between planes			
(1)–(2)	80.6	(1)–(3)	73.8
(2)–(4)	25.6	(3)–(5)	12.7
(1)–(6)	6.1		
Distances (Å) from plane (6)			
Se	0.112(1)	Se′	−0.256(1)
$[Te_2(esu)_4X_2]X_2$ (orh.)			
Plane (1): Te, Se, Se′		Plane (3): Se, C(1), N(1), N(2)	
(2): Te, Se, C(1)		(4): Te, X(1), Te″, X(1′)	
	X = Br		X = I
Angles (°) between planes			
(1)–(2)	77.0		77.9
(2)–(3)	22.8		21.5
(1)–(4)	6.5		4.7
Distances (Å) from plane (4)			
Se	0.212(1)		0.158(1)

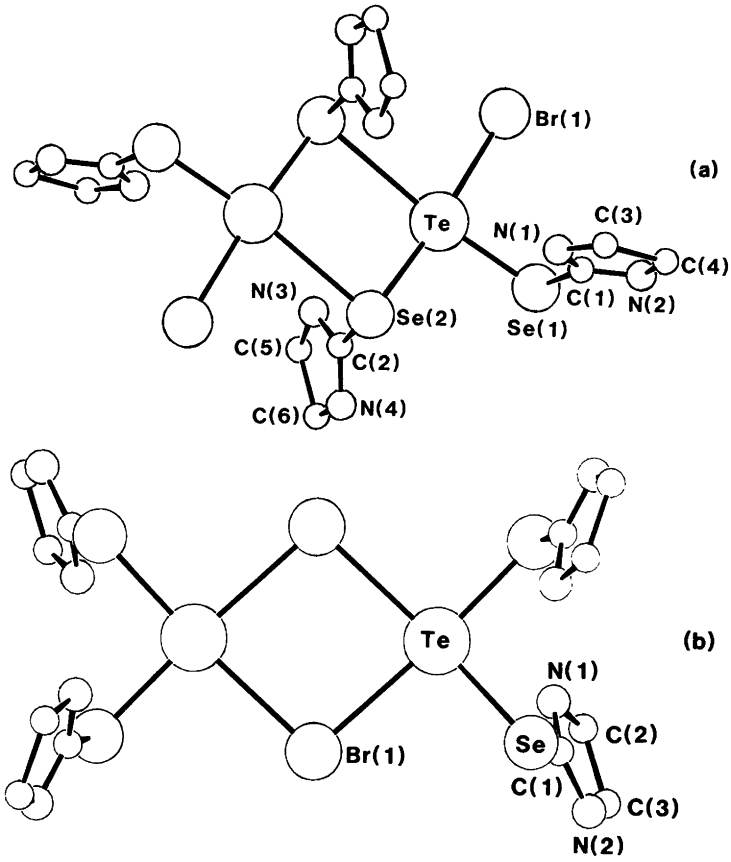

Fig. 1. The two isomers of the $[Te_2(esu)_4Br_2]^{2+}$ ion: (a) di-Se-bridged in the triclinic form, and (b) di-Br-bridged as it occurs in the monoclinic and orthorhombic forms. The 222 symmetry in the latter is shown here.

Table 9. Se···X distances (Å) and angles (°). Primed atoms as in Tables 5–8.

$[Te_2(esu)_4X_2]X_2$ (tric.)					
		X = Cl		X = Br	
Se(1)···X(1)[a]		3.674(1)		3.632(1)	
C(1)–Se(1)···X(1)[a]		160.7(1)		164.6(3)	
Se(2)···X(2)		3.494(1)		3.523(1)	
C(2)–Se(2)···X(2)		178.2(1)		177.9(2)	
$[Te_2(esu)_4Br_2]Br_2$ (mon.)					
Se···Br(2)	3.501(1)		C(1)–Se···Br(2)		172.1(3)
Se′···Br(1′)[b]	3.581(1)		C(1′)–Se′···Br(1′)		174.4(3)
			Se′···Br(1′)···Se[c]		175.1(1)
$[Te_2(esu)_4X_2]X_2$ (orh.)					
		X = Br		X = I	
Se···X(2)		3.534(1)		3.715(1)	
C(1)–Se···X(2)		172.6(3)		173.0(3)	
Se···X(2)···Se[d]		174.5(1)		173.7(1)	

[a,b]X(1) and Br(1′) over symmetry centres in ½,0,0 and 0,0,½, respectively. [c,d]Se′ or Se on either side of the two-fold axis.

Table 10. Bond lengths (Å) and angles (°) in isomorphous pairs or triads of tellurium(II) complexes.[a]

Pair	Complex	Te–L	Te–X	L–Te–X	$10^3\Delta$(Cl/Br)	$10^3\Delta$(I/Br)	Ref.
(1)	$[Te_2(esu)_4Cl_2]Cl_2$	2.664(1)	2.701(1)	175.57(3)	16		This work
	$[Te_2(esu)_4Br_2]Br_2$	2.648(1)	2.855(1)	174.76(4)			
(2)	*cis*-$Te(tmsu)_2Cl_2$	2.677(1)	2.753(1)	172.81(2)	−1		4
	cis-$Te(tmsu)_2Br_2$	2.678(1)	2.898(1)	173.96(2)			
(3)	*cis*-$Te(tu)_2Cl_2$	2.457(1)	2.936(1)	172.50(2)	−19		4
(4)	*cis*-$Te(tu)_2Br_2$	2.476(1)	3.038(1)	171.73(2)		45	
	cis-$Te(tu)_2I_2$	2.521(1)	3.162(1)	171.92(2)			
(5)	$[Te_2(esu)_4Br_2]Br_2$	2.582(1)	3.086(1)	173.99(4)		36	This work
	$[Te_2(esu)_4I_2]I_2$	2.618(1)	3.251(1)	173.47(4)			
(6)	$Te_2(tmtu)_2Cl_4$	2.425(1)	3.217(2)	171.64(5)	−16		7
(7)	$Te_2(tmtu)_2Br_4$	2.537(1)	3.267(1)	172.01(1)		32	
	$Te_2(tmtu)_2I_4$	2.473(2)	3.360(1)	175.19(4)			
(8)	$Te_2(tmsu)_2Cl_4$	2.537(1)	3.267(1)	172.01(1)	−13		7
(9)	$Te_2(tmsu)_2Br_4$	2.550(1)	3.343(1)	173.29(2)		25	
	$Te_2(tmsu)_2I_4$	2.575(1)	3.431(1)	174.89(1)			

[a] X = Cl, Br or I; L = *trans*-ligand: Te–L = Te–S or Te–Se; Δ(Cl/Br) and Δ(I/Br): see text.

Te–Br 2.855(1) Å, they are shorter than in *cis*-$Te(tmsu)_2X_2$ [2.753(1) and 2.898(1) Å],[4] although longer than in centrosymmetric *trans*-$Te(tmtu)_2X_2$ [2.584(2) and 2.737(3) Å].[6] They occur *trans* to bridging esu ligands located at Te–Se distances of 2.664(1) and 2.648(1) Å, respectively. The longer bridges, with Te–Se bond lengths of 3.285(1) and 3.338(1) Å, occur *trans* to terminal esu ligands located at Te–Se distances of 2.550(1) and 2.534(1) Å, for X = Cl and Br, respectively.

In the monoclinic and orthorhombic crystals, the Te–X bonds are bridging and the bridges are symmetrical. With bond lengths of 3.068(1)–3.126(1) Å, and 2.565(1)–2.582(1) Å, the Te–Br bonds are longer and the *trans*-positioned Te–Se bonds to terminal esu groups are shorter, respectively, than the bonds in the terminal Br and bridging Se system of the triclinic isomer.

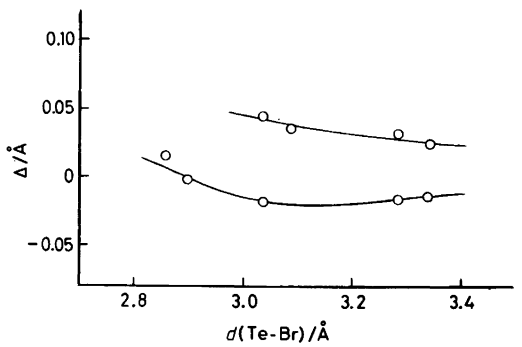

Fig. 2. trans-Influence of I and Cl relative to Br. Upper curve: Δ(I/Br); lower: Δ(Cl/Br).

Intermolecular contacts. Short Se···X approaches occur, with C–Se···X angles of 160–178° (see Table 9). The X^- ions [labelled X(2)] participate, as do the coordinated X ligands in the triclinic and monoclinic crystals. In the cases where X is located on a two-fold axis, nearly linear C–Se···X···Se–C systems result. In triclinic $Te_2(tmsu)_2X_4$, Se···X approaches also occur.[7]

The shortest Te···X^- distances are 4.094(1), 4.212(1), 4.044(1), 4.195(1) and 4.325(1) Å in complexes **1–5**, respectively.

Relative trans-*influence of Cl, Br and I.* In complexes **1** and **2**, Te–Se bond lengths are 2.664(1) and 2.648(1) Å *trans* to Cl and Br, respectively, and in **4** and **5**, 2.582(1) and 2.618(1) Å *trans* to Br and I, respectively. Data for these and other complexes are listed in Table 10. As in the case of thio and seleno ligands,[8] in order to minimize differences arising from lattice forces we compare isomorphous pairs of complexes. They contain L–Te–X systems in which X is Cl, Br or I and

the *trans*-ligand L is the same for both members of each pair. The difference Δ(Cl/Br) = [*d*(Te–L) *trans* to Cl] – [*d*(Te–L) *trans* to Br] is a measure of the relative *trans*-influence of Cl and Br, and similarly for Δ(I/Br). In Fig. 2, Δ(Cl/Br) and Δ(I/Br) are plotted against *d*(Te–Br). The data cover bond length ranges Te–Cl 2.701(1) – 3.267(1), Te–Br 2.855(1) – 3.343(1) and Te–I 3.162(1) – 3.431(1) Å.

Iodine has the largest *trans*-influence. The range is rather small, but the slope of the plot indicates that with decreasing *d*(Te–I) and *d*(Te–Br), the Δ(I/Br) curve will rise further to a maximum before descending to zero at Te–I and Te–Br single-bond distances. This parallels the form of the ΔL_{tr} curve for thio and seleno ligands.[8]

With regard to Cl and Br, the *trans*-influence order is clearly Br > Cl for the longest Te–Cl and Te–Br distances, for pairs (3), (6) and (8). However, for pair (2) there is no significant difference, and for pair (1), Δ(Cl/Br) is positive. Thus, provided the trend is genuine, a reversal takes place at bond lengths around Te–Cl 2.75 and Te–Br 2.90 Å, Br having the greater *trans*-influence at longer Te–Cl and Te–Br distances and Cl the greater *trans*-influence at shorter distances.

trans-Influence in tellurium(II) complexes follows from the 3*c*–4*e* bonding scheme based on tellurium 5*p* orbitals. Two ligands at an angle of 180° share the same *p* orbital; if one ligand is more firmly bound, then the bond to the *trans*-ligand must be weaker.[9] The Te–Cl, Te–Br and Te–I bonds are partly ionic: the electron density in the non-bonding molecular orbital of the 3*c*–4*e* system resides on the ligand atoms. The polarization theory of *trans* effects, developed with reference to transition metal complexes,[10] is an electrostatic theory. It "leads to the wrong prediction that Cl^- will have a larger *trans* effect than I^-".[11] The present data indicate that electrostatic effects play a role at short Te–Cl distances in tellurium(II) complexes.

References

1. Foss, O. and Fossen, S. *Acta Chem. Scand. 15* (1961) 1618.
2. Herland, P., Lundeland, M. and Marøy, K. *Acta Chem. Scand., Ser. A 30* (1976) 719.
3. 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.
4. Foss, O. and Maartmann-Moe, K. *Acta Chem. Scand., Ser. A 41* (1987). 121.
5. Foss, O., Kjøge, H. M. and Marøy, K. *Acta Chem. Scand. 19* (1965) 2349; Foss, O., Maartmann-Moe, K. and Marøy, K. *Acta Chem. Scand., Ser. A 40* (1986) 685.
6. Foss, O. and Maartmann-Moe, K. *Acta Chem. Scand., Ser. A 40* (1986) 675.
7. Eide, J., Foss, O., Maartmann-Moe, K. and Marøy, K. *Acta Chem. Scand., Ser. A 41* (1987). 67.
8. Foss, O., Henjum, J., Maartmann-Moe, K. and Marøy, K. *Acta Chem. Scand., Ser. A 41* (1987). 77.
9. Foss, O. *Acta Chem. Scand. 16* (1962) 779; In: Andersen, P., Bastiansen, O. and Furberg, S., Eds., *Selected Topics in Structure Chemistry,* Universitetsforlaget, Oslo 1974, pp. 145–173; *Pure Appl. Chem. 24* (1970) 31; see also Shustorovich, E. M. and Busaev, Yu. A. *Inorg. Chem. 15* (1976) 1142; Shustorovich, E. *Ibid. 18* (1979) 1030; *J. Am. Chem. Soc. 100* (1978) 7513; *101* (1979) 792.
10. Grinberg, A. A. *Acta Physicochem. USSR 3* (1935) 573.
11. Basolo, F. and Pearson, R. G. *Mechanisms of Inorganic Reactions,* 2nd. ed., Wiley, New York 1967, p. 370.

Received July 18, 1986.