The Structures of Two Crystalline Forms of

Di-μ-bromobis-{diethylenethioureatellurium(II)} Dibromide

PER HERLAND, MAGNE LUNDELAND and KJARTAN MARØY

Department of Chemistry, University of Bergen, N-5014 Bergen-Univ., Norway

Di-μ-bromobis{diethylenethioureatellurium(II)} dibromide, $[Te_2(etu)_4Br_2]Br_2$, forms two crystalline modifications, one orthorhombic (I) and one monoclinic (II). The former has space group $Fddd$ (No. 70), with unit cell $a = 14.454(5)$ Å, $b = 31.258(10)$ Å, $c = 12.057(5)$ Å, $Z = 8$, and the latter has space group $C2/c$ (No. 15), with unit cell $a = 26.734(8)$ Å, $b = 11.437(4)$ Å, $c = 9.321(4)$ Å, $\beta = 101.97(6)°$, $Z = 4$.

The structure determinations were carried out using single-crystal diffractometer data. The refinements, based on 831 non-zero reflections for I and 2349 for II, converged at R values of 0.043 and 0.032, respectively.

Each tellurium atom is bound to two sulfur atoms and two bromine atoms in a distorted square-planar cis arrangement. The two bromine atoms are situated on a twofold axis of symmetry, and bridge two tellurium atoms. In the orthorhombic form, the two tellurium atoms are also situated on a twofold axis. The two $S - Te - Br$ systems have the bond lengths $S - Te = 2.495(3)$ Å, $Te - Br = 3.042(2)$ Å in the orthorhombic form, and $S - Te = 2.491(2)$ and $2.481(2)$ Å, $Te - Br = 3.015(1)$ and $3.079(1)$ Å in the monoclinic form. The $S - Te - Br$ angles are, in the same order, $175.75(8)$, $178.68(5)$, and $170.51(5)°$.

In preparing complexes of divalent tellurium with ethylenethiourea, Foss and Fossen [1] isolated four different bromides of which three had the apparent composition $Te(etu)_2Br_2$. The crystal structure of one of these was published together with that of the isomorphous diiodo complex,[2] and these structures have later been refined using diffractometer data.[3] In these crystals the tellurium atoms are situated at centres of symmetry, and the complexes are trans square-planar. The crystal structure analyses of the two other $Te(etu)_2Br_2$ complexes have now been carried out. Some

features of the structures have been briefly reported earlier.[4] The present work forms part of the extensive studies on linear three-atom systems centered on divalent tellurium, selenium, and sulfur which are being carried out at this department.[5,6]

EXPERIMENTAL

The intensity data, and diffraction angles for unit cell dimensions, were measured on a Siemens automatic single-crystal diffractometer using MoKα radiation (Nb-filtered) and a scintillation counter.

The crystals used for the measurements were of samples prepared by Foss and Fossen [1] which had been kept in a refrigerator. The crystal used of the orthorhombic form was a prism with (010) predominant, 0.045 mm thick, and 0.115 and 0.195 mm along the a and c axes, respectively. The crystal of the monoclinic form was a prism along the c axis, 0.326 mm long, with distances between the (100), between the (110), and between the (1̄0) boundary faces of 0.082, 0.095 and 0.095 mm, respectively. Each crystal was mounted with the c axis approximately parallel to the ϕ axis of the diffractometer.

The five-value procedure and $\theta - 2\theta$ scan technique, with scan width of 0.80°, were used. The maximum scan time per degree was 24 s.

Two reflections of medium strength were measured two times each at intervals of 50 reflections. The net intensities were brought to a common scale by means of these reference reflections, which showed no systematic variations.

Reflections with net intensity below three times its standard deviation were assigned an intensity equal to this limit and were labelled as unobserved. These reflections were included in the refinements and the calculation of R values when $|F_c|$ was greater than the observable limit.

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Table 1. Atomic coordinates, in fractions of cell edges. Standard deviations in parentheses.

	x	y	z

Orthorhombic di-μ-bromobis{diethylenethio-ureatellurium(II)} dibromide. Origin at a centre of symmetry, at 1/8 1/8 1/8 from 222

	x	y	z
Te	1/8	1/8	0.31237(7)
Br	1/8	0.05955(5)	1/8
Br⁻	1/8	0.43705(5)	1/8
S	0.11637(22)	0.06835(9)	0.45775(22)
N(1)	0.29695(73)	0.09136(34)	0.49197(95)
N(2)	0.25923(69)	0.02672(30)	0.54806(75)
C(1)	0.23112(67)	0.06248(37)	0.50014(77)
C(2)	0.38628(105)	0.07530(47)	0.53864(131)
C(3)	0.35905(87)	0.02980(37)	0.58013(89)

Monoclinic di-μ-bromobis{diethylenethioureatellurium(II)} dibromide. Origin at a centre of symmetry

	x	y	z
Te	0.06839(1)	0.17088(4)	0.43729(4)
Br	0	0.35462(8)	1/4
Br'	0	−0.00446(8)	1/4
Br⁻	0.18045(3)	0.32672(7)	0.27303(8)
S	0.12664(6)	0.31301(15)	0.59152(19)
S'	0.11143(6)	0.00040(14)	0.57482(19)
N(1)	0.07233(24)	0.25228(50)	0.79804(67)
N(2)	0.10756(23)	0.42350(46)	0.82977(60)
N(1')	0.18975(20)	0.06349(47)	0.43993(58)
N(2')	0.19708(21)	−0.10821(48)	0.54525(60)
C(1)	0.09982(22)	0.32898(56)	0.74633(67)
C(2)	0.05811(31)	0.29228(65)	0.93738(79)
C(3)	0.08183(28)	0.41411(58)	0.95525(72)
C(1')	0.16828(23)	−0.01342(54)	0.51320(62)
C(2')	0.23836(27)	0.02006(63)	0.41211(79)
C(3')	0.24594(28)	−0.09357(69)	0.50132(89)

Absorption corrections [7] were carried out in addition to Lorentz and polarization corrections.

The scattering factor curves used were those listed in *International Tables for X-Ray Crystallography*,[8] Table 3,3. 1A. The curves for tellurium, bromine, bromide, and sulfur were corrected for anomalous dispersion using the values given by Cromer,[9] and taking the amplitude as the corrected value.

The structures were solved through Patterson and Fourier maps.

The refinements were carried out by means of a full-matrix least squares program, and in the course of the refinements the intensities were corrected for secondary extinction according to Zachariasen.[10] The extinction correction program used has a fixed values of one for the absorption term, and C was found to be 0.54×10^{-7} for I and 1.29×10^{-7} for II.

Difference electron density maps revealed the positions of all the hydrogen atoms in II, but of only two of the six symmetry independent ones in I. The hydrogen atoms are not included in the structure factor calculations.

The final atomic coordinates and thermal parameters are listed in Tables 1 and 2, respectively. Lists of observed and calculated structure factors are available from author K. M. on request.

The program for drawing illustrations is written by C. K. Johnson, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A. The other programs are partly of a set made available by the Chemical Department of X-Ray Crystallography, Weizmann Institute of Science, Rehovoth, Israel, and partly written at this Department. An IBM 360/50H computer was used for the calculations.

CRYSTAL DATA

Orthorhombic	Monoclinic
$[Te_2(etu)_4Br_2]Br_2$	$[Te_2(etu)_4Br_2]Br_2$
Fddd (No. 70)	*C2/c* (No. 15)
$a = 14.454(5)$ Å	$a = 26.734(8)$ Å
$b = 31.258(10)$ Å	$b = 11.437(4)$ Å
$c = 12.057(5)$ Å	$c = 9.321(4)$ Å
	$\beta = 101.97(6)°$
$Z = 8$	$Z = 4$
$\varrho_{calc} = 2.40$ g/cm³	$\varrho_{calc} = 2.30$ g/cm³
$\mu(MoK\alpha) = 87.5$ cm⁻¹	$\mu(MoK\alpha) = 85.5$ cm⁻¹
2010 refl. within $\theta = 28°$	3397 refl. within $\theta = 28°$
831 refl. with $I > 3\sigma(I)$	2349 refl. with $I > 3\sigma(I)$
$R = 0.043$	$R = 0.032$

RESULTS

Distances and angles are listed in Table 3. A view of the complex cation is shown in Fig. 1, and the unit cell contents are shown in Figs. 2 and 3. The marked and unmarked atoms, used for the monoclinic form, refer to atoms which in the orthorhombic form are related to each other by the twofold axis through the tellurium atoms.

In the earlier published [2] monoclinic modification of Te(etu)₂Br₂, the arrangement is *trans* square-planar with the tellurium atoms situated at symmetry centres. Also in the present complexes, two bromine atoms and two sulfur atoms are coordinated to tellurium in an approximately square-planar arrangement. The arrangement is, however, *cis*, and the two bromine atoms are situated on a twofold axis of symmetry and thus bridge two tellurium atoms. The result is a dinuclear cation of

Table 2. Thermal parameters expressed in the form $\exp[-2\pi^2(h^2a^{-2}U_{11}+...+2hka^{-1}b^{-1}U_{12}+...)]$. All values have been multiplied by 10^4. Standard deviations are given in parentheses.

|	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Orthorhombic di-μ-bromobis{diethylenethioureatellurium(II)} dibromide						
Te	301(5)	299(5)	326(5)	36(6)	0	0
Br	504(10)	347(9)	409(8)	0	0	− 43(10)
Br⁻	414(8)	331(8)	462(8)	0	0	−· 17(10)
S	414(16)	303(13)	440(15)	− 30(15)	79(12)	− 26(15)
N(1)	427(61)	417(64)	805(75)	− 122(59)	204(59)	− 205(56)
N(2)	568(64)	299(55)	425(53)	55(47)	96(47)	− 67(49)
C(1)	299(55)	413(65)	214(44)	− 29(44)	13(46)	24(42)
C(2)	613(97)	514(79)	1095(119)	40(81)	428(82)	− 442(99)
C(3)	493(88)	359(60)	479(63)	65(57)	− 10(49)	− 160(56)
Monoclinic di-μ-bromobis{diethylenethioureatellurium(II)} dibromide						
Te	306(2)	271(2)	331(2)	26(2)	2(2)	107(2)
Br	498(6)	291(6)	423(6)	0	0	35(5)
Br'	402(6)	297(5)	498(6)	0	0	79(5)
Br⁻	585(4)	380(4)	493(4)	5(4)	19(4)	225(4)
S	416(9)	325(9)	469(9)	− 81(8)	− 47(8)	154(8)
S'	358(9)	312(8)	456(10)	59(7)	92(7)	143(7)
N(1)	642(44)	473(36)	508(39)	− 243(31)	− 137(30)	304(34)
N(2)	609(39)	293(29)	412(33)	− 60(28)	− 70(26)	94(30)
N(1')	408(32)	369(30)	424(33)	28(25)	82(26)	204(27)
N(2')	482(36)	369(30)	489(37)	− 146(28)	− 81(27)	227(30)
C(1)	354(32)	259(29)	421(35)	− 15(31)	6(32)	86(27)
C(2)	757(56)	455(42)	413(41)	− 180(38)	− 165(35)	270(41)
C(3)	627(49)	321(36)	331(39)	10(32)	14(29)	120(36)
C(1')	377(36)	307(33)	280(34)	− 26(29)	− 11(27)	62(28)
C(2')	402(39)	475(42)	533(46)	124(34)	99(36)	203(34)
C(3')	527(49)	526(50)	804(61)	− 220(39)	− 240(44)	400(46)
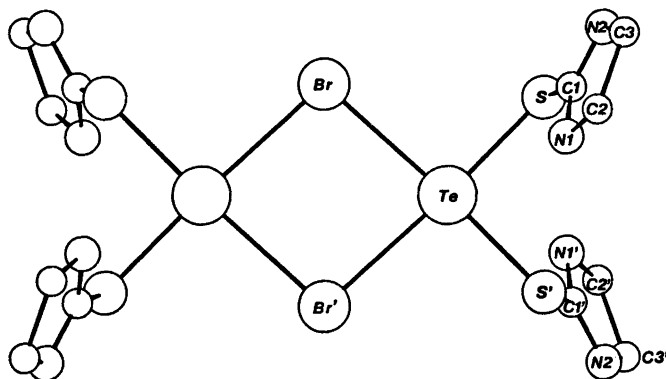
Fig. 1. A view of the di-μ-bromobis{diethylenethioureatellurium(II)} cation as seen normal to the coordination plane of the tellurium atoms.

composition [(etu)₂TeBr₂Te(etu)₂]²⁺. The sulfur atoms are moved slightly out of the TeBr₂Te-plane, the angle between this plane and the TeS₂ plane being 4.0° in I and 3.4° in II.

In the orthorhombic crystals the tellurium atoms are also situated on twofold axes of symmetry. The deviations from this twofold symmetry in the monoclinic crystals are

Table 3. Bond lengths (Å) and angles (deg.). Standard deviations are given in parentheses.

	Orthorhombic form	Monoclinic form	
Te − Br	3.048(2)	3.079(1)	3.015(1)
Te − S	2.495(3)	2.491(2)	2.481(2)
∠Be − Te − Br	84.32(5)	84.74(3)	
∠S − Te − S	90.73(9)	92.70(6)	
∠S − Te − Br(*cis*)	92.54(7)	96.23(5)	86.39(5)
∠S − Te − Br(*trans*)	175.75(8)	178.68(5)	170.51(5)
∠Te − Br − Te	95.68(5)	93.93(3)	96.60(3)
S − C(1)	1.745(10)	1.749(7)	1.740(7)
C(1) − N(1)	1.315(15)	1.300(9)	1.316(9)
C(1) − N(2)	1.322(15)	1.323(8)	1.327(8)
N(1) − C(2)	1.495(19)	1.499(10)	1.464(9)
N(2) − C(3)	1.497(16)	1.479(10)	1.457(10)
C(2) − C(3)	1.558(19)	1.526(10)	1.534(11)
∠Te − S − C(1)	103.5(4)	103.3(2)	104.1(3)
∠S − C(1) − N(1)	126.4(8)	126.6(5)	128.0(4)
∠S − C(1) − N(2)	120.6(7)	122.0(5)	120.4(4)
∠N(1) − C(1) − N(2)	113.0(9)	111.4(6)	111.6(5)
∠C(1) − N(1) − C(2)	111.5(10)	112.3(6)	111.3(5)
∠C(1) − N(2) − C(3)	110.8(8)	111.3(5)	110.8(5)
∠N(1) − C(2) − C(3)	102.1(10)	101.5(6)	102.4(6)
∠N(2) − C(3) − C(2)	102.7(9)	103.4(5)	103.0(6)
N(1)···Br⁻	3.494(11)		3.374(5)
∠C(1) − N(1)···Br⁻	148.4(7)		146.8(4)
∠C(2) − N(1)···Br⁻	99.2(7)		101.8(4)
N(2)···Br⁻	3.533(10)	3.559(6)	3.368(6)
∠C(1) − N(2)···Br⁻	128.1(6)	126.3(4)	127.0(4)
∠C(3) − N(2)···Br⁻	120.8(6)	122.3(3)	120.4(4)
N(1)···Br		3.408(6)	
∠C(1) − N(1)···Br		149.5(4)	
∠C(2) − N(1)···Br		97.4(4)	

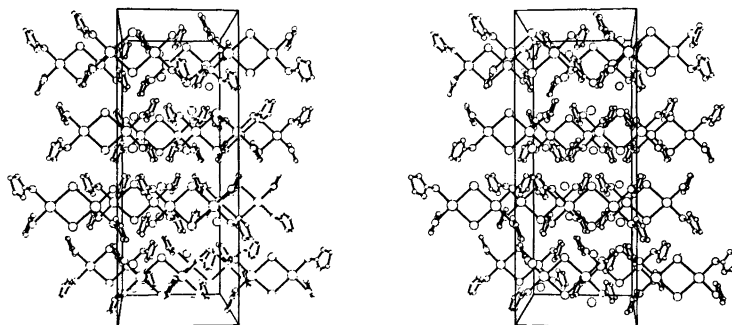*Fig. 2.* A stereoscopic view of the cell packing in the orthorhombic crystals of $[Te_2(etu)_4Br_2]Br_2$ as seen normal to the *a* plane.

illustrated by the differences in dimensions in the two halves of the cation; the Te − Br bond lengths differ by 0.064 Å, the Te − S bond lengths by 0.010 Å, the *cis* S − Te − Br angles by 9.84°, the *trans* S − Te − Br angles by 8.17°, and the Te − Br − Te angles by 2.67°. The averaged dimensions in the monoclinic crystals agree well with the dimensions in the orthorhombic crystals.
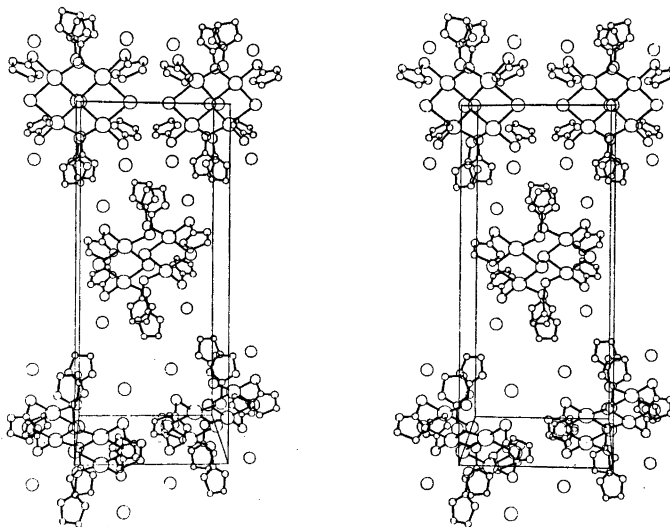
Fig. 3. A stereoscopic view of the cell packing in the monoclinic crystals of [Te₂(etu)₄Br₂]Br₂ as seen normal to the *c* plane.

When the dimensions of the present dimeric *cis* complexes are compared to those of the monomeric *cis* complex Te(trtu)₂Br₂,[11] the most obvious difference is found in the $Br-Te-Br$ angle, which is 96.24(7)° in the latter, while in the former they are 84.32(5) and 84.74(3)°, *cf.* Table 3. The bromine atoms are closer together and the tellurium atoms are further apart than in a square arrangement. Since the Te⋯Te distances are as large as about 4.50 Å, the reason for the distortion is more likely to be the preference of a bond angle at bromine larger than 90°, than the space requirements of the tellurium atoms. The dimerization seems to have a small lengthening effect on the $Te-Br$ bonds, which are 2.994(2) Å in Te(trtu)₂Br₂.[11]

As seen from Table 3, each nitrogen atom seems to form a hydrogen bond with a bromide ion or a bromine atom. The bromide ions involved in these contacts are in the orthorhombic crystals at $\frac{1}{2}-x, y-1/4, 1/4+z$ and $x,y-\frac{1}{2}, \frac{1}{2}+z$ relative to the coordinates of Table 1. In the monoclinic crystals, the bromide ions are, in the order listed, at $x,1-y, \frac{1}{2}+z; x,y,z; x, -y,\frac{1}{2}+z$, and Br is at $x, -y, \frac{1}{2}+z$ relative to the coordinates of the table. The sums of the bond angles at nitrogen are in the range 358.2 − 359.9°.

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