

The Crystal and Molecular Structures of *cis* Square-planar Complexes of Tellurium Dichloride and Dibromide with Trimethylenethiourea

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The crystal and molecular structures of *cis*-dichloro- and *cis*-dibromobis(trimethylenethiourea)tellurium(II), $\text{Te}(\text{trtu})_2\text{Cl}_2$ (I) and $\text{Te}(\text{trtu})_2\text{Br}_2$ (II), have been determined by X-ray methods. The least squares refinement based on 933 observed reflections for I and 809 observed reflections for II converged at R values of 0.055 and 0.065, respectively.

The space group is $C2/c$ (No. 15), with $Z=4$, and unit cell, $a=16.492(5)$ Å, $b=7.606(4)$ Å, $c=14.515(6)$ Å, $\beta=120.20(3)^\circ$ for I, and $I2/c$ (No. 15), with $Z=4$, and unit cell, $a=16.118(6)$ Å, $b=7.880(4)$ Å, $c=14.312(6)$ Å, $\beta=117.60(4)^\circ$ for II.

The dimensions of the distorted square-planar *cis* TeS_2X_2 groups are: $\text{Te}-\text{S}=2.465(4)$ Å, $\text{Te}-\text{Cl}=2.964(4)$ Å in I, and $\text{Te}-\text{S}=2.499(5)$ Å, $\text{Te}-\text{Br}=2.994(2)$ Å in II.

The present structure determinations form part of the extensive studies on linear three-atom systems centered on divalent tellurium, selenium, and sulfur which are being carried out at this institute.^{1,2}

The complexes of tellurium dichloride and dibromide with trimethylenethiourea, $\text{Te}(\text{trtu})_2\text{Cl}_2$ and $\text{Te}(\text{trtu})_2\text{Br}_2$, belong to the square-planar complexes where *cis-trans* isomerism is possible. When the configuration around tellurium is square-planar *trans*, the tellurium atoms usually lie in crystallographic centres of symmetry, whereas the tellurium atoms usually lie on crystallographic twofold axes when the arrangement is square-planar *cis*.¹ From a preliminary crystallographic investigation it was concluded that the present complexes belong to the latter type of configuration.³

EXPERIMENTAL

The crystals of $\text{Te}(\text{trtu})_2\text{Cl}_2$ (I) and $\text{Te}(\text{trtu})_2\text{Br}_2$ (II) used for the present studies were of samples prepared for the earlier investigations,³ which had been kept in a refrigerator.

The unit cell dimensions were redetermined by means of a least squares program, using the diffraction angles of 82 reflections in I and 79 reflections in II, measured from zero-layer Weissenberg photographs around the b and c axes. The derived values are, $a=16.492(5)$ Å, $b=7.606(4)$ Å, $c=14.515(6)$ Å, $\beta=120.20(3)^\circ$ for I, and $a=16.118(6)$ Å, $b=7.880(4)$ Å, $c=14.312(6)$ Å, $\beta=117.60(4)^\circ$ for II.

The intensity data were collected by the multiple-film technique. Integrated zero-layer and equi-inclination photographs were taken with $\text{CuK}\alpha$ radiation (Ni-filtered) for the $h0l-h3l$, $hk0$ and hkl reflections. Out of 1001 attainable independent reflections for I, and 1003 for II, 933 and 809, respectively, were strong enough to be observed with measurable intensities; the unobserved reflections were set equal to the observable limit. The reflections were estimated visually on the upper and lower parts of the films. At high angles, only α_1 reflections were estimated, and the resulting intensities were increased by 2–50 %, according to an experimental scale.

Lorentz and polarization corrections were carried out, and absorption corrections were done by the method described by Busing and Levy⁴ and modified by Coppens *et al.*⁵ For I, $\mu=211$ cm^{-1} and for II, $\mu=241$ cm^{-1} . The crystals of I are monoclinic prisms extended along the b axis. Two crystals were used for collection of intensity data; the one rotated about the b axis was 0.24 mm long and had a cross section of 0.06×0.08 mm^2 , and the one rotated about the c axis was cut such that the distances between the pairs of faces were 0.08–0.09 mm. Only one crystal of II was used; a monoclinic

plate (100) with distances between pairs of faces 0.07 mm. The number of grid points used for absorption corrections were in the range 5–600.

The observed structure factors were eventually corrected for secondary extinction according to Zachariassen.⁶ The absorption term in the expression for F_{corr} was put equal to one, and C was found to be 0.88×10^{-7} and 0.63×10^{-7} for the crystals of I, rotated about the b and c axes, respectively, and 1.95×10^{-7} for the crystal of II.

The scattering factors used were those given in *International Tables for X-Ray Crystallography*,⁷ Table 3.31B for Te and Br, and Table 3.3.1A for Cl, S, N, and C. The factors for Te, Br, Cl, and S were corrected for anomalous dispersion using the $\Delta f'$ and $\Delta f''$ values given by Cromer,⁸ and taking the amplitude of f as the corrected value.

Least squares refinements were carried out with a full-matrix program, minimizing the function

$$r = \sum W(|F_o| - K|F_c|)^2$$

with $W = [(a_1 K)^2 + (a_2 F_o)^2 / 4W_o]^{-1}$. Here W_o is based on the reliability of the individual intensities, and the constants a_1 and a_2 were put equal to 5 and 1, respectively, for I, and 10 and 1, respectively, for II. Unobserved reflections were included with $|F_o|$ equal to the observable limit when $|F_c|$ exceeded this value.

The programs used for calculation of unit cell dimensions, film data processing, absorption corrections, two-dimensional Fourier summations, and least squares refinement were made available by the Chemical Department of X-Ray Crystallography, Weizmann Institute of Science, Rehovoth, Israel. The program used for drawing of illustrations is written by C. K. Johnson, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A. The other programs used are written by K. Åse and K. Maartmann-Moe, both of this Department. The calculations were carried out on an IBM 360/50H computer.

THE STRUCTURE ANALYSES

The tellurium atoms in both crystals lie on twofold axes of symmetry $(0, y, \frac{1}{2})$ and their y coordinates were found from $hk0$ Patterson maps. The approximate positions of all atoms, except hydrogen, were evaluated from $h0l$ and $hk0$ electron density maps, starting with signs based on tellurium contributions only. One of the strongest reflections, 400, in both structures turned out to have sign opposite of the tellurium contribution.

The three-dimensional least squares refinements were started with coordinates derived from the projections. Isotropic thermal param-

Table 1. Atomic coordinates, in fractions of cell edges, and isotropic thermal parameters, in the form $\exp[-8\pi^2 U(\sin^2 \theta/\lambda^2)]$. Standard deviations are given in parentheses.

	x	y	z	U
Dichlorobis(trimethylenethiourea)tellurium(II)				
Te	0	0.1032(2)	1/4	
Cl	0.1304(2)	-0.1601(5)	0.2454(2)	
S	0.1216(2)	0.3238(6)	0.2848(2)	
N(1)	0.1275(6)	0.1822(18)	0.1195(7)	0.0521(23)
N(2)	0.1351(6)	0.4876(17)	0.1334(7)	0.0477(22)
C(1)	0.1283(6)	0.3319(21)	0.1677(8)	0.0410(23)
C(2)	0.1391(8)	0.1773(25)	0.0243(10)	0.0604(32)
C(3)	0.1055(8)	0.3501(22)	-0.0340(9)	0.0568(30)
C(4)	0.1479(8)	0.5098(23)	0.0405(9)	0.0581(31)
Dibromobis(trimethylenethiourea)tellurium(II)				
Te	0	0.1275(2)	1/4	
Br	0.1340(1)	-0.1261(3)	0.2400(1)	
S	0.1141(3)	0.3535(7)	0.2645(3)	
N(1)	0.1137(9)	0.2138(22)	0.0945(11)	0.0550(37)
N(2)	0.1250(9)	0.5133(22)	0.1092(11)	0.0519(37)
C(1)	0.1178(9)	0.3598(29)	0.1450(11)	0.0469(36)
C(2)	0.1221(11)	0.2241(28)	-0.0070(13)	0.0573(47)
C(3)	0.1834(10)	0.3739(26)	-0.0009(12)	0.0559(41)
C(4)	0.1413(11)	0.5335(28)	0.0158(13)	0.0547(43)

Table 2. Anisotropic thermal parameters expressed in the form $\exp[-2\pi^2(h^2\alpha^{-2}U_{11} + \dots + 2hka^{-1} \times b^{-1}U_{13} + \dots)]$. 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}
Dichlorobis(trimethylenethiourea)tellurium(II)						
Te	643(6)	321(8)	503(6)	0	0	345(5)
Cl	755(18)	300(19)	845(20)	51(16)	-15(22)	408(16)
S	1022(22)	412(24)	708(19)	-225(20)	-197(21)	608(18)
Dibromobis(trimethylenethiourea)tellurium(II)						
Te	621(9)	308(10)	485(8)	0	0	308(6)
Br	817(12)	364(13)	834(14)	121(13)	-23(18)	405(11)
S	859(27)	376(27)	567(22)	-220(30)	-144(33)	456(20)

eters were used for all atoms in the first refinement cycles, and then anisotropic parameters were introduced for Te, Br, Cl, and S. Secondary extinction corrections were carried out, and then additional least squares refinement until the maximum shift of a parameter was about one tenth of its standard deviation. The final R value ($\sum||F_o| - |F_c|| / \sum|F_o|$) was 0.055 for I and 0.065 for II. Unobserved reflections are included when $|F_c|$ is greater than the observable limit.

Final three-dimensional difference electron density maps revealed the positions of some of the hydrogen atoms. An attempt was made to refine the coordinates of the hydrogen atoms bonded to nitrogen in the dichloro complex, but without success as the atoms were shifted to unreasonable positions.

The final atomic coordinates together with the isotropic thermal parameters of N and C are listed in Table 1, and the anisotropic parameters of the other atoms are listed in Table 2. Lists of observed and calculated structure factors are available from author K. M. on request.

RESULTS

Bond lengths and angles, from the atomic coordinates of Table 1, are given in Table 3 and Figs. 1 and 2. Views of the cell contents are shown in Figs. 3 and 4.

The two complexes, $\text{Te}(\text{trtu}_2\text{Cl}_2)$ (I) and $\text{Te}(\text{trtu}_2\text{Br}_2)$ (II), crystallize in unit cells of nearly the same dimensions when space group $I2/c$ is chosen for II instead of $C2/c$ for I. The compounds, though not isomorphous, are nearly

Table 3. Atomic distances (Å) and angles (deg.) of the trimethylenethiourea groups and the halogen-nitrogen approaches. X = Cl, Br. Standard deviations are given in parentheses.

	Dichloro complex	Dibromo complex		Dichloro complex	Dibromo complex
S-C(1)	1.758(13)	1.738(18)	$\angle \text{Te-S-C}(1)$	105.4(4)	107.3(6)
C(1)-N(1)	1.333(20)	1.344(27)	$\angle \text{S-C}(1)-\text{N}(1)$	119.3(10)	119.3(13)
C(1)-N(2)	1.312(20)	1.340(27)	$\angle \text{S-C}(1)-\text{N}(2)$	117.3(9)	116.8(13)
N(1)-C(2)	1.487(20)	1.522(27)	$\angle \text{N}(1)-\text{C}(1)-\text{N}(2)$	123.4(11)	123.9(15)
N(2)-C(4)	1.474(19)	1.485(27)	$\angle \text{C}(1)-\text{N}(1)-\text{C}(2)$	122.5(12)	117.6(15)
C(2)-C(3)	1.509(23)	1.516(29)	$\angle \text{C}(1)-\text{N}(2)-\text{C}(4)$	122.0(9)	121.6(15)
C(3)-C(4)	1.541(21)	1.499(30)	$\angle \text{N}(1)-\text{C}(2)-\text{C}(3)$	108.4(12)	109.3(14)
			$\angle \text{N}(2)-\text{C}(4)-\text{C}(3)$	109.2(12)	109.6(15)
			$\angle \text{C}(2)-\text{C}(3)-\text{C}(4)$	112.6(10)	109.4(15)
N(1)⋯X	3.168(14)	3.315(17)	$\angle \text{C}(1)-\text{N}(1)\cdots\text{X}$	113.9(8)	112.8(11)
			$\angle \text{C}(2)-\text{N}(1)\cdots\text{X}$	122.9(9)	128.0(11)
N(2')⋯X	3.156(13)	3.369(17)	$\angle \text{C}(1')-\text{N}(2')\cdots\text{X}$	122.8(8)	122.6(11)
			$\angle \text{C}(4')-\text{N}(2')\cdots\text{X}$	115.2(9)	115.4(11)

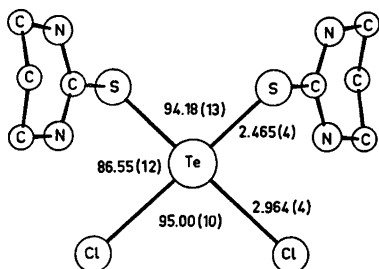


Fig. 1. The *cis*-dichlorobis(trimethylenethiourea)tellurium(II) molecule as seen normal to the plane of the TeS₂Cl₂ coordination group.

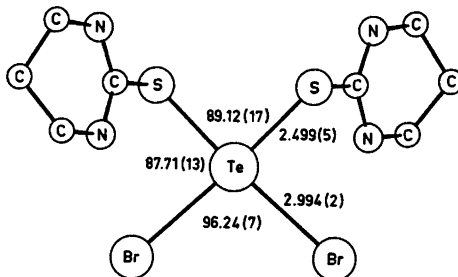


Fig. 2. The *cis*-dibromobis(trimethylenethiourea)tellurium(II) molecule as seen normal to the plane of the TeS₂Br₂ coordination group.

isostructural, as also indicated by the similarity of the *h0l* and *hk0* zones of reflections.³ As seen from the figures, the middle carbon atom of the trimethylene chain is moved out of the plane through the other non-hydrogen atoms of the thiourea group, towards Te in I and away from Te in II. This difference may be due to space requirements of the trimethylene groups and is connected with the different locations of the symmetry elements in the two unit cells.

The tellurium atoms are each bonded to two sulfur atoms and two halogen atoms in a distorted square-planar *cis* arrangement. The Te-X bonds are bent out of the TeS₂ plane, to opposite sides of the plane. The configuration is similar to that of the analogous thiourea complexes Te(tu)₂Cl₂ and Te(tu)₂Br₂.⁹ The deviation from planarity is larger in the dichloro than in the dibromo complex, the angle between the TeS₂ and TeX₂ planes being 15.5° in

I and 9.3° in II. The S-Te-X three-atom systems deviate from linearity as the angle at Te is 168.61(9)° in I and 172.41(11)° in II. When the present *cis* Te(trtu)₂Br₂ is compared to the *trans* Te(etu)₂Br₂,^{10,11} where Te-S = 2.657(2) Å and Te-Br = 2.765(1) Å, one finds that the Te-S bonds are 0.158 Å shorter in the *cis* complex, whereas the Te-Br bonds are 0.229 Å longer. This illustrates the relative stronger *trans* bond lengthening effect of a thiourea group than of a halogen atom.¹

In the *trans* square-planar complexes of Te(etu)₂Br₂ and Te(etu)₂I₂,¹¹ Te-Br = 2.765(1) Å and Te-I = 2.956(1) Å. The difference between these bond lengths is in accordance with the difference in single covalent bond radii of iodine and bromine, 0.19 Å.¹² The covalent bond radii of bromine and chlorine differ by 0.15 Å,¹² whereas the difference between the Te-Br and Te-Cl bond lengths in the present *cis*

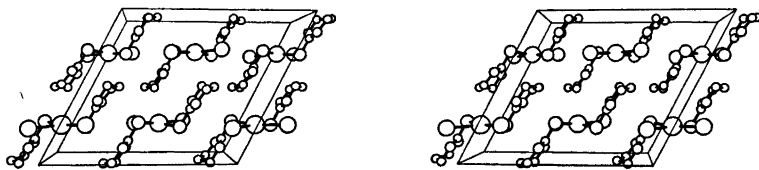


Fig. 3. A stereoscopic view of the cell packing in *cis*-Te(trtu)₂Cl₂ as seen normal to the *b* plane.

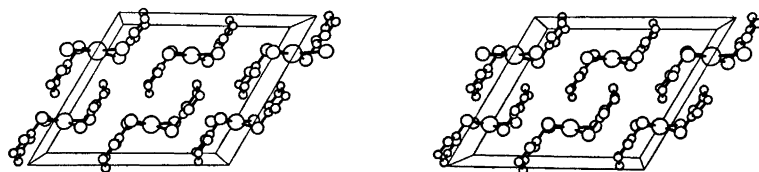


Fig. 4. A stereoscopic view of the cell packing in *cis*-Te(trtu)₂Br₂ as seen normal to the *b* plane.

complexes is only 0.03 Å. Bromine is thus more strongly bonded to tellurium than is chlorine, and this has a small but significant effect on the *trans*-positioned Te-S bond, which is 2.499(5) Å in the dibromo and 2.456(4) Å in the dichloro complex.

The bond lengths and angles of the trimethylene-thiourea ligands are, within the rather large standard deviations, in accordance with those of trimethylenethiourea.²⁸ The thioamide groups, SCN₂, are planar within the errors, and make angles of 70.6° with the TeS₂ plane in I and 66.8° in II. The least squares plane of N(1), N(2), C(2), and C(4) passes at a distance of 0.62 Å from C(3) in I and 0.68 Å in II, and at a distance of 0.03 Å from C(1) in I and 0.05 Å in II. In I, C(1) and C(3) are on opposite sides of the plane, whereas in II they are on the same side of the plane.

Each halogen atom seems to be hydrogen-bonded to two nitrogen atoms, one of the same molecule and one of the molecule with coordinates, *x*, *y* - 1, *z*. In Table 3, primes are used to denote atoms of the latter molecule. The least squares planes of the two thioamide groups connected to the same halogen atom are thus parallel and the halogen atom is situated between the planes. The distance between the planes is 0.38 Å in I and 0.55 Å in II. The hydrogen positions derived from the difference electron density maps are in accordance with the assumed hydrogen bonds. The observed N-H...X angles are in the range 165-176°. The hydrogen bonds are directed out of the TeS₂ plane and may be the cause of the deviations from planarity of the TeS₂X₂ groups. If so, it may explain the greater distortion in the dichloro than in the dibromo complex, the hydrogen bonds in the former being stronger.

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Received September 20, 1974.