Acta Chemica Scandinavica A 29 (1975) 141—148

The Crystal Structure of the Monoclinic Form of *trans*-Tetrachlorobis(tetramethylthiourea)tellurium(IV). An Example of Structural Change in the Solid State

STEINAR ESPERÅS, JOHN W. GEORGE,* STEINAR HUSEBYE and ØYVIND MIKALSEN

Chemical Institute, University of Bergen, N-5014 Bergen-Universitetet, Norway

Monoclinic *trans*-tetrachlorobis(tetramethylthiourea)tellurium(IV), $TeCl_4(C_5H_{12}N_2S)_2$, forms dark, red prismatic crystals, elongated along *c*, with $a = 14.009(3)$ Å, $b = 14.708(3)$ Å, $c = 10.053(2)$ Å, $\beta = 90.37(2)°$ and $Z = 4$. Data were collected by counter methods and the structure solved by a Patterson synthesis and refined by least-squares methods to a conventional *R* value of 3.5 %. The molecules are monomeric and the coordination around the central tellurium atom is distorted octahedral. Some relevant bond lengths and angles are: Te – S1 = 2.726(1) Å, Te – S2 = 2.649(1) Å, Te – Cl1 = 2.455(1) Å, Te – Cl2 = 2.530(2) Å, Te – Cl3 = 2.601(1) Å, Te – Cl4 = 2.544(2) Å, and ∠S1 – Te – Cl3 = 105.9°.

Conversion of the originally orthorhombic crystals to the monoclinic form is very slow, and takes place in the solid state. It is accompanied by small changes in cell dimensions, by significant changes in some bond lengths and angles and by rather large changes in the packing of the molecules. Also, the stereochemically inert lone pair on tellurium may have become stereochemically active during the transformation.

The solution of this structure is part of a study of the stereochemical role of the lone electron pair in complexes with central atoms possessing an $(n-1)d^{10}\ ns^2$ electronic configuration.[1–7] During our work on the structure of orthorhombic *trans*-tetrachlorobis(tetramethylthiourea)tellurium(IV), it was found that a several years old sample contained mostly monoclinic crystals, whereas the crystals were orthorhombic in fresh samples.[1] During exposure to X-rays, some orthorhombic crystals were transformed during a couple of weeks and the transformation could be followed as shifts and intensity changes of the reflections on Weissenberg films.

This structure investigation was undertaken to see which changes had taken place in the crystals and if they could be related to any stereochemical activity of the lone pair of electrons on the tellurium atom.[1,4,8–11]

Table 1. Unit cell dimensions of *trans*-$TeCl_4(tmtu)_2$ before and after transformation.

Orthorhombic form – *Pbca*	Monoclinic form – $P2_1/n$ (present investigation)
b (Å) 13.87(3)	*a* 14.009(3)
a (Å) 14.74(3)	*b* 14.708(3)
c (Å) 10.06(2)	*c* 10.053(2)
β (°) 90	90.37(2)
Vol (Å³) 2058	2069
Z 4	4

EXPERIMENTAL

The crystals used were taken from the same sample as were the crystals used for determining the structure of the orthorhombic form of tetrachlorobis(tetramethylthiourea)tellurium(IV).[1] During the intervening four and a half years, most of the crystals had become monoclinic.

For data recording, a Siemens papertape-controlled single crystal diffractometer (AED-1) was used. The diffractometer was operated as a three-circle instrument, using Mo$K\alpha$ radiation.

* Present address: Dept. of Chemistry, University of Massachusetts, Amherst, Mass. 01002, USA.

Table 2. Atomic coordinates for monoclinic *trans*-tetrachlorobis(tetramethylthiourea)tellurium(IV) in fractions of cell edges. Standard deviations in brackets.

	x	*y*	*z*
Te	0.00104(2)	0.23600(2)	0.19402(3)
S1	0.15607(9)	0.25791(10)	0.03470(13)
S2	−0.15671(8)	0.20313(9)	0.32973(12)
Cl1	−0.02828(11)	0.10722(10)	0.04384(14)
Cl2	−0.09265(12)	0.33767(12)	0.03779(16)
Cl3	0.01023(11)	0.36590(10)	0.36910(15)
Cl4	0.10261(11)	0.13725(11)	0.34707(14)
C1	−0.2209(3)	0.1139(3)	0.2560(4)
C2	−0.1153(7)	−0.0013(7)	0.3520(11)
C3	−0.2195(3)	−0.0405(4)	0.1624(6)
C4	−0.3892(6)	0.0735(6)	0.2142(10)
C5	−0.3285(5)	0.2252(5)	0.1539(9)
C6	0.2399(3)	0.3096(3)	0.1373(4)
C7	0.1635(6)	0.4594(5)	0.1151(8)
C8	0.2643(6)	0.4239(5)	0.3114(7)
C9	0.4121(5)	0.3129(7)	0.1858(8)
C10	0.3297(5)	0.1674(5)	0.1568(8)
N1	−0.1911(3)	0.0288(3)	0.2615(4)
N2	−0.3055(3)	0.1335(3)	0.2009(4)
N3	0.2267(3)	0.3943(3)	0.1824(5)
N4	0.3210(3)	0.2650(3)	0.1673(4)
H1	−0.101(6)	0.038(6)	0.416(8)
H2	−0.054(6)	−0.011(5)	0.305(8)
H3	−0.130(5)	−0.050(5)	0.387(7)
H4	−0.157(5)	−0.061(4)	0.134(6)
H5	−0.247(7)	−0.007(7)	0.080(9)
H6	−0.263(6)	−0.079(5)	0.195(8)
H7	−0.440(7)	0.115(7)	0.259(10)
H8	−0.410(6)	0.052(5)	0.135(8)
H9	−0.378(5)	0.023(5)	0.270(8)
H10	−0.359(5)	0.254(5)	0.217(7)
H11	−0.367(5)	0.221(4)	0.071(7)
H12	−0.272(5)	0.254(5)	0.129(7)
H13	0.146(5)	0.434(5)	0.024(8)
H14	0.202(5)	0.518(5)	0.113(7)
H15	0.113(6)	0.469(5)	0.167(7)
H16	0.216(5)	0.450(4)	0.366(6)
H17	0.315(5)	0.469(5)	0.302(6)
H18	0.291(4)	0.368(5)	0.354(6)
H19	0.433(5)	0.305(5)	0.275(8)
H20	0.404(5)	0.373(5)	0.165(7)
H21	0.455(6)	0.294(5)	0.117(8)
H22	0.266(5)	0.139(5)	0.168(7)
H23	0.369(5)	0.153(5)	0.082(7)
H24	0.380(5)	0.156(5)	0.236(7)

Intensity data were collected using a scintillation counter, the "five-value" measurement, and $\theta-2\theta$ scan technique.[12] Reflections out to $2\theta=56°$ were scanned with scan speed 2.5° per min with automatic setting of greater speed for strong reflections. Attenuation filters were automatically inserted in the beam to reduce counting losses. The reflections were scanned between $\theta_1=\theta-0.41°$ and $\theta_2=\theta+0.41°$, where θ is the Bragg angle for the α_1 peak. Two reference reflections were measured at intervals of 50 reflections. Of the 4958 reflections measured, 4028 had intensities greater than twice the standard deviations and were labelled as observed. The very strong reflection $\bar{1}\bar{1}\bar{1}$ was not recorded due to an error occurring during data collection.

The intensities were corrected for Lorentz and polarization effects and for absorption ($\mu=21.9$ cm^{-1}).[13] The crystal used for data collection had the following dimensions measured as distances from a common origin to crystal faces: 100 and $\bar{1}00$; 37 μ, 010 and $0\bar{1}0$; 42 μ, 001; 17 μ, $\bar{2}21$, $2\bar{2}1$, $\bar{2}\bar{2}1$ and 221; 78 μ.

Accurate unit cell dimensions were based on measurements of 20 high-order reflections and determined by a least-squares procedure. The calculated and observed densities are 1.71 and 1.70 g/cm^3, respectively.

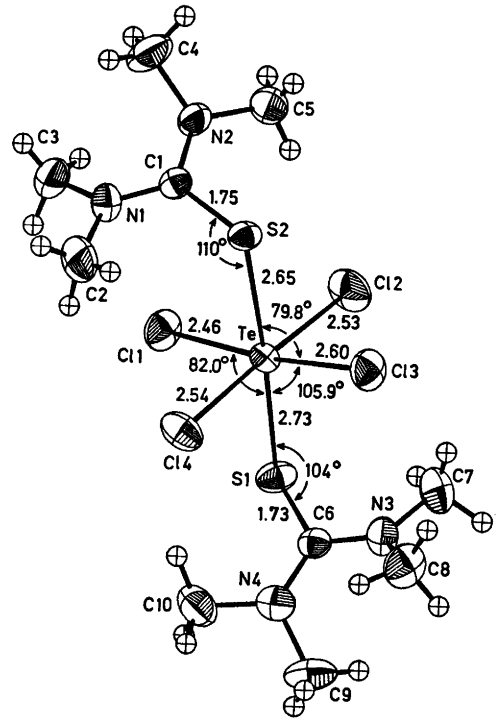

Fig. 1. Monoclinic *trans*-tetrachlorobis(tetramethylthiourea)tellurium(IV) as seen along the *c*-axis. Distances are in Å, and unlabelled spheres represent hydrogen atoms. The other atoms are represented by 50 % probability thermal ellipsoids.

Table 3. Components of atomic vibration tensors, $U \times 10^3$, in Å^2, with standard deviations, referred to crystallographic axes. For hydrogen, the expression used is $\exp[-8\pi^2 U(\sin^2\theta/\lambda^2)]$. For the other atoms, the expression is $\exp[-2\pi^2(h^2a^2U_{11}+\cdots+2hka^{-1}b^{-1}U_{12}+\cdots)]$.

Te	30.22(0.15)	32.13(0.16)	28.11(0.15)	(U_{11}, U_{22}, U_{33})
	4.68(0.13)	−0.56(0.13)	−0.58(0.10)	(U_{12}, U_{23}, U_{13})
S1	35.6(0.6)	59.6(0.9)	38.0(0.6)	
	−7.4(0.6)	−9.4(0.6)	8.3(0.5)	
S2	30.3(0.6)	41.2(0.7)	35.3(0.6)	
	−1.7(0.5)	−8.1(0.5)	4.6(0.5)	
Cl1	61.2(0.9)	48.3(0.8)	48.2(0.8)	
	−6.8(0.7)	−16.7(0.6)	3.6(0.6)	
Cl2	62.4(1.0)	66.8(1.0)	60.8(0.9)	
	16.2(0.8)	25.4(0.8)	−9.4(0.8)	
Cl3	62.0(0.9)	45.7(0.8)	54.0(0.8)	
	0.7(0.7)	−14.1(0.6)	−5.2(0.7)	
Cl4	52.8(0.9)	64.4(0.9)	46.4(0.8)	
	19.2(0.7)	11.0(0.7)	−7.2(0.6)	
C1	35.0(2.6)	36.2(2.6)	30.8(2.4)	
	−2.92(2.0)	3.4(1.9)	1.1(2.0)	
C2	75.3(5.6)	48.2(4.9)	82.7(6.5)	
	10.8(4.1)	23.1(4.8)	−17.7(4.9)	
C3	58.1(2.1)	44.1(2.8)	76.3(3.7)	
	−9.7(1.9)	−10.5(2.5)	3.1(2.2)	
C4	51.8(4.4)	72.0(5.1)	84.7(6.1)	
	−26.8(3.8)	13.7(4.7)	−19.4(4.2)	
C5	49.5(3.8)	50.5(3.9)	81.6(5.5)	
	2.3(3.2)	8.5(3.8)	−25.0(3.8)	
C6	32.2(2.5)	40.1(2.7)	31.6(2.4)	
	−2.4(2.0)	7.9(2.0)	3.3(1.9)	
C7	74.4(5.2)	43.8(3.7)	68.6(4.8)	
	12.1(3.6)	11.2(3.2)	−2.5(4.1)	
C8	71.6(4.9)	62.1(4.5)	51.6(3.3)	
	−7.4(3.9)	−17.9(3.3)	−3.8(3.4)	
C9	35.4(3.4)	101.1(6.5)	54.5(4.3)	
	−8.5(3.6)	6.7(4.1)	−8.0(3.0)	
C10	58.6(4.1)	56.9(3.9)	80.9(5.2)	
	18.3(3.2)	15.9(3.4)	22.3(3.8)	
N1	52.5(2.8)	32.5(2.4)	45.6(2.6)	
	2.2(2.0)	3.9(1.9)	−1.6(2.1)	
N2	38.7(2.4)	39.0(2.0)	55.1(2.7)	
	−6.9(1.7)	5.0(1.8)	−12.0(2.0)	
N3	53.7(2.9)	34.7(2.4)	46.0(2.6)	
	−0.6(2.1)	−0.2(2.0)	−5.1(2.1)	
N4	43.2(2.2)	54.1(2.6)	38.2(2.2)	
	1.4(2.0)	6.1(2.0)	0.2(1.7)	

H1	56(33)	H7	101(37)	H13	49(22)	H19	53(24)
H2	84(28)	H8	50(25)	H14	51(22)	H20	42(21)
H3	50(23)	H9	47(23)	H15	44(23)	H21	67(26)
H4	21(17)	H10	40(20)	H16	24(18)	H22	45(20)
H5	136(34)	H11	39(19)	H17	31(18)	H23	52(23)
H6	41(26)	H12	34(23)	H18	37(18)	H24	54(20)

STRUCTURE ANALYSIS

The structure was solved by conventional heavy atom methods. Full-matrix least-squares refinement was performed by using a program which minimizes the expression $r = \sum W(|F_o| - K|F_c|)^2$. K is a scale factor and W, the weight of a reflection, is the reciprocal of the variance of F_o. With isotropic temperature factors for all atoms (hydrogen not included) the R-factor, $R = \sum||F_o| - K|F_c||/\sum|F_o|$ reached a value of 0.08. With anisotropic temperature factors for the heavier atoms the R factor became 0.047. From a model and a difference

Table 4. Intramolecular bond lengths (Å) based on the coordinates of Table 1. Standard deviations in brackets.

Te – S1	2.726(1)	C6 – N3	1.338(5)
Te – S2	2.649(1)	C6 – N4	1.345(6)
Te – Cl1	2.455(1)	N1 – C2	1.462(10)
Te – Cl2	2.530(2)	N1 – C3	1.478(6)
Te – Cl3	2.601(1)	N2 – C4	1.474(9)
Te – Cl4	2.544(2)	N2 – C5	1.464(8)
S1 – C6	1.734(5)	N3 – C7	1.466(8)
S2 – C1	1.752(5)	N3 – C8	1.464(7)
C1 – N1	1.321(5)	N4 – C9	1.468(9)
C1 – N2	1.337(6)	N4 – C10	1.444(8)

map, all hydrogen positions were found. With anisotropic temperature factors for all atoms except hydrogen (isotropic), the structure was refined to its final R-value of 0.036. No spurious peaks were found in the final difference map.

Observed and calculated structure factors following the last refinement cycle can be obtained from the author St. Husebye upon request. Atomic scattering factors were taken from the *International Tables.*[14] Those for tellurium, sulfur and chlorine were corrected for anomalous dispersion, using the expression $f=[(f_o+\Delta F')^2+(\Delta f'')^2]^{\frac{1}{2}}$, where the values of $\Delta f'$ and $\Delta f''$ were taken from Cromers calculations.[15] Final atomic coordinates are listed in Table 2 and components of atomic vibration tensors in Table 3. Interatomic distances and angles are found in Tables 4 – 7.

RESULTS AND DISCUSSION

Molecular shape. The structure of one molecule of monoclinic *trans*-tetrachlorobis-(tetramethylthiourea)tellurium(IV) is shown in Fig. 1. The central tellurium atom is bonded to the two sulfur atoms of the tetramethylthiourea groups and to the four chlorine atoms in a distorted octahedral configuration. The bond lengths and bond angles (excluding hydrogen) are shown in Tables 4 and 5. The main deviations from a perfect octahedral structure are apparent in two of the pairs of ligand-tellurium bonds *trans* to each other, and in three bond angles on tellurium deviating considerably from 90°. These bonds and angles are Te – S1 = 2.726(1)Å and Te – S2 = 2.649(1) Å; Te – Cl1 = 2.455(1) Å and Te – Cl3 = 2.601 Å and ∠S1 – Te – Cl3 = 105.95(5)°, ∠S1 – Te – Cl1 = 81.99(5)° and ∠S2 – Te – Cl3 = 79.82(4)°. Also the interplanar angle, $TeCl_4$/TeCl2Cl4S1S2, is only 80.7°.

Comparison with the orthorhombic modification. The structure of orthorhombic *trans*-tetrachlorobis(tetramethylthiourea)tellurium-(IV) has been solved earlier in this laboratory.[1] The conversion of the crystals from an orthorhombic to a monoclinic form is accompanied by certain changes in unit cell parameters, molecular structure and in the packing of the molecules in the crystals. However, there appears to be no change in the shape of the crystals.

The unit cell parameters for the two modifications A (Orthorhombic) and B (Monoclinic) are

Table 5. Intramolecular bond angles (°), with standard deviations in brackets.

∠S1 – Te – S2	174.06(0.04)	∠Te – S2 – C1	110.3(0.2)
∠S1 – Te – Cl1	81.99(0.05)	∠S2 – C1 – N1	122.1(0.3)
∠S1 – Te – Cl2	88.71(0.05)	∠S2 – C1 – N2	117.7(0.3)
∠S1 – Te – Cl3	105.94(0.05)	∠C1 – N1 – C2	122.8(0.4)
∠S1 – Te – Cl4	88.76(0.04)	∠C1 – N1 – C3	122.8(0.3)
∠S2 – Te – Cl1	92.24(0.05)	∠C2 – N1 – C3	113.7(0.4)
∠S2 – Te – Cl2	89.80(0.05)	∠C1 – N2 – C4	122.5(0.5)
∠S2 – Te – Cl3	79.82(0.04)	∠C1 – N2 – C5	121.7(0.4)
∠S2 – Te – Cl4	92.84(0.04)	∠C4 – N2 – C5	114.0(0.5)
∠Cl1 – Te – Cl2	89.44(0.05)	∠C6 – N3 – C7	122.4(0.4)
∠Cl1 – Te – Cl3	172.07(0.05)	∠C6 – N3 – C8	121.8(0.4)
∠Cl1 – Te – Cl4	91.28(0.05)	∠C7 – N3 – C8	115.3(0.4)
∠Cl2 – Te – Cl3	90.53(0.05)	∠C6 – N4 – C9	121.8(0.5)
∠Cl2 – Te – Cl4	177.24(0.05)	∠C6 – N4 – C10	122.7(0.4)
∠Cl3 – Te – Cl4	89.14(0.05)	∠C9 – N4 – C10	114.3(0.5)
∠Te – S1 – C6	104.0(0.2)		

Table 6. Some short intramolecular distances in Å.

Te – Cl	3.647(5)	S2 – Cl2	3.656(2)
Te – C6	3.566(5)	S2 – Cl3	3.368(2)
S1 – Cl1	3.405(2)	S2 – Cl4	3.763(2)
S1 – Cl2	3.677(2)	Cl1 – C2	3.508(2)
S1 – Cl3	4.232(2)	Cl – Cl4	3.575(2)
S1 – Cl4	3.688(2)	Cl2 – Cl3	3.645(2)
S2 – Cl1	3.681(2)	Cl3 – Cl4	3.611(2)

listed in Table 1. From photographic data, the axes *a*, *b*, *c* in B corresponds to axes *b*, *a*, $-c$, respectively, in A. The only significant changes in unit cell parameters are thus found in the β angle and the *a* axis (B). They are both larger than the corresponding unit cell dimensions in A. Also the cell volume is larger in the more stable modification, B.

The changes in molecular structure is more striking. First, the center of symmetry observed in the molecules of the orthorhombic form, A, is not preserved during conversion to the monoclinic form, B. The average lengths of the Te – Cl and Te – S bonds change very little, being 2.528 and 2.669 Å, respectively, for A, as compared to 2.533 and 2.688 Å, respectively, for B. However, whereas the three linear three-center S – Te – S and Cl – Te – Cl systems are symmetric and exactly linear in A, two of them are quite asymmetric in B, both with regard to bond lengths and bond angles, although their overall lengths are not significantly different from the corresponding

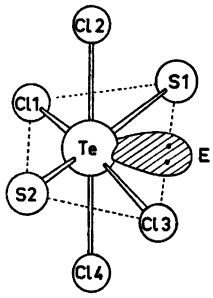

Fig. 2. The possible location of the lone pair of electrons, E, in the complex.

lengths found in A. In the monoclinic form of *trans*-tetrachlorobis(tetramethylthiourea)tellurium(IV), (B), the difference in bond lengths are 0.077 and 0.145 Å, respectively, for the bond pairs constituting the S1 – Te – S2 and Cl1 – Te – Cl3 three-center systems. It is probable that the two bonds that are elongated, Te – S1 and Te – Cl3, are the same that make up one of the two very large bond angles of 98.5° in A. One of these two, ∠S1 – Te – Cl3(B), upon transformation to the monoclinic form B, increases with 7.4°, whereas the other decreases with 6.5°. Another significant change is found in the Te – S – C angles. These are both 109.0(8)° in A, whereas ∠Te – S1 – C6 = 103.97(2)° and ∠Te – S2 – Cl = 110.3(2)° in B.

The large difference between the two sulfur valency angles may be a consequence of the changes in the Te – S bonds. The increase in

Table 7. Some short intermolecular distances in Å.

S1 – S2	$\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$-\frac{1}{2}+z$	3.395(2)
S1 – H10		»		3.20(7)
S2 – C6	$-\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$\frac{1}{2}+z$	3.428(5)
Cl1 – Cl1	$-x$,	$-y$,	$-z$	3.371(2)
Cl1 – H18	$-\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$-\frac{1}{2}+z$	3.18(6)
Cl1 – H19		»		3.04(8)
Cl2 – H14	$-x$,	$1-y$,	$-z$	3.02(8)
Cl2 – H24	$-\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$-\frac{1}{2}+z$	3.05(8)
Cl3 – H8	$-\frac{1}{2}-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$	3.07(8)
Cl3 – H8	$\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$\frac{1}{2}+z$	3.14(8)
Cl3 – H11		»	$\frac{1}{2}+z$	2.93(7)
Cl3 – H23	$-\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$\frac{1}{2}+z$	2.95(7)
Cl4 – H17	$\frac{1}{2}-x$,	$-\frac{1}{2}+y$,	$\frac{1}{2}-z$	3.11(6)
Cl4 – H3	$-x$,	$-y$,	$1-z$	2.99(7)
Cl4 – H11	$\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$\frac{1}{2}+z$	3.10(7)
H5 – H16	$-\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$-\frac{1}{2}+z$	2.36(12)
H7 – H24	$-1+x$,	y,	z	2.58(12)

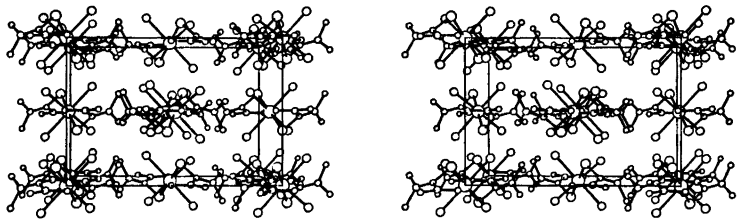

Fig. 3. A stereoscopic view of the structure of orthorhombic *trans*-tetrachlorobis(tetramethylthiourea)tellurium(IV) showing the unit cell packing. The *a* axis is horizontal, the negative *c* axis is vertical and the *b* axis points up from the paper.

the Te – S1 bond length lessens the repulsion between the tetramethylthiourea methyl groups and the chlorine atoms, thus the Te – S1 – C6 angle decreases relative to the corresponding angle in A. The opposite holds for the Te – S2 – C angle.

Lone pair activity and bonding. The seventh valency electron pair on tetravalent tellurium has previously been shown to be stereochemically inert in octahedral complexes.[9–11] This was also assumed to be the case for the orthorhombic form of *trans*-tetrachlorobis(tetramethylthiourea)tellurium(IV), (A), and has recently been indicated also from Mössbauer spectra.[16] Thus the deviation from perfect octahedral symmetry found in A, demonstrated by the S′ – Te – Cl2 and S – Te – Cl2′ angles of 98.5°,[1] probably is due to packing effects. The Mössbauer data also indicate that the bonding in the three linear S – Te – S and Cl – Te – Cl systems in A is of the three-center four-electron type, involving *p*-orbitals only on the central tellurium atom.[16]

The increased distortion from octahedral symmetry in B as compared to A may possibly be due to packing effects. But there is a characteristic feature that indicates lone pair activity, namely the aforementioned lengthening of the two bonds that constitute the large S1 – Te – Cl3 angle in B. This fact can be explained if one assumes that the lone pair of valency electrons on tellurium in form A more or less squeezes through one of the two "cracks" in the valency shell presented by the large S – Te – Cl angles in direction of the corresponding S – Cl octahedral edge. According to VSEPR theory,[9] the lone pair-bond pair repulsions would then tend to increase the Te – S1 and Te – Cl3 bond lengths and at the same time increase the S1 – Te – Cl3 angle when going from A to B. This situation is indicated in Fig. 2. Such an AB_6E structure with idealized C_{2v} symmetry has only slightly higher energy than the C_{3v} structure with the lone pair above the center of one of the octahedral faces.[17] As a result of the bond elongations, one finds a corresponding contraction of bonds *trans* to the two elongated ones. Such *trans* effects are earlier found in *cis*-square-planar complexes of divalent tellurium and interpreted as a result of one ligand atom orbital overlapping more effectively with a

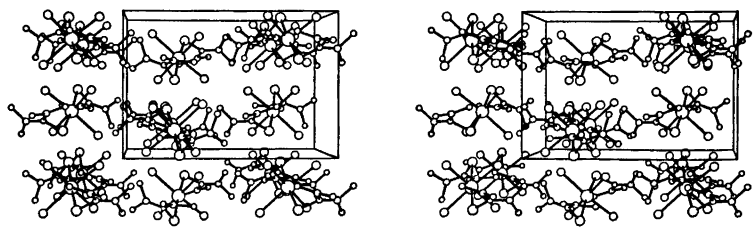

Fig. 4. A stereoscopic view of the structure of monoclinic *trans*-tetrachlorobis(tetramethylthiourea)tellurium(IV) showing the unit cell packing. The *b* axis is horisontal, the *c* axis is vertical and the *a* axis points up from the paper.

Table 8. Least squares planes through parts of the molecule. (Weights; Te:6, S and Cl:3, C and N:1).

No. of plane	Atoms defining plane	Equation of plane
1	TeCl1Cl2Cl3Cl4	$11.780x + 4.183y - 4.684z = 0.052$
2	TeCl1Cl3S1S2	$7.298x - 8.770y + 6.106z = -0.890$
3	TeCl2Cl4S1S2	$3.202x + 11.725y + 5.603z = 3.820$
4	S1C6N3N4	$-6.326x - 5.580y + 8.147z = -2.142$
5	S2C1N1N2	$-6.639x - 2.162y + 8.759z = 3.487$

No. of plane	Distances of atoms from planes in Å				
1	Te: 0.038,	Cl1: −0.142,	Cl2: 0.092,	Cl3: −0.133,	Cl4: 0.106
2	Te: 0.012,	Cl1: 0.010,	Cl3: 0.008,	S1: −0.021,	S2: −0.022
3	Te: 0.037,	Cl2: 0.055,	Cl4: 0.065,	S1: −0.102,	S2: −0.092
4	S1: −0.002,	C6: 0.017,	N3: −0.006,	N4: −0.006,	
5	S2: 0.002,	C1: −0.025,	N1: 0.010,	N4: 0.009	

Interplanar angles (°):
1 − 2 = 90.7, 1 − 3 = 80.7, 2 − 3 = 90.9, 2 − 4 = 61.0, 2 − 5 = 68.2.

common *p*-orbital on the central atom than the one *trans* to it.[18,19]

Mössbauer spectra have later been obtained for the monoclinic form of *trans*-tetrachlorobis-(tetramethylthiourea)tellurium(IV), (B), to find out if they can be interpreted in terms of some tellurium *s*-orbital character in the tellurium-ligand bonds in agreement with the above.[20] However, the bonding also here is mainly of the three-center four-electron type. In a recent structure determination of the compound $TeCl_4.PCl_5$, the tellurium atoms were found to be coordinated to six chlorine atoms in a distorted octahedral configuration.[21] Two of the ligands are bridging with an average Te − Cl bond length of 2.79 Å. For the bonds between tellurium and terminal chlorines, the average length is 2.43 Å. Thus the lone pair is here probably located on the octahedral edge between the two bridging chlorines. The Te − Cl bonds *trans* to the long ones are significantly shorter than the other bonds from tellurium to terminal chlorines. The lone pair activity is also reflected in the tellurium bond angles.

Molecular packing. The packing of the complex molecules both in the orthorhombic modification and the monoclinic one are shown as stereo pairs in Figs. 3 and 4, respectively. It can clearly be seen that there are great changes in the packing as a result of the transformation from one form to the other, in spite of the small changes in cell dimensions. The A molecules have the tellurium atom at a center of symmetry and are related through screw axes and glide planes whereas the B molecules are interrelated through screw axes, glide planes and centers of symmetry.

In both cases, the normal to the $TeCl_4$ plane is roughly parallel (makes an angle below 30°) to the viewing direction, and along *c* the molecules are stacked so that every other one is one half axis length above or below the next one. For the A molecules, the twofold screw axis parallel to *b* prevents near contacts between thiourea sulfur atoms on neighbour molecules (Min. S···S contact is 5.59 Å). For the B molecules, there is no screw axis in the corresponding direction; also the molecular S − Te − S axis in the B molecules is tilted nearly the same angle relative to the *bc* plane. This makes possible a short intermolecular S···S approach of only 3.40 Å in the *c*-direction.

The change in packing can also be visualized by looking at the positions of the central tellurium atoms in the four molecules in the unit cells. In A, the tellurium atoms are situated at 0,0,0; 0,½,½; ½,½,0; ½,0,½. In B, after moving the origin to the tellurium position in the asymmetric unit and interchanging *b* and *a*

plus c and $-c$, one gets 0,0,0; 0.028,½,½; ½,0.498,−0.112; 0.528,0.002,0.388 as coordinates for the tellurium atoms, referred to the original A-cell. Thus the center of the molecules are moved very little in the a and b directions during the conversion, but every other molecule has moved 1.1 Å in the c direction.

Such solid state transformations have been observed earlier, especially in organic compounds, but they usually occur at elevated temperatures.[22]

Other distances and angles. The C−S distances in the two tetramethylthiourea groups in monoclinic *trans*-tetrachlorobis(tetramethylthiourea)tellurium(IV) are not significantly different, C6−S1 and C1−S2 being 1.734(5) and 1.752(5) Å, respectively. These values are normal for complexes containing tetramethylthiourea ligands.[1,19] However, the shorter bond corresponds to a long S−Te bond and *vice versa*, so the difference may be real. The C−N partial double bond lengths vary between 1.321 and 1.345 Å with 1.335 Å as the average, while the C−N single bonds from nitrogen to methyl carbon vary in length between 1.444 and 1.478 Å with 1.465 Å as the average. The above values are normal for tetramethylthiourea ligands.

All twentyfour hydrogen atoms refined satisfactorily. The C−H bond lengths vary between 0.82 and 1.07 Å with standard deviations ranging from 0.07 to 0.10 Å. Their average length is 0.96 Å.

The angles on the nitrogen atoms correspond to sp^2 hybridization on these atoms, the same do the angles on C1 and C6.

The tetramethylthiourea groups have a roughly planar SCN_2 skeleton (Table 8), but the carbon atoms in methyl groups bonded to the nitrogen atoms, are located above or below the SCN_2 plane, in order to minimize steric repulsion. Each nitrogen atom is bonded to three carbon atoms and the resulting NC_3 groups are all nearly planar. The interplanar angles for neighbouring NC_3 groups have an average value of 130.7° and the interplanar NC_3/SCN_2 angles on the same ligand have an average value of 153.5°.

REFERENCES

1. Husebye, S. and George, J. W. *Inorg. Chem. 8* (1969) 313.
2. Esperås, S., Husebye, S. and Sværen, S. E. *Acta Chem. Scand. 25* (1971) 3539.
3. Esperås, S. and Husebye, S. *Acta Chem. Scand. 26* (1972) 3293.
4. Husebye, S. and Sværen, S. E. *Acta Chem. Scand. 27* (1973) 763.
5. Esperås, S. and Husebye, S. *Acta Chem. Scand. 27* (1973) 706.
6. Esperås, S., George, J. W., Husebye, S. and Mikalsen, Ø. *Acta Chem. Scand. 27* (1973) 1089.
7. Esperås, S. and Husebye, S. *Acta Chem. Scand. 27* (1973) 1827.
8. Urch, D. S. *J. Chem. Soc.* (1964) 5775.
9. Gillespie, R. J. *J. Chem. Educ. 47* (1970) 18.
10. Cox, J. J. and Whiston, C. D. *Educ. Chem. 7* (1970) 234.
11. Wynne, K. J. *J. Chem. Educ. 50* (1973) 328.
12. Troughton, P. G. H. *Siemens Rev.* XXXVII (1970), Fourth Special Issue, p. 9.
13. Coppens, P., Leiserowitz, L. and Rabinovich, D. *Acta Crystallogr. 18* (1965) 1035.
14. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. III, p. 204.
15. Cromer, D. T. *Acta Crystallogr. 18* (1965) 17.
16. Cheyne, B. M., Jones, C. H. W. and Vasudek, P. *Can. J. Chem. 50* (1972) 3677.
17. Cotton, F. A. and Wilkinson, G. *Advanced Inorganic Chemistry*, 3rd Ed., Interscience, New York 1972, p. 140.
18. Foss, O. *Acta Chem. Scand. 16* (1962) 779.
19. Foss, O. In Andersen, P., Bastiansen, O. and Furberg, S., Eds., *Selected Topics in Structure Chemistry*, Universitetsforlaget, Oslo 1967, p. 145.
20. Jones, C. H. W. *Private communication.*
21. Krebs, B., Buss, B. and Berger, W. *Z. Anorg. Allg. Chem. 397* (1973) 1.
22. Paul, I. C. and Curtin, D. Y. *Accounts Chem. Res. 6* (1973) 217.

Received July 8, 1974.