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The Crystal and Molecular Structure of *trans*-Tetrabromo- and *trans*-Tetrachlorobis(tetramethylthiourea)tellurium(IV)

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Both *trans*-tetrabromo- and *trans*-tetrachlorobis(tetramethylthiourea)tellurium(IV), $TeX_4(C_5H_{12}N_2S)_2$ (X = Br, Cl), are dark red substances forming orthorhombic crystals of space group symmetry Pbca and having four molecules per unit cell. Measured and calculated densities are 2.21 and 2.19 and 1.70 and 1.72 g cm^{-3}, for the bromide and chloride, respectively. The unit cell dimensions of the bromide are $a = 14.98 \pm 0.03$ Å, $b = 13.88 \pm 0.03$ Å, and $c = 10.40 \pm 0.02$ Å. For the chloride these are $a = 14.74 \pm 0.03$ Å, $b = 13.87 \pm 0.03$ Å, and $c = 10.06 \pm 0.02$ Å. Diffraction data for 861 and 596 independent, observed reflections for the bromide and chloride, repesctively, were collected using Cu Kα radiation and the multiple-film Weissenberg technique. Reflection intensities were estimated visually. In determining the structure of the bromide Patterson projections on *h*0*l* and *hk*0 revealed the approximate positions of Te, Br, and S atoms. The positions of the C and N atoms were found by three-dimensional Fourier methods, and full-matrix, three-dimensional, least-squares refinement led to a final, conventional *R* value of 0.090. The refinement of the chloride proceeded, using trial atomic positions corresponding to those of the bromide structure, to an *R* value of 0.083. As required by tellurium's occupancy of a center of symmetry in the unit cell, the two sulfur atoms of each molecule are in *trans* positions. With the four halogen atoms they form a slightly distorted octahedral arrangement around the tellurium atom. The Te–S bond lengths of 2.707 ± 0.01 and 2.699 ± 0.008 Å in the bromide and chloride, respectively, are significantly longer than the sum of the covalent radii, but the Te–Br distances of 2.707 ± 0.007 and 2.686 ± 0.007 Å and the Te–Cl distances of 2.536 ± 0.008 and 2.520 ± 0.008 Å are in accord with the covalent radii sums.

Introduction

The geometry of four- and six-coordinated tellurium(IV) molecules and ions is subject to possible distortion effects arising from the presence of an unshared electron pair associated with tellurium(IV). For those four-coordinated species whose structures have been investigated, a configuration consistent with a stereochemically active role for this electron pair has been found. Thus, crystalline α-dimethyltellurium dichloride[2] $(CH_3)_2TeCl_2$, and tellurium(IV) chloride, $TeCl_4$, either in the gas phase[3] or in benzene solution,[4] have been described as trigonal-bipyramidal molecules with the electron pair occupying one of the equatorial positions. In six-coordinated species, however, the electron pair appears to play no detectable role in determining the disposition of ligand atoms or groups about the central atom and a regular octahedral configuration results. X-Ray crystallographic examination provides such evidence for hexachlorotellurates[5,6] and hexabromotellurates[7,8] and confirmation is afforded by the results of nuclear quadrupole resonance,[9,10] vibrational,[11] and Mössbauer[12] spectroscopic investigations. This paper describes the complete structural investigation of two isomorphous examples of six-coordinated tellurium(IV) complexes, *trans*-tetrabromo- and *trans*-tetrachlorobis(tetramethylthiourea)tellurium(IV), $(C_5H_{12}N_2S)_2TeX_4$ (X = Br, Cl).

Experimental Section

The dark red, platelike bromide crystals used were those previously prepared by a solution reaction of tellurium dioxide, tetramethylthiourea, and hydrobromic acid in an aqueous methanol–hydrochloric acid medium.[13] The space group is Pbca, $Z = 4$, and the cell dimensions are $a = 14.98 \pm 0.03$ Å, $b = 13.88 \pm 0.03$ Å, and $c = 10.40 \pm 0.02$ Å. The measured and calculated densities are 2.21 and 2.19 g cm^{-3}, respectively.[13]

Using a multiple-film technique, integrated zero-layer and equiinclination Weissenberg photographs of *h*0*l* and *hkl*, with l = 0 through 6, were taken employing Cu Kα radiation. Reflection intensities were estimated visually. Although exposure times up to 150 hr were used, the crystals were so small that only 861 of 1625 independent reflections having $\theta \leq 0.985$ were observed. While the Cu Kα radiation used to collect the intensity data results in a rather high μ (230 cm^{-1}), no absorption correction was applied because of the small crystal dimensions. However, the usual Lorentz and polarization corrections were made. Computations were carried out using a set of programs made available by the Weizmann Institute, Rehovoth, Israel, and modified for use on the University of Bergen's IBM 360-50 H computer by Dr. Dove Rabinovich. The least-squares program in this set provides full-matrix refinement.

The red, prism-shaped chloride crystals were obtained by the addition of methanol to a hydrochloric acid solution of tellurium dioxide and tetramethylthiourea.[13] Space group examination of a number of crystals which had been stored in a refrigerator for 7 years demonstrated the presence of a space group other than Pbca, but orthorhombic crystals isomorphous with the bromide complex were found in a fresh sample of the material. The cell dimensions are $a = 14.74 \pm 0.03$ Å, $b = 13.87 \pm 0.03$ Å, and $c = 10.06 \pm 0.02$ Å, and the measured and calculated densities are 1.70 and 1.72 g cm^{-1}, respectively.[13]

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Intensity data for *hkl*, with k = 0, 1, 3, and *hkl*, with l = 0, 1, 3, were obtained for the chloride crystals in the manner described above for the bromide complex. Of the total of 997 independent reflections obtainable using Cu Kα radiation 596 were observed. Corrections for the Lorentz effect, polarization, and secondary extinction were applied. The very small size of the crystals used limited absorption effects (μ = 185 cm^{-1}), and no absorption correction was made. Computations, including a full-matrix, least-squares refinement (SFLS version 1968), on the chloride complex were made using a library of programs prepared by Mr. Knut Maartmann-Moe of the Chemical Institute, University of Bergen.

Structure Determination and Refinement

The space group of these compounds requires that each of the four tellurium atoms in the unit cell occupies a special position coincident with a center of symmetry. Attention was directed first to the structure of the bromide complex. Using Patterson projections on *h*0*l* and *hk*0 the approximate positions of the bromine and sulfur atoms were determined. A Fourier diagram, using signs based upon the heavy-atom contributions alone, was then prepared for each of these projections and, together with a model constructed using assumed bond lengths and angles, it was possible to locate tentatively most of the carbon and nitrogen atoms. Full-matrix, least-squares refinement of the structure was then begun. Successive repetition of the technique of alternate Fourier analysis and least-squares refinement failed, however, to fix satisfactorily the positions of all seven carbon and nitrogen atoms in the asymmetric unit. This was indicated by the failure to reduce the reliability index, R, defined as $\Sigma(||F_o| - |F_c||)/\Sigma|F_o|$, below 0.20. Unobserved reflections are included when F_c exceeds the F_o associated with the minimum observable intensity. No effort was made to locate hydrogen atoms, and no account was taken of them in any part of the computations.

Examination of a three-dimensional Fourier map of one-eighth of a unit cell made possible the immediate location of all atomic positions. A few cycles of least-squares refinement, with isotropic temperature factors assigned to all atoms, yielded an R of 0.12. Duplicate reflections were then removed, anisotropic temperature factors were applied to tellurium, bromine, and sulfur atoms, and, after a series of eight refinement cycles, the R index reached its final value of 0.090.

The least-squares program employed in the refinement of the bromide structure minimizes the expression $\Sigma w[|F_o| - b|F_c|]^2/\Sigma w|F_o|^2$, where b is a variable scale factor in the computation and w, the relative weight assigned to a reflection, is determined as the inverse of the square of the standard deviation of the observation, $1/\sigma^2(F)$. $\sigma^2(F)$ is evaluated as $(ba_1)^2 + [(a_2F_o)^2/4y]$, where y is a variable related to the reliability with which the intensity of a given reflection is measured, and a_1 and a_2 are constants fixed at 3.0 and 1.0, respectively.

The chloride structure determination was begun in a straightforward way by assigning trial positions to the atoms of the asymmetric unit according to the positions found for the corresponding atoms of the bromide complex. Using *hk*0 and *h*0*l* intensity data an R value of 0.20 was immediately obtained. Addition of data for the remaining four layers and removal of duplicate reflections were followed by three cycles of full-matrix, least-squares refinement yielding R = 0.10. After introduction of anisotropic temperature factors for tellurium, sulfur, and chlorine atoms three refinement cycles gave R = 0.085. The final R value of 0.083 was obtained after the application of a correction for secondary extinction. The least-squares program used for the chloride structure refinement minimizes $\Sigma w[|F_c| - |F_o|]^2$, where w, the weight assigned a reflection, is defined by the expression $a/(a + b|F_o| + c|F_o|^2)$. As used here, a = 160, b = 1, and c = 0.002.

The final positional parameters and their estimated standard deviations for all atoms in the asymmetric units of the complexes are given in Tables I and II. Components of atomic vibration tensors are shown in Table III. Shifts in these parameters during the final refinement cycle of each structure determination were less than 5% of the corresponding estimated standard deviations.

Table I

Atomic Coordinates for *trans*-Tetrabromobis(tetramethylthiourea)tellurium(IV) in Fractions of Cell Edges[a]

	x	y	z
Te	0	0	0
S	0.0418 (5)	−0.1651 (6)	0.1248 (8)
Br_1	0.1144 (2)	0.1003 (3)	0.1506 (4)
Br_2	0.1223 (2)	−0.0093 (3)	−0.1884 (4)
C_1	0.1126 (16)	−0.2357 (18)	0.0283 (27)
N_1	0.1957 (14)	−0.2057 (15)	0.0007 (24)
C_2	0.2415 (20)	−0.2396 (24)	−0.1196 (30)
C_3	0.2456 (22)	−0.1321 (23)	0.0706 (31)
N_2	0.0847 (14)	−0.3206 (15)	−0.0087 (23)
C_4	0.1432 (19)	−0.4028 (21)	−0.0306 (30)
C_5	−0.0138 (20)	−0.3444 (22)	−0.0206 (33)

[a] Tellurium is at a center of symmetry. Estimated standard deviations (×10^4) are given in parentheses.

Table II

Atomic Coordinates for *trans*-Tetrachlorobis(tetramethylthiourea)tellurium(IV) in Fractions of Cell Edges[a]

	x	y	z
Te	0	0	0
S	0.0438 (3)	−0.1625 (4)	0.1329 (6)
Cl_1	0.1086 (4)	0.0980 (5)	0.1415 (7)
Cl_2	0.1161 (4)	−0.0113 (5)	−0.1833 (7)
C_1	0.1165 (11)	−0.2323 (15)	0.0341 (22)
N_1	0.1987 (10)	−0.2010 (13)	−0.0010 (17)
C_2	0.2427 (14)	−0.2326 (21)	−0.1281 (36)
C_3	0.2435 (14)	−0.1201 (20)	0.0728 (28)
N_2	0.0844 (10)	−0.3192 (12)	−0.0072 (18)
C_4	0.1473 (14)	−0.4021 (18)	−0.0182 (25)
C_5	−0.0110 (14)	−0.3450 (18)	−0.0084 (28)

[a] Tellurium is at a center of symmetry. Estimated standard deviations (×10^4) are given in parentheses.

Final observed and calculated structure factors are listed in Tables IV and V. Commonly used atomic

TABLE III

COMPONENTS OF ATOMIC VIBRATION TENSORS, U, IN Å^2 (STANDARD DEVIATIONS IN PARENTHESES) REFERRED TO CRYSTALLOGRAPHIC AXES[a]

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
			$(C_5H_{12}N_2S)_2TeBr_4$			
Te	44.04 (1.1)	50.46 (1.1)	46.47 (2.0)	−2.65 (1.3)	−3.82 (1.7)	1.59 (1.3)
S	56.02 (4.2)	58.36 (4.4)	48.95 (5.8)	2.13 (3.7)	−0.82 (4.6)	9.71 (4.1)
Br_1	72.34 (2.0)	72.23 (2.1)	83.27 (3.0)	−10.71 (1.8)	−14.36 (2.2)	−14.51 (2.2)
Br_2	66.86 (1.9)	94.55 (2.8)	78.98 (3.1)	8.42 (2.2)	5.84 (2.2)	18.09 (1.9)
C_1			46.78 (6.3)			
N_1			55.61 (5.9)			
C_2			71.03 (9.0)			
C_3			71.51 (9.1)	u values		
N_2			51.66 (5.6)			
C_4			60.89 (8.1)			
C_5			70.09 (9.1)			
			$(C_5H_{12}N_2S)_2TeCl_4$			
Te	27.95 (0.7)	39.90 (0.8)	36.20 (1.0)	−2.18 (1.4)	0.85 (0.4)	−0.19 (0.3)
S	37.33 (2.1)	39.22 (2.4)	41.42 (2.9)	−2.79 (3.8)	3.36 (1.2)	1.46 (0.9)
Cl_1	47.29 (2.5)	60.23 (3.5)	59.58 (4.6)	−13.10 (4.6)	−6.06 (1.7)	−3.38 (1.2)
Cl_2	53.14 (2.9)	78.00 (4.7)	47.87 (3.9)	−0.48 (4.9)	8.37 (1.5)	4.13 (1.3)
C_1			32.54 (4.2)			
N_1			36.39 (3.7)			
C_2			62.11 (7.8)			
C_3			52.87 (6.5)	u values		
N_2			34.32 (3.5)			
C_4			46.55 (5.3)			
C_5			47.01 (5.5)			

[a] All values have been multiplied by 10^3. For Te, S, Br, and Cl atoms the expression used is $\exp\{-2\pi^2[U_{11}(ha^*)^2 + U_{22}(kb^*)^2 + U_{33}(lc^*)^2 + a^*b^*hkU_{12} + 2b^*c^*klU_{23} + 2a^*c^*hlU_{31}]\}$. For C and N atoms the expression used is $\exp(-2\pi^2u^2H^2)$.

scattering factor data for tellurium,[14] bromine,[15] chlorine,[16] sulfur,[16] carbon,[17] and nitrogen[17] were employed. No correction for anomalous dispersion was introduced.

Description of the Structures

The previously reported space group determinations of these complexes[13] suggested the occupancy of centers of symmetry by tellurium atoms. There is no indication that such centers could be false centers resulting from a statistical distribution of nonsymmetric molecules, and, therefore, a stereochemical role for the unshared electron pair associated with the tellurium atom is ruled out.

Figure 1 is a representation of a single molecule of the bromide complex viewed down the crystallographic c axis, and Figure 2 shows the chloride molecule viewed up the crystallographic a axis. As may be seen from these figures and from the values of bond lengths and angles listed in Tables VI and VII the halogen and sulfur atoms are distributed in an approximate *trans*-octahedral manner about the tellurium atom. As required by tellurium's occupancy of a center of symmetry the S–Te–S′ grouping is linear, and the departure of the S′–Te–X_2 angle from 90° must be interpreted as resulting from lattice-packing effects, rather than as a possible distortion induced by the unshared electron pair.

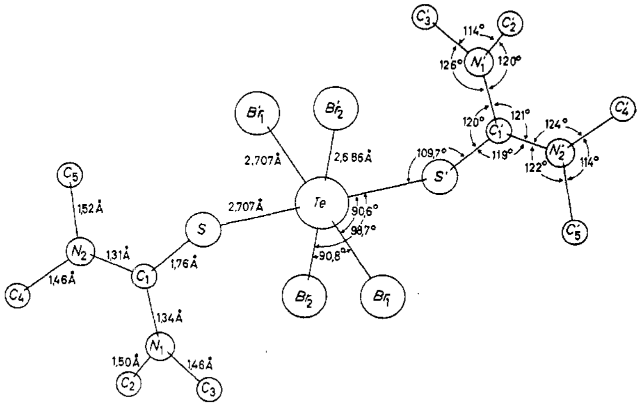

Figure 1.—The $(C_5H_{12}N_2S)_2TeBr_4$ molecule at (0, 0, 0) viewed down the crystallographic c axis.

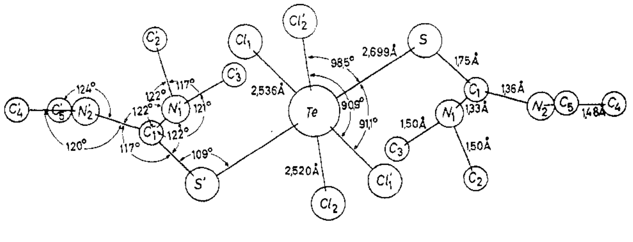

Figure 2.—The $(C_5H_{12}N_2S)_2TeCl_4$ molecule at (0, 0, 0) viewed up the crystallographic a axis.

The resulting short S–Br_2 and S–Cl_2 contact distances of 3.51 and 3.41 Å (see Table IX) are probably influential in each case in opening the Te–S–C_1 angle to about 109°. This latter value lies at the upper end of the

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TABLE IV

OBSERVED AND CALCULATED STRUCTURE FACTORS (×10) FOR $(C_5H_{12}N_2S)_2TeBr_4$[a]

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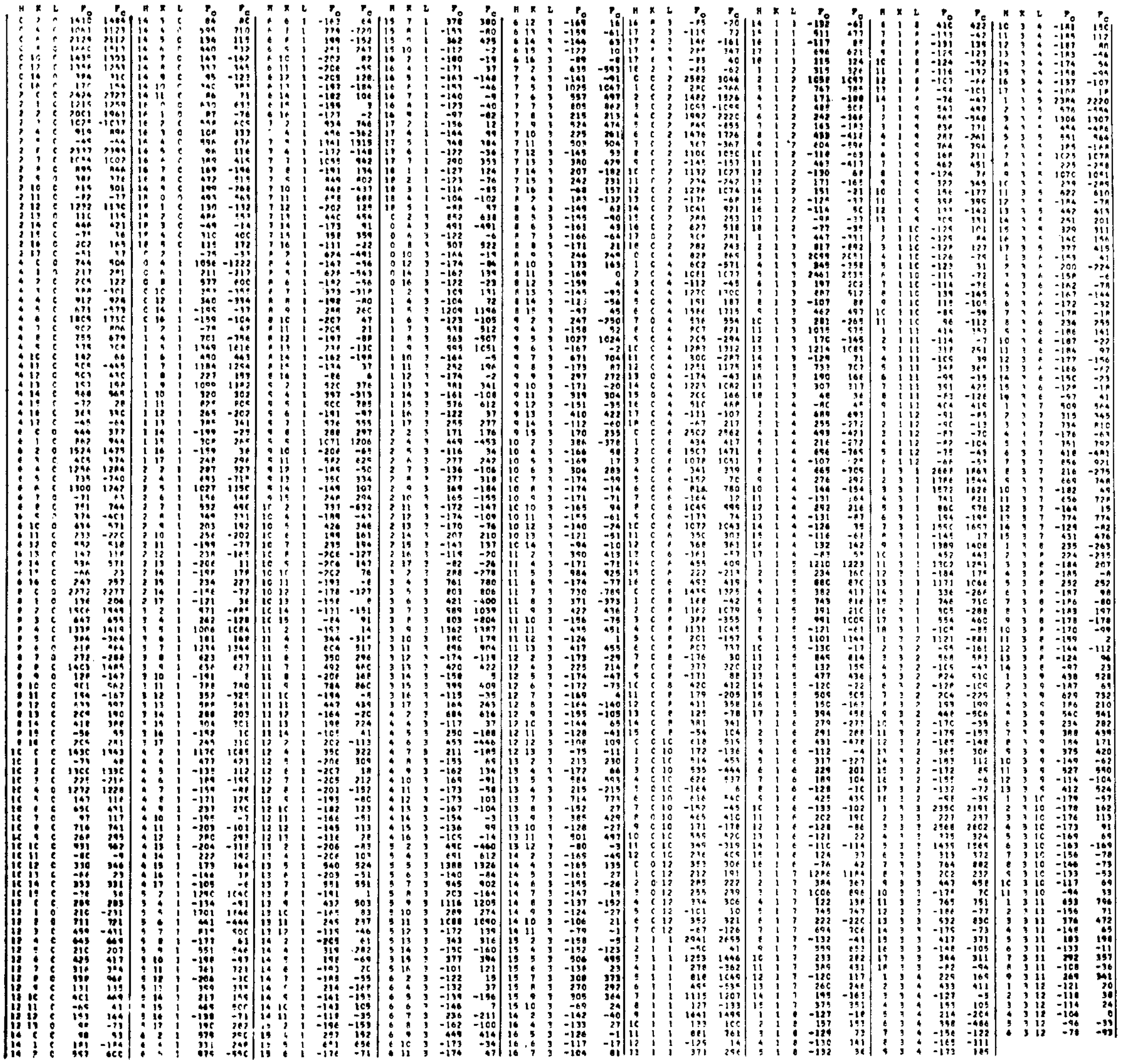
[a] Unobserved reflections are denoted by negative F_o values.

TABLE V

OBSERVED AND CALCULATED STRUCTURE FACTORS (×10) FOR $(C_5H_{12}N_2S)_2TeCl_4$[a]



[a] Unobserved reflections are denoted by negative F_o values.

TABLE VI

BOND LENGTHS AND ANGLES AND THEIR STANDARD DEVIATIONS IN *trans*-TETRABROMOBIS(TETRAMETHYLTHIOUREA)TELLURIUM(IV)[a]

Bonds, Å		Angles, deg	
Te–S	2.707 ± 0.01	Br_1–Te–Br_2	90.8 ± 0.1
Te–Br_1	2.707 ± 0.007	S′–Te–Br_1	90.6 ± 0.2
Te–Br_2	2.686 ± 0.007	S′–Te–Br_2	98.7 ± 0.2
S–C_1	1.76 ± 0.03	Te–S–C_1	109.7 ± 0.9
C_1–N_1	1.34 ± 0.03	S–C_1–N_1	120.5 ± 1.9
C_1–N_2	1.31 ± 0.03	S–C_1–N_2	118.5 ± 1.9
N_1–C_2	1.50 ± 0.04	C_1–N_1–C_2	120.3 ± 2.3
N_1–C_3	1.46 ± 0.04	C_1–N_1–C_3	125.8 ± 2.4
N_2–C_4	1.46 ± 0.04	C_1–N_2–C_4	124.0 ± 2.2
N_2–C_5	1.52 ± 0.04	C_1–N_2–C_5	122.1 ± 2.2
		N_1–C_1–N_2	120.8 ± 2.3
		C_2–N_1–C_3	113.6 ± 2.3
		C_4–N_2–C_5	113.7 ± 2.1

[a] Esd values for Te–S and Te–Br distances have been corrected to include standard deviations in cell dimensions.

TABLE VII

BOND LENGTHS AND ANGLES AND THEIR STANDARD DEVIATIONS IN *trans*-TETRACHLOROBIS(TETRAMETHYLTHIOUREA)TELLURIUM(IV)[a]

Bonds, Å		Angles, deg	
Te–S	2.699 ± 0.008	Cl_1–Te–Cl_2	90.9 ± 0.2
Te–Cl_1	2.536 ± 0.008	S′–Te–Cl_1	91.1 ± 0.2
Te–Cl_2	2.520 ± 0.008	S′–Te–Cl_2	98.5 ± 0.2
S–C_1	1.75 ± 0.02	Te–S–C_1	109.0 ± 0.8
C_1–N_1	1.33 ± 0.02	S–C_1–N_1	121.7 ± 1.6
C_1–N_2	1.36 ± 0.03	S–C_1–N_2	116.8 ± 1.3
N_1–C_2	1.50 ± 0.04	C_1–N_1–C_2	121.5 ± 1.8
N_1–C_3	1.50 ± 0.03	C_1–N_1–C_3	120.9 ± 1.8
N_2–C_4	1.48 ± 0.03	C_1–N_2–C_4	119.6 ± 1.6
N_2–C_5	1.45 ± 0.03	C_1–N_2–C_5	123.9 ± 1.7
		N_1–C_1–N_2	121.5 ± 1.8
		C_2–N_1–C_3	116.8 ± 1.7
		C_4–N_2–C_5	114.5 ± 1.7

[a] Esd values for Te–S and Te–Cl distances have been corrected to include standard deviations in cell dimensions.

TABLE VIII

BOND LENGTHS AND ANGLES IN CRYSTALLINE TETRAMETHYLTHIOUREA[a]

Bonds, Å		Angles	
S–C_1	1.68 ± 0.01		
C_1–$N_1(N_2)$	1.37 ± 0.01	C_1–N–$C_3(C_5)$	126° 36′
N–$C_2(C_4)$	1.46 ± 0.01	C_1–N–$C_2(C_4)$	115° 47′
N–$C_3(C_5)$	1.47 ± 0.01	$C_2(C_4)$–N–$C_3(C_5)$	115° 49′

[a] Values from ref 21.

TABLE IX

BOND LENGTHS IN TETRAMETHYLTHIOUREA COMPLEXES OF TELLURIUM(II)[22]

Complex	S–C, Å	C_1–N, Å
$Te(tmtu)Br_2$	1.75 ± 0.02	1.32–1.35
$Te(tmtu)Cl_2$	1.79 ± 0.06	1.36–1.40
trans-$Te(tmtu)_2(SeCN)_2$	1.74 ± 0.03	1.34–1.39

TABLE X

NONBONDED INTRAMOLECULAR DISTANCES (Å)

	$(C_5H_{12}N_2S)_2TeBr_4$		
Te–C_1	3.69[a]	S–N_2	2.65[a]
Te–C_3	4.18	C_1–C_2	2.47[a]
Br_1–Br_2	3.84[a]	C_1–C_3	2.50[a]
Br_1–C_3	3.87	C_1–C_4	2.44[a]
Br_2–S	3.51[a]	C_1–C_5	2.47[a]
Br_2–C_1	3.87	C_2–C_3	2.48[a]
Br_2–C_2	3.73	C_2–C_4	2.86
Br_2–C_3	3.69	N_1–C_4	2.87
S–C_3	3.14	N_2–C_2	2.85
S–C_5	3.03	N_1–N_2	2.31[a]
S–N_1	2.70[a]	C_4–C_5	2.49[a]
	$(C_5H_{12}N_2S)_2TeCl_4$		
Te–C_1	3.67[a]	S–N_2	2.66[a]
Te–C_3	4.02	C_1–C_2	2.47[a]
Cl_1–Cl_2	3.55[a]	C_1–C_3	2.47[a]
Cl_1–C_3	3.69	C_1–C_4	2.46[a]
Cl_2–S	3.41[a]	C_1–C_5	2.48[a]
Cl_2–C_1	3.77	C_2–C_3	2.55[a]
Cl_2–C_2	3.64	C_2–C_4	2.96
Cl_2–C_3	3.53	N_1–C_4	2.90
S–C_3	3.06	N_2–C_2	2.89
S–C_5	3.01	N_1–N_2	2.35[a]
S–N_1	2.70[a]	C_4–C_5	2.47[a]

[a] Two atoms bonded to a common atom.

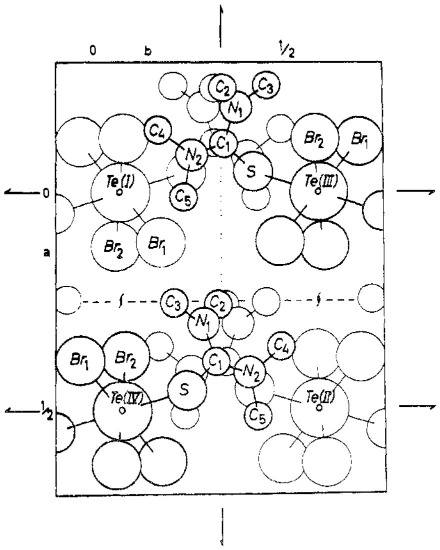


Figure 3.—The molecular arrangement of $(C_5H_{12}N_2S)_2TeBr_4$ looking down the *c* axis. Te(I) and Te(II) are at $z = 0$; Te(III) and Te(IV) are at $z = {}^1/_2$.

range of sulfur valency angles[18] (where sulfur is joined to two other atoms only). The averages of the Te–Br and Te–Cl distances in the two complexes are in good agreement with reported bond lengths in hexabromo-[7,8] and hexachlorotellurate[5,6] species. The Te–S distance of 2.707 ± 0.01 Å in the bromide complex is also significantly greater than the sum of the octahedral radii of tellurium(IV), proposed[19] as 1.54–1.56 Å from observations on measured Te–X distances in TeX_6^{2-} species, and the single bond covalent radius of sulfur, 1.04 Å. While this might result from interaction with the large bromine atoms in the equatorial plane of the complex, it should be noted that the corresponding distance in the isomorphous chloride, in which the steric effect of the halogen atoms should be much less pronounced, is 2.699 ± 0.008 Å. Arguments based upon tellurium orbital hybridization changes, *e.g.*, a small s character of the tellurium orbital used to bond to sulfur resulting in an increase in the Te–S distance, do not appear entirely satisfactory for it would then be expected that the increased s character of the orbitals used in Te–X bond formation would result in bond lengths observably shorter than those of TeX_6^{2-}. This, however, is not the case. An alternative view of the tellurium bond system as being composed of a four-electron, three-centered S–Te–S arrangement making use of p orbitals only from the three atoms, plus a square-planar disposition of Te–X bonds, offers no descriptive advantages. It is interesting that the Te(IV)–S distances are very similar to those occurring in centrosymmetric square-planar Te(II) complexes and also are about equal to the average Te–S bond length in species containing asymmetric, linear, three-centered S–Te(II)–S bond systems, despite the greater charge associated with tellurium(IV).[19]

Application of a standard significance test[20] to the differences between comparable bond lengths in the tetramethylthiourea parts of the complexes and to the differences between these distances and those reported for crystalline tetramethylthiourea[21] (Table VIII) results in the following conclusions. (a) In keeping with the donor action of sulfur toward tellurium, the C–S distances in the complexes are significantly greater than the C–S distance in crystalline tetramethylthiourea. (b) A shortening of the C_1–N distances in the complexes might be anticipated if redistribution of charge around C_1 resulted in increased π character for C_1–N when sulfur bonds to tellurium. Comparison of observed C_1–N bond lengths in the complexes with those

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TABLE XI

INTERMOLECULAR NONBONDED DISTANCES, Å. THE TELLURIUM ATOM OF THE MOLECULE TO WHICH A SPECIFIED ATOM BELONGS IS INDICATED BY THE ROMAN NUMERAL (SEE FIGURE 3)

$(C_5H_{12}N_2S)_2TeBr_4$		$(C_5H_{12}N_2S)_2TeCl_4$	
Br_1(I)–C_2(IV)	3.76	Cl_1(I)–C_2(IV)	3.70
Br_2(I)–C_3(IV)	3.75	Cl_2(I)–C_3(IV)	3.69
Br_2(IV)–C_4(II)	3.78	Cl_2(IV)–C_4(II)	3.61
S(II)–C_5(IV)	3.78	S(II)–C_5(IV)	3.70
C_2(IV)–C_3(II)	3.68	C_2(IV)–C_3(II)	3.64
C_3(IV)–C_5(II)	3.66	C_3(IV)–C_5(III)	3.71
C_3(I)–C_4(II)	3.74	C_3(I)–C_4(II)	3.55
		C_1(II)–C_2(IV)	3.91

in the crystalline ligand seems to support such a prediction, but the differences in bond lengths are not clearly significant. (c) The N–CH_3 distances differ insignificantly, both from each other in the complexes and from the corresponding bond lengths in the crystalline ligand.

The structures of a few tetramethylthiourea complexes of tellurium(II) have been determined, and S–C bond lengths and the ranges of C_1–N distances are listed in Table IX.[22] The results for these complexes also suggest a significantly longer S–C bond than that found in the free ligand.

Considerably more data regarding complexes of thiourea are available, and it is interesting that in some cases, bis(thiourea)silver(I) chloride,[23] *trans*-dichlorotetrakis(thiourea)cobalt(II),[24] and tris(thiourea)zinc(II) sulfate,[25] for example, the S–C distances are in close agreement with the value reported for the free ligand.[26] However, for other complexes such as mono(thiourea)cadmium(II) sulfate dihydrate,[27] bis(thiourea)nickel(II) thiocyanate,[28] and bis(thiourea)zinc chloride,[29] there is uncertainty regarding the significance of the apparent elongation of the C–S linkage.

In Table X the nonbonded intramolecular contact distances shorter than the sum of the van der Waals radii are listed. Many of these, which are marked, involve atoms which are bonded to a common atom, and interatomic distances substantially less than the van der Waals radii sum are expected.[30] The S–C and several of the Br–C and Cl–C contact distances given in the table are quite short, however. For each complex the close approach of the two $(CH_3)_2N$– groups bonded to C is illustrated by the very short C_2–C_4, N_1–C_4, and N_2–C_2 distances. That strong forces are operating in this region of the structure is also apparent from the small value for the C_2–N_1–C_3 and C_4–N_2–C_5 angles.

Figure 3 is a view down the crystallographic *c* axis of the bromide showing the molecular packing. A comparable arrangement exists for the chloride.

In Table XI the intermolecular contact distances shown are also pronouncedly below the van der Waals radii sums and add further support to the suggestion of a moderate degree of atomic crowding in these lattices.

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