

Crystallographic and Structural Data on Two Highly Coordinated Te(IV) Compounds

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Crystals of the two compounds, tetrakis[*N*-(2-hydroxyethyl)-*N*-methylthiocarbamate]tellurium(IV), $\text{Te}[\text{HOCH}_2\text{CH}_2(\text{CH}_3)\text{NCS}_2]_4$, and bromotris[*N*-(2-hydroxyethyl)-*N*-methylthiocarbamate]tellurium(IV), $\text{TeBr}[(\text{HOCH}_2\text{CH}_2(\text{CH}_3)\text{NCS}_2)_3]$, have been prepared. The structures of the two compounds have been determined by means of three-dimensional X-ray crystallographic methods. The unit cell dimensions of $\text{Te}[\text{HOCH}_2\text{CH}_2(\text{CH}_3)\text{NCS}_2]_4$ are $a=b=19.535(7)$ Å, $c=7.558(2)$ Å and the crystals are tetragonal with space group $I4_1/a$ and $Z=4$. Data were collected on a CAD-4 diffractometer and refined to an R -value of 0.042.

The space group symmetry requires that the tellurium atoms lie on fourfold inversion axes. They are dodecahedrally coordinated to the eight sulfur atoms of the four ligands, with Te–S bond lengths of 2.714(2) and 2.758(2) Å to each ligand. The molecules are held together by hydrogen bonds between the hydroxyl groups.

The unit cell dimensions of $\text{TeBr}[(\text{HOCH}_2\text{CH}_2(\text{CH}_3)\text{NCS}_2)_3]$ are $a=6.42(2)$ Å, $b=14.48(4)$ Å, $c=25.91(5)$ Å, $\beta=91.2(2)^\circ$ and $Z=4$; the space group is $P2_1/c$. Due to small crystals of poor quality the structure did not refine satisfactorily. However, the results show a regular pentagonal bipyramidal molecule with bromine in an axial position.

Dialkyldithiocarbamate anions are strong nucleophiles and form stable binary complexes with both divalent and tetravalent tellurium.¹ Mixed complexes with other ligands have so far been prepared mostly with aromatic groups like phenyl as the second ligand.^{2,3} The phenyl group has a very strong *trans* effect which causes distortion from the regular coordination geometry in tellurium complexes.^{3,4}

Replacement of an alkyl group hydrogen atom with a hydroxyl group in a dialkyldithiocarbamate ion reduces the nucleophilicity of that ligand. This is due to the fact that the electron releasing ability of the alkyl group is reduced. On the basis of the above it has been argued that it should be possible to prepare mixed halogenide-dithiocarbamate complexes of tellurium, and several such complexes have now been prepared by Aravamudan *et al.*⁵ Among these are seven-coordinate complexes of Te(IV) with three methyl β -hydroxyethylthiocarbamate ligands and halogenide or thiocyanate ions as the fourth ligand. The present investigation was carried out to get a closer look at the result of introducing the *N*-(2-hydroxyethyl)-*N*-methylthiocarbamate ligand in tellurium complexes and also to study the structure of a seven-coordinate tellurium(IV) complex with halogenide instead of a strongly distorting phenyl group as a ligand.

EXPERIMENTAL

An aqueous solution of sodium *N*-(2-hydroxyethyl)-*N*-methylthiocarbamate was added to tellurium dioxide dissolved in dilute hydrobromic acid in the molar ratio 3:1. The orange precipitate was recrystallized from a 1:1 mixture of benzene and ethanol. Two types of very small yellow, prismatic crystals were obtained. The final structures showed that they were $\text{Te}[\text{HOCH}_2\text{CH}_2(\text{CH}_3)\text{NCS}_2]_4$, $\text{Te}(\text{motc})_4$ and $\text{TeBr}[(\text{HOCH}_2\text{CH}_2(\text{CH}_3)\text{NCS}_2)_3]$, $\text{TeBr}(\text{motc})_3$.

For recording of intensity data for $\text{Te}(\text{motc})_4$, the CAD-4 diffractometer at the Department of Chemistry, Institute of Mathematical and Physical Sciences, University of Tromsø, Norway, was used. It was equipped with a graphite monochromator. Data were collected using the $\theta-2\theta$ scan technique

with a scan angle of $(0.75 + 0.35 \tan \theta)^\circ$. With MoK_α radiation, 932 out of 1340 independent reflections with $2\theta < 50^\circ$ and $I > 2\sigma(I)$ were observed and used in the analysis. The crystal used for data collection was $0.010 \times 0.010 \times 0.021$ cm. The author is greatly indebted to Mr. L. K. Hansen at the Department of Chemistry, University of Tromsø, for collecting the data.

Accurate cell dimensions were based on 25 precisely centered high order reflections and determined by a least squares procedure. The crystal data are $a = b = 19.535(7)$ Å, $c = 7.558(2)$ Å, $Z = 4$, $d_m = d_x = 1.68$ g/cm³. Based on systematic extinctions hkl for $h+k+l=2n+1$, $hk0$ for $h, k=2n+1$ and $00l$ for $l \neq 4n$, the space group is $I4_1/a$.

Crystal data for $\text{TeBr}(\text{motc})_3$ are $a = 6.42(2)$ Å, $b = 14.48(4)$ Å, $c = 25.91(5)$ Å, $\beta = 91.2(2)^\circ$, $Z = 4$, $d_m = 1.85$ g/cm³, $d_x = 1.82$ g/cm³. Based on extinctions $h0l$ for $l=2n+1$ and $0k0$ for $l=2n+1$ the space group is $P2_1/c$.

Data were collected in the same manner as described above for $\text{Te}(\text{motc})_4$. The crystal used had the dimensions $0.004 \times 0.006 \times 0.028$ cm.

STRUCTURE ANALYSIS OF

$\text{Te}[\text{HOCH}_2\text{CH}_2(\text{CH}_3)\text{NCS}_2]_4$

The asymmetric unit contains only a quarter of a formula unit. The origin was chosen at a center of symmetry. This requires that the tellurium atom lies on a fourfold inversion axis in the special position $4a$, which gave tellurium coordinates of 0, $1/4$, $1/8$. Consecutive structure factor calculations and Fourier syntheses revealed the positions of all other non-hydrogen atoms. A difference map after a few cycles of full-matrix least squares refinement gave the positions of all hydrogen atoms. The structure was then refined to a final conventional R value of 0.042. The corresponding R_w is 0.032 with $w = 1/\sigma_f^2$. All atoms, except hydrogen, were given anisotropic temperature factors. No peaks above $0.3 \text{ e}^-/\text{Å}^3$ were observed in the final difference map.

The computer programs used were from the X-ray 1972 package.⁶ Scattering factors for tellurium were taken from the International Tables⁷ while those for the other atoms were as incorporated in the program package.⁶ The scattering factors for sulfur and tellurium were corrected for anomalous dispersion using $\Delta f'$ and $\Delta f''$ from the International Tables.⁷ The intensities were corrected for Lorentz, polarization and absorption effects ($\mu = 17.5 \text{ cm}^{-1}$). Observed and calculated structure factors can be obtained from the author upon request. Final

Table 1. Final atomic coordinates with standard deviations.

Atom	x	y	z
Te	0	1/4	1/8
S1	0.1269(1)	0.1992(1)	0.0629(2)
S2	0.0766(1)	0.2242(1)	0.4240(2)
C1	0.1405(4)	0.1980(4)	0.2884(9)
N	0.2005(3)	0.1768(3)	0.3539(8)
C2	0.2552(5)	0.1490(6)	0.2409(16)
C3	0.2141(5)	0.1800(5)	0.5461(11)
C4	0.1885(5)	0.1182(5)	0.6409(13)
O	0.2234(4)	0.0580(3)	0.5906(9)
H1	0.247(6)	0.114(5)	0.229(17)
H2	0.270(4)	0.188(4)	0.159(11)
H3	0.319(6)	0.155(5)	0.345(19)
H4	0.264(4)	0.183(4)	0.543(10)
H5	0.192(3)	0.222(3)	0.592(8)
H6	0.142(4)	0.116(4)	0.626(12)
H7	0.194(4)	0.128(3)	0.785(14)

Table 2. Thermal parameters, $U \times 10^3$ in Å² with standard deviations. The expression used for all atoms except hydrogen is $\exp\{-2\pi^2[h^2a^{-2}U_{11} + \dots + 2klb^{-1}c^{-1}U_{13}]\}$. For hydrogen the expression $\exp[-8\pi^2U(\sin^2\theta/\lambda^2)]$ was used.

	$(U_{11}, U_{22}, U_{33}, U_{12}, U_{13}, U_{23})$				
Te	36.2(0.9)	36.2	37.6(0.5)		
	0	0	0		
S1	44.7(1.2)	58.3(1.3)	36.5(1.1)		
	3.4(1.0)	7.5(0.9)	-5.6(1.0)		
S2	52.2(1.3)	80.6(1.6)	33.5(1.1)		
	21.4(1.2)	1.3(0.9)	-2.1(1.0)		
C1	35.8(4.3)	36.2(4.1)	45.5(4.5)		
	-0.7(3.4)	1.8(3.5)	1.0(3.4)		
N	44.1(3.7)	44.2(3.6)	44.0(3.7)		
	4.0(2.8)	-1.5(3.3)	0.4(3.3)		
C2	41.5(5.5)	65.1(6.6)	87.2(7.2)		
	10.2(4.8)	20.5(5.1)	-0.4(6.1)		
C3	56.6(5.4)	61.5(5.8)	46.3(5.0)		
	8.0(4.7)	-14.2(4.1)	-4.7(4.5)		
C4	79.5(7.1)	72.2(6.6)	39.7(5.0)		
	23.5(5.3)	-2.3(5.1)	-12.1(5.0)		
O	115.6(5.7)	61.8(4.2)	55.2(4.2)		
	22.8(4.1)	-27.8(4.0)	-2.3(3.4)		
	U	U	U		
H1	183(63)	H4	69(27)	H7	56(23)
H2	96(27)	H5	38(18)	H8	72(38)
H3	192(55)	H6	79(28)		

Table 3. Bond lengths (Å) and bond angles (°) with standard deviations.

Te—S1	2.714(2)	S1—Te—S2	65.11(6)
Te—S2	2.758(2)	S2—Te—S6	69.90(7)
S1—C1	1.733(8)	S1—Te—S5	160.00(6)
S2—C1	1.703(3)	Te—S1—C1	88.9(3)
C1—N	1.328(10)	Te—S2—C1	88.1(3)
N—C2	1.470(13)	S1—C1—S2	117.9(4)
N—C3	1.473(13)	S1—C1—N	120.6(6)
C3—C4	1.509(17)	S2—C1—N	121.5(6)
C4—O	1.414(13)	C1—N—C2	122.0(7)
O—H8	1.12(9)	C1—N—C3	120.0(8)
		C2—N—C3	118.0(8)
		N—C3—C4	112.5(10)
		C3—C4—O	111.6(9)
		C4—O—H8	115(4)

Table 4. Some intramolecular distances (Å).

S1—S4	3.650(3)	S1—S3	3.896(3)
S2—S3	3.516(3)	S1—S5	5.346(3)
S2—S6	3.159(3)		

atomic coordinates and thermal parameters are listed in Tables 1 and 2, respectively. Interatomic distances and angles are listed in Tables 3–4.

RESULTS AND DISCUSSION

The structure of $\text{Te}(\text{motc})_4$, is shown in Fig. 1. All eight sulfur atoms of the four equivalent ligands are bonded to the central tellurium atom in a slightly distorted dodecahedral D_{2d} configuration. The structure is quite similar to those found in other eight-coordinate tellurium dithiocarbamates.^{8,9} A dodecahedral configuration in a complex with four bidentate ligands having a small "bite" corresponds to the energetically most favourable distribution of eight electron pairs in the valency shell of the central atom.^{9–11}

The ninth electron pair must, therefore, be stereochemically inactive in the sense that it does not occupy a position in the coordination polyhedron. Earlier structural work shows that the lone pair of electrons on a central tellurium(IV) atom most often is stereochemically inert when the coordination number is six or higher.

The two intersecting TeS_4 trapezoids making up the dodecahedron are planar to within 0.065 Å. Their interplanar angle is 90° , the same as in an ideal dodecahedron. For eight-coordinate complexes, dodecahedral and square antiprismatic configurations are almost equally probable. Factors such as multidentate character of ligands and ligand bite may decide the symmetry.¹¹ There are eight

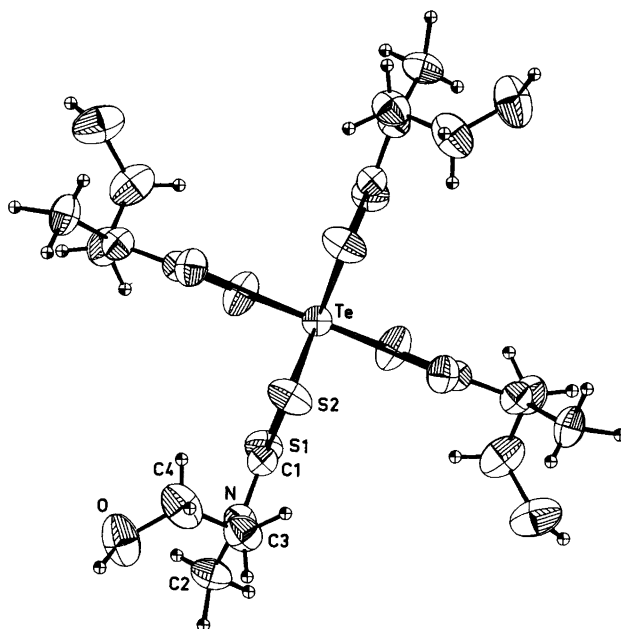


Fig. 1. The $\text{Te}(\text{motc})_4$ molecule as seen along c . The smallest spheres indicate hydrogen atoms.

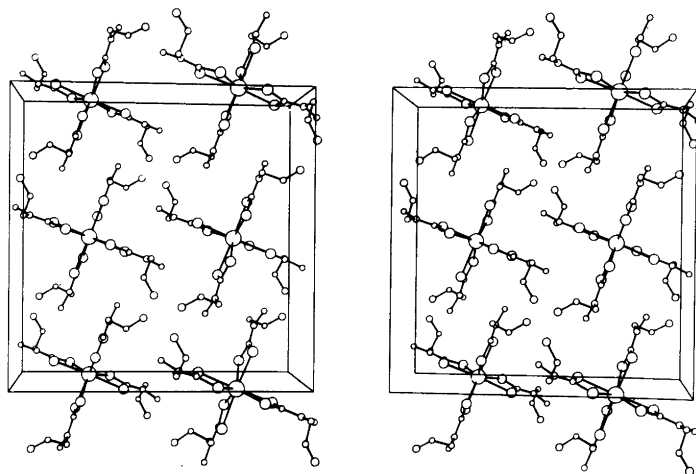


Fig. 2. Stereo drawing of the packing of the $\text{Te}(\text{motc})_4$ molecules. One unit cell is outlined, with a vertical, b horizontal and c up from the paper plane. Hydrogen atoms are omitted.

corners in a dodecahedron, four of type A and four of type B.¹⁰ A and B are not equivalent so that the distance $\text{MA} > \text{MB}$ where M represents the center of the dodecahedron. In the present investigation, chelation is along edges m with S1 and S2 at B and A positions respectively. The Te–S1 and Te–S2 bond lengths are 2.714(2) and 2.758(2) Å respectively, giving an MA/MB ratio of 1.02. The angles these bonds make with the fourfold inversion axis are called θ_A and θ_B ¹⁰ and their values are found to be 35.0 and 80.0° respectively. The “best” values of the D_{2d} dodecahedron are 1.03, 35.2 and 73.5° for MA/MB, θ_A and θ_B respectively.¹⁰ It may also be noted that the above parameters found for $\text{Te}(\text{motc})_4$ are nearly identical with the corresponding ones found for the diethylhydithiocarbamate, $\text{Te}(\text{dtc})_4$ ⁸ and they agree well with values found in dodecahedral complexes of transition metal ions with bidentate ligands.^{9,12} In the ligand the bond lengths are normal, C1–S1, C1–S2 and C1–N being 1.733(8), 1.703(8), and 1.328(10) Å respectively, indicating some double bond character in all the three bonds. The bond angles at C1 and N correspond to sp^2 hybridization and demonstrate the usual mesomeric shift of charge density from nitrogen to sulfur found in dithiocarbamate complexes. The tellurium-ligand angles within a trapezoid are close to those of $\text{Te}(\text{dtc})_4$. With an S2–Te–S2' angle of only 69.90(7)°, the S2–S2' nonbonded distance is only 3.159(3) Å. This is close to 3.17 Å, the minimum value found in $\text{Te}(\text{dtc})_4$.

It has been tentatively proposed that such a small value is indicative of easy disproportionation into the divalent tellurium bis(dithiocarbamate) and the corresponding thiuramdisulfide.⁸ This disproportion-

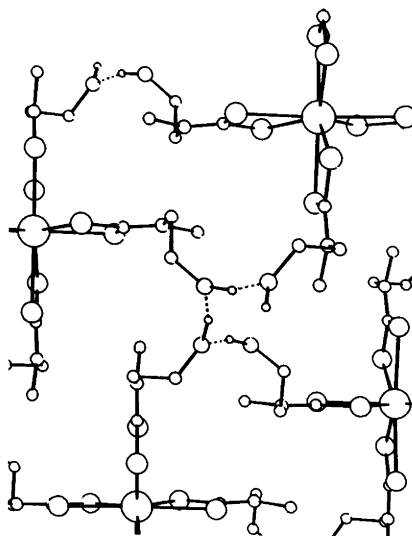


Fig. 3. Detail of the molecular packing with part of the hydrogen bond helix indicated in the center. The hydrogen bonds are dotted and are joining to four molecules around a fourfold screw axis. These are further joined to other molecules above and below to form an endless helix of hydrogen bonds parallel to c .

tionation in hot solution is not found in the present case and may be due to a stabilizing effect of hydrogen bonding. The O—H and the average C—H bond lengths are 1.12 and 0.94 Å, respectively.

Molecular packing. The packing of the molecules is shown in Fig. 2, looking down the *z*-axis. Fourfold screw axes parallel to *z* lie midway between inversion centers, each center being midway between two neighbour molecules. Hydroxyl groups from neighbour molecules approach each other closely around the fourfold screw axes (Fig. 3), forming hydrogen bonds knitting the molecules together in a helixlike fashion. Each hydroxyl group functions as both a hydrogen bond donor and acceptor so that every molecule partakes in four hydrogen bond spirals knitting the molecules together in a three-dimensional network. These hydrogen bonds are relatively strong, the O···O and H8···O distances being 2.581(10) and 1.49(9) Å, respectively. The angle O—H···O is 178°. Apart from the hydrogen bonding, there are no especially short intermolecular contacts.

The introduction of a hydroxyl group in one of the alkyl groups of the dialkyldithiocarbamate ligand in dodecahedral tetrakis(dialkyldithiocarbamato)-tellurium(IV) complexes thus has a small effect upon the molecular structure. On the other hand, it affects the molecular packing through hydrogen bonding. Also the solubility, especially in polar media is greatly enhanced.⁵

THE STRUCTURE OF



Based on a low quality data set and the heavy atom method, the structure of TeBr(motc)₃ was solved. It did not refine satisfactorily and the final *R* (anisotropic Te, Br and S, isotropic O, N and C) for 2106 observed reflections was 12.8%. The corresponding coordinates for these atoms are listed in Table 5, while the molecule is shown in Fig. 4.

The compound has a pentagonal bipyramidal structure with an axial bromine atom. Again the lone pair of electrons seems to be stereochemically inert. The main deviation from perfect geometry is due to the small S—S bite in the dithiocarbamate ligands and the structure is very similar to that of the tris(dimethyldithiocarbamato)iodoruthenium-(IV) complex.¹³ Thus S3 is forced more than 0.5 Å

Table 5. Parameters for TeBr(motc)₃.

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Te	0.2630(4)	0.2517(2)	0.1118(1)
Br	0.0668(10)	0.3285(4)	0.1983(2)
S1	0.570(2)	0.1757(9)	0.1616(5)
S2	0.163(2)	0.0861(8)	0.1560(4)
S3	-0.075(2)	0.1934(8)	0.0489(5)
S4	0.375(2)	0.1733(8)	0.0309(5)
S5	0.157(2)	0.4086(8)	0.0572(5)
S6	0.562(2)	0.3741(7)	0.1092(5)
C1	0.402(7)	0.090(3)	0.184(2)
N1	0.476(6)	0.028(3)	0.216(1)
C2	0.698(7)	0.022(3)	0.234(2)
C3	0.325(9)	-0.053(4)	0.228(2)
C4	0.703(9)	0.053(4)	0.288(2)
O1	0.668(6)	0.152(2)	0.297(1)
C5	0.111(6)	0.162(3)	0.017(2)
N2	0.071(5)	0.106(2)	-0.032(1)
C6	-0.158(7)	0.093(3)	-0.048(2)
C7	0.235(7)	0.068(3)	-0.066(2)
C8	0.262(9)	0.119(4)	-0.116(2)
O2	0.268(6)	0.210(2)	-0.112(1)
C9	0.396(8)	0.441(3)	0.073(2)
N3	0.465(5)	0.535(2)	0.062(1)
C10	0.664(7)	0.566(3)	0.083(2)
C11	0.326(7)	0.600(3)	0.041(2)
C12	0.188(8)	0.650(3)	0.074(2)
O3	0.321(5)	0.712(2)	0.110(1)

Thermal parameters listed as in Table 2.

Te	41.0(1.3)	27.7(1.1)	29.2(1.1)		
	-2.0(1.6)	-1.4(0.9)	-3.4(1.6)		
Br	78.9(4.0)	77.4(4.0)	73.9(4.0)		
	5.9(3.4)	14.5(3.2)	-24.4(3.3)		
S1	45.8(6.5)	53.7(7.2)	69.3(8.3)		
	-7.2(6.3)	-13.1(6.1)	11.0(6.7)		
S2	27.3(5.1)	39.9(6.1)	57.3(7.4)		
	-3.3(4.9)	2.1(5.0)	4.3(5.3)		
S3	16.7(4.7)	54.8(7.5)	68.5(8.2)		
	-7.3(5.1)	-3.1(5.1)	-4.1(6.1)		
S4	34.4(5.7)	50.2(6.9)	60.2(8.0)		
	-5.5(5.5)	3.0(5.4)	9.8(6.2)		
S5	33.1(5.7)	37.6(6.1)	59.0(7.8)		
	5.2(5.1)	-11.7(5.4)	3.3(5.4)		
S6	28.0(5.2)	34.2(5.6)	62.4(7.5)		
	0.8(4.8)	-6.4(5.2)	2.7(5.4)		
C1	2.7(1.0)	C5	2.1(1.0)	C9	5.6(1.3)
N1	6.2(1.1)	N2	3.3(0.9)	N3	3.0(0.9)
C2	5.1(1.2)	C6	6.1(1.3)	C10	5.2(1.2)
C3	12.1(1.7)	C7	5.0(1.2)	C11	3.3(1.1)
C4	12.5(1.7)	C8	11.1(1.5)	C12	5.7(1.2)
O1	14.0(1.1)	O2	12.8(1.0)	O3	7.6(0.9)

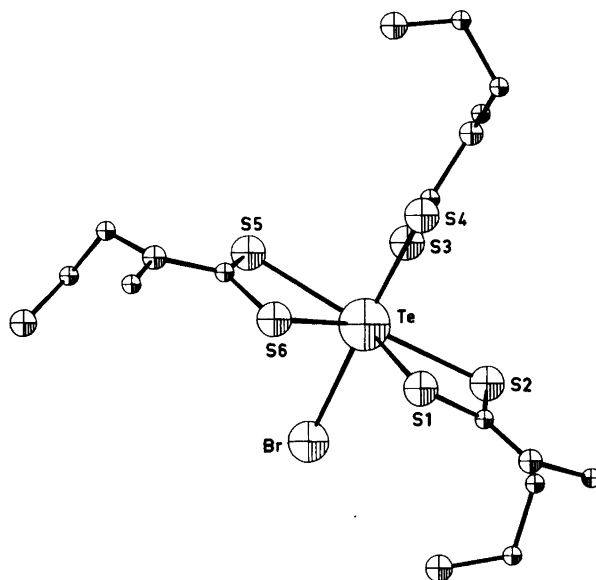


Fig. 4. A molecule of $\text{TeBr}(\text{motc})_3$, as seen along a . Unlabelled atoms are in order of decreasing size oxygen, nitrogen and carbon.

up above the equatorial plane so that angle $\text{Br}-\text{Te}-\text{S4}$ may approach 180° . Its value is found to be $170.2(3)^\circ$. $\text{Te}-\text{S4}$ is 2.51 \AA , as compared to an axial $\text{Te}-\text{S}$ bond of $3.228(4) \text{ \AA}$ in $\text{Te}(\text{Et}_2\text{NCS}_2)_3\text{Ph}^3$ where the strong *trans* effect of an axial phenyl group is operating. The average $\text{Te}-\text{S}_{\text{eq}}$ bond length is 2.71 \AA in both of these seven-coordinate tellurium(IV) compounds. The $\text{Te}-\text{Br}$ bond length is found to be 2.83 \AA .

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