

A Tellurium(IV) Complex with a TeS₇ Coordination Sphere

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As part of the work on highly coordinated Te(IV) compounds, the crystal structure of tris[*N*-(2-hydroxyethyl)-*N*-methylthiocarbamate]thiocyanatotellurium(IV), [Te{HOCH₂CH₂(CH₃)NCS₂}₃·SCN], has been determined by three-dimensional X-ray crystallographic methods. The crystals were prepared according to Aravamudan *et al.*¹ and found to be monoclinic with $a=6.378(2)$ Å, $b=17.710(4)$ Å, $c=11.128(2)$ Å, $\beta=99.99(2)^\circ$, $Z=2$, $D_m=1.70$ g/cm³ and $D_x=1.71$ g/cm³. An elemental analysis for S and O gave S, found 35.13%, required 35.37%; O, found 7.59%, required 7.54%.

Table 1. Atomic coordinates with standard deviations.

	x	y	z
Te	0.2316(1)	1/4	0.4204(1)
S1	0.1330(4)	0.1012(1)	0.4373(2)
S2	0.4956(6)	0.1588(3)	0.3410(5)
S3	0.1330(4)	0.3988(1)	0.4373(2)
S4	0.5200(6)	0.3385(2)	0.3507(5)
S5	-0.0507(5)	0.2486(11)	0.5856(3)
S6	0.4220(4)	0.2440(5)	0.6383(3)
S7	-0.0626(6)	0.2569(7)	0.1928(4)
O1	0.205(4)	-0.082(2)	0.130(3)
O2	0.372(5)	0.533(2)	0.092(3)
O3	0.396(3)	0.347(1)	0.918(2)
N1	0.391(2)	0.015(1)	0.321(1)
N2	0.406(2)	0.484(1)	0.352(1)
N3	0.176(2)	0.225(1)	0.804(1)
N4	-0.023(2)	0.104(1)	0.106(2)
C1	0.347(2)	0.831(1)	0.360(1)
C2	0.574(3)	0.004(1)	0.258(2)
C3	0.274(2)	-0.052(1)	0.336(1)
C4	0.111(4)	-0.062(2)	0.236(2)
C5	0.351(2)	0.415(1)	0.381(1)
C6	0.252(3)	0.548(1)	0.376(2)
C7	0.603(3)	0.499(1)	0.295(2)
C8	0.524(4)	0.494(1)	0.154(2)
C9	0.178(2)	0.237(1)	0.688(1)
C10	-0.032(3)	0.220(1)	0.854(2)
C11	0.380(3)	0.220(1)	0.899(2)
C12	0.394(3)	0.282(1)	0.985(2)
C13	-0.056(3)	0.167(1)	0.140(2)

From systematic extinctions, $0k0$, $k=2n+1$, the space group is $P2_1$ or $P2_1/m$.

From 1601 observed reflections [$I > 2\sigma(I)$], the Te and S atoms were located using Patterson and Fourier methods and assuming the space group to be $P2_1$. Based on the positions of these atoms, tellurium is seven-coordinate and bonded to the six sulfur atoms of the three bidentate ligands and to the sulfur atom of the thiocyanate ion in a pentagonal bipyramidal configuration. During the refinement, it soon became apparent that there was extensive disorder in the structure, and realistic parameters for the light atoms were not obtained, even when various forms of disorder were assumed. An attempt to refine the structure in space group $P2_1/c$ with a doubled c -axis also failed. The reason for this attempt was that the reflection pattern for [TeClL₃]·2H₂O,² excluding reflections hkl with $l=2n+1$, is very similar to that for the present compound.

Also the cell parameters are similar when c is doubled in the latter and it was therefore assumed that every other layer line (corresponding to $l=2n+1$ in [TeClL₃]·2H₂O) might be too weak to be observed.

Refinement was finally attempted in space group $P2_1/m$. The approach that gave the best results was as follows. The structure of [TeClL₃]·2H₂O, space group $P2_1/c$, was chosen as starting point. A stacking of unit cells for that compound with every other cell given a translation of $c/2$ along c gives the space group $P2_1/m$ with c halved. Then Cl and H₂O were replaced by SCN. These changes resulted in a completely disordered, molecular structure with pairs of molecules, each with occupancy 0.5, being related by a mirror plane. The refinement with anisotropic temperature factors for Te and S was then completed and the final R -factor was 5.1%. Some of the final bond lengths and angles for the -CH₂OH groups were still deviating

Table 2. Some bond lengths (Å) and angles (°) with standard deviations.^a

Te-S1	2.72	S1-Te-S2	65.8
Te-S2	2.60	S3-Te-S4	68.0
Te-S3	2.72	S5-Te-S6	67.9
Te-S4	2.64	S2-Te-S4	75.1
Te-S5	2.79	S1-Te-S5	77.2
Te-S6	2.52	S3-Te-S5	77.3
Te-S7	2.88	S6-Te-S7	168.5
S7-C13	1.70	Te-S7-C13	102.4
C13-N4	1.20	S7-C13-N4	171.2

^a E.s.d.'s are: Te-S, 0.02 Å for S₂ and S₄ and 0.01 Å for the others; S-C and C-N, 0.03 Å; S-Te-S and Te-S-C, 1.0°; S-C-N, 2.0°.

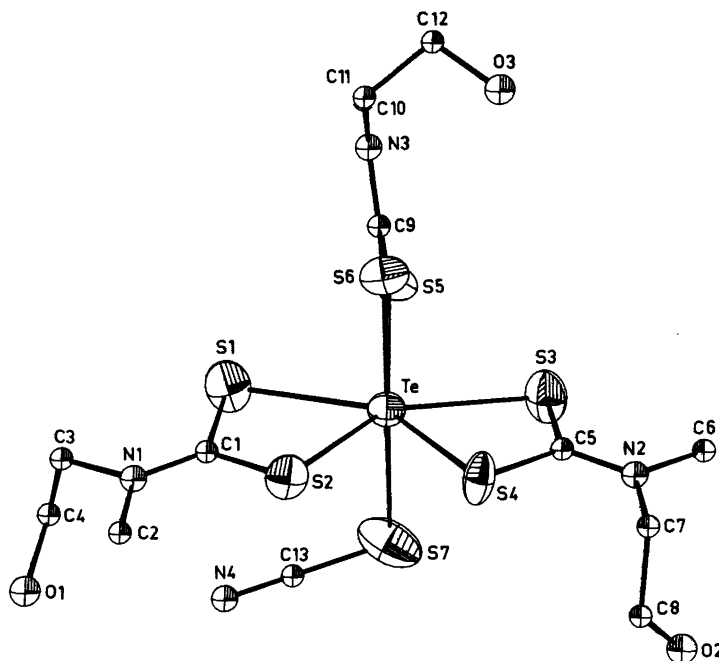


Fig. 1. The molecule as seen along *a*.

significantly from normal values, likewise the temperature parameters for the oxygen atoms were high. This indicates some residual disorder in the structure.

The pentagonal bipyramidal (PB) molecules (Fig. 1) have near C_s symmetry, with the equatorial sulfur-atom of the unique bidentate ligand ($S5_{eq}$, $S6_{ax}$) moved *ca.* 0.6 Å up above the equatorial $TeS1S2S3S4$ plane. There is a near mirror plane defined by Te , $S5$, $S6$, $S7$, and the structure closely resembles that of $[TeCl_3] \cdot 2H_2O$, with the C and N atoms of $-SCN$ partly replacing H_2O . Selected bond lengths and angles are shown in Table 2. The main structural differences between the chloride and the thiocyanate is that, in the latter, the unique

ligand is closer to the equatorial plane giving an $S_{ax}-Te-S(CN)_{ax}$ angle of only 168.5° , *ca.* 6° smaller than $S_{ax}-Te-Cl_{ax}$ in the chloride.² Also the $Te-S(CN)$ bond is very long and weak, being 2.88(1) Å as compared to a long corresponding $Te-Cl$ bond of 2.772(1) Å in the chloride.² In some of the seven-coordinate $Te(IV)$ complexes with three bidentate dithiocarbamate ligands and one monodentate halogenide or pseudohalogenide ligand, there appears to be a *cis* effect operating. In three of these compounds there is a direct relation between the $Te-X$ and $Te-S5$ bond lengths with a short $Te-X$ bond corresponding to a long $Te-S5$ bond and *vice versa*. Surprisingly the $Te-S6$ bond length is remarkably constant (Table 3). The com-

Table 3. Some selected bond parameters in seven-coordinate pentagonal, bipyramidal $Te(IV)$ complexes.

Compound ^a	$Te-X_{ax}$	$Te-S5_{eq}$	$Te-S6_{ax}$	Δ
$[TeL_3Cl]^3$	2.686(4)	2.874(4)	2.512(4)	0.15
$[TeL_3Cl] \cdot 2H_2O^2$	2.772(1)	2.835(1)	2.493(1)	0.23
$[TeL_3SCN]$	2.88(1)	2.79(1)	2.52(1)	0.29

^a $L' = Et_2NCS_2^-$, $L = HOCH_2CH_2(Me)NCS_2^-$, $\Delta = r_{Te} + r_X - l_{Te-X}$, where r_{Te} is taken as the octahedral radius of $Te(IV) = 1.55$ Å. $X =$ halogen or SCN . For the three compounds there is a near linear relationship between Δ and the length of $Te-S5$.

compound $[\text{TeL}_3\text{Br}] \cdot 2\text{H}_2\text{O}$ has been prepared following a procedure described in the literature.¹ The crystals are isomorphous with those of the thiocyanate described in the present investigation, with $a=6.422(2)$ Å, $b=17.822(8)$ Å, $c=11.005(6)$ Å, $\beta=100.06(3)^\circ$ and $Z=2$. A preliminary X-ray study shows a structure with nearly the same bond lengths and angles as found in the anhydrous compound⁴ and of course very similar to the isomorphous thiocyanate.

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1. Aravamudan, G., Janakiram, C. and Sejekan, B. G. *Phosphorus Sulfur* 5 (1978) 185.
2. Husebye, S. and Thowsen, A. G. *Acta Chem. Scand. A* 35 (1981). *In press.*
3. Deuten, K., Schnabel, W. and Klar, G. *Phosphorus Sulfur* 9 (1980) 93.
4. Husebye, S. *Acta Chem. Scand. A* 33 (1979) 485.

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