6. Banfield, J. E., Davies, W., Ennis, B. C., Middleton, S. and Porter, Q. N. *J. Chem. Soc.* 1956 2603.
7. Fields, D. L., Miller, J. B. and Reynolds, D. D. *J. Org. Chem.* 27 (1962) 2749.
8. Smith, L. I. and Tess, R. W. H. *J. Am. Chem. Soc.* 66 (1944) 1523.

Received October 21, 1971.

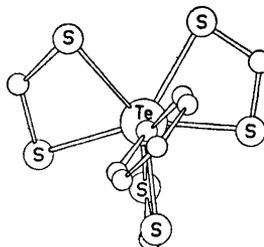*Fig. 1.* The $[Te(Et_2NCS_2)_3C_6H_5]$ molecule (I), seen along the normal to the equatorial TeS_5 plane. All Et_2N- groups are omitted, and the smallest spheres represent carbon atoms.

On the Crystal Structures of Two Highly Coordinated Tellurium(IV) Complexes

STEINAR ESPERÅS, STEINAR HUSEBYE and STEIN EGIL SVÆREN

Chemical Institute, University of Bergen, 5000 Bergen, Norway

The crystal structures of the two complexes, tris(diethyldithiocarbamato) phenyltellurium(IV), $[Te(Et_2NCS_2)_3C_6H_5]$, and tetrakis(diethyldithiocarbamato)tellurium(IV), $[Te(Et_2NCS_2)_4]$, have been determined by three-dimensional X-ray crystallographic methods.

The yellow crystals of $[Te(Et_2NCS_2)_3]C_6$-$H_5]$, (I), are monoclinic with $a = 10.791(5)$ Å, $b = 16.090(6)$ Å, $c = 18.417(9)$ Å $\beta = 117.63(6)°$ and $Z = 4$. Density, calc. 1.52, found 1.51 g/cm^3; space group $P2_1/c$.

Intensities of 4183 reflections greater than the background were recorded with a Siemens AED-1 diffractometer, using $MoK\alpha$-radiation. The structure was solved by conventional heavy atom methods. No absorption correction was applied. Full-matrix least squares refinement with anisotropic temperature factors for Te and S, excluding hydrogen atoms, has given an R value of 6.2 %. The coordination around the central tellurium atom is shown in Fig. 1.

The orange crystals of $[Te(Et_2NCS_2)_4]$, (II), are orthorhombic with $a = 19.805(2)$ Å, $b = 9.371(2)$ Å, $c = 35.178(4)$ Å and $Z = 8$.

Density, calc. and found 1.46 g/cm^3; space group $Pna2_1$. On basis of a three-dimensional Patterson synthesis and packing considerations, the space group $Pna2_1$ was chosen instead of $Pnma$, thus giving two molecules in the asymmetric unit. The Patterson synthesis gave the x and y coordinates of the two Te atoms and also the difference in their z-coordinates. The value of z for Te1 was arbitrarily chosen as 0.000, and the structure then solved by successive Fourier syntheses. It is being refined by full-matrix least squares methods, based at present on 2645 observed diffractometer reflections obtained with $CuK\alpha$ radiation. The R value, with absorption correction undertaken, and with anisotropic temperature factors only for Te, is at present 8.8 %. The content of one asymmetric unit is shown in Fig. 2.

From the figures, it is seen that in the complexes I and II, the central Te atom is, respectively, seven- and eight-coordinated. In I, the coordination is best described as distorted pentagonal bipyramidal, in II as distorted dodecahedral.

Thus the coordination around the central Te atoms in I and II is not that expected on the basis of distributions of 8 and 9 valence electron pairs, respectively, according to the VSEPR theory.[1] The structures found here can to a first approximation be explained by assuming the $5s$ lone pair to be stereochemically inert. This is as found for octahedral hexahalotellurates.[1]

The main distortion in $[Te(Et_7NCS_2)_3$-$C_6H_5]$, (I), the long $Te-S$ bond of 3.23 Å *trans* (144.6°) to the phenyl group ($Te-C = 2.12$ Å), may be due to the strong *trans* effect of the latter, rather than to the lone pair. Also the narrow $S-S$ "bite" distance
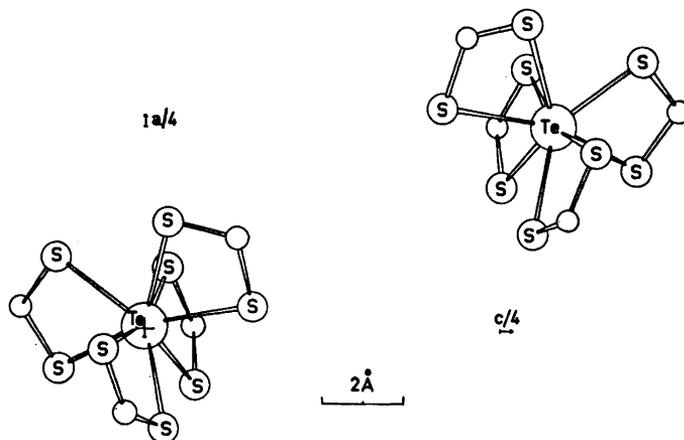
Fig. 2. The two [Te(Et$_2$NCS$_2$)$_4$] molecules (II) in the asymmetric unit, seen along *b*. All Et$_2$N— groups are omitted and the smallest spheres represent carbon atoms.

in the dithiocarbamate ligand makes it difficult for it to span an axial and an equatorial position in the complex without distorting the regular geometry. The two equatorial ligands are nearly coplanar with the approximately planar TeS$_4$ equatorial group and the two other ligands are at nearly right angles to it.

In [Te(Et$_2$NCS$_2$)$_4$], (II), there are two ligands in each of two similar, interlocking trapezoids which are roughly at right angles to each other. The coordination in such a nearly planar trapezoid is similar to that found in corresponding divalent tellurium complexes.[2,3] Upon heating in solution, II decomposes to give the divalent tellurium compound and the corresponding disulphide.

The dithiocarbamate ligands are, as mentioned above, nearly planar. This planarity does not include the H atoms and the methyl groups.

A characteristic feature of the two complexes is the large Te—S bond lengths. Excluding the very long axial Te—S bond of 3.23 Å in I, the five equatorial Te—S bond lengths lie in the range of 2.606 to 2.816 Å ($\sigma = 0.003$ Å) with an average of 2.71 Å. In the two molecules of II, the Te—S bond lengths have values between 2.61 and 2.88 Å, the average here being 2.74 Å. These values are much larger than those expected on basis of the octahedral radius of Te(IV), 1.54 – 1.56 Å,[4] and the covalent radius of S, 1.04 Å.

This may in part be due to a strong antibonding effect of the 5s lone pair[5,6] and to increasing contribution of high energy 5d orbitals to the bonding. Steric factors probably also play a role, especially in II where the crowding is greatest.

1. Gillespie, R. J. *J. Chem. Educ.* **47** (1970) 18.
2. Husebye, S. *Acta Chem. Scand.* **24** (1970) 2198.
3. Fabiani, C., Spagna, R., Vaciago, A. and Zambonelli, L. *Acta Cryst.* **B 27** (1971) 1499.
4. Foss, O. In Andersen, P., Bastiansen, O. and Furberg, S., Eds., *Selected Topics in Structure Chemistry*, Universitetsforlaget, Oslo 1967, p. 145.
5. Urch, D. S. *J. Chem. Soc.* **1964** 5775.
6. Lawton, S. L. and Kokotailo, G. T. *Nature* **221** (1969) 550.
                    Received October 20, 1971.