The Crystal Structure of Monoclinic *trans*-Tetrachlorobis-(tetramethylthiourea)tellurium (IV)

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Dark red, prism-shaped crystals of *trans*-tetrachlorobis(tetramethylthiourea)tellurium(IV), $[TeCl_4(C_5H_{12}N_2S)_2]$, are obtained by recrystallization from methanol.[1] In a fresh sample the crystals belong to the orthorhombic crystal system, but upon standing they become monoclinic.[2] The structure of the orthorhombic crystals have earlier been determined by Husebye and George [2] by means of three-dimensional X-ray methods, using the multiple-film technique. The present investigation is concerned with monoclinic crystals belonging to a five-year-old sample. The following unit cell parameters were found: $a = 14.009(3)$ Å, $b = 14.708(3)$ Å, $c = 10.053(2)$ Å, $\beta = 90.37(2)°$ and $Z = 4$. The measured and calculated densities are 1.70 and 1.71 g/cm^3, respectively, and the space group is $P2_1/n$. For comparison, the cell dimensions in the orthorhombic structure with space group *Pbca* are: $a = 14.74(3)$ Å, $b = 13.87(3)$ Å, $c = 10.06(2)$ Å, and $Z = 4$, *i.e.*, only one axis is significantly different.

The intensity data of 4028 reflections greater than background were recorded by means of a Siemens AED-1 single-crystal diffractometer using Mo$K\alpha$-radiation. The structure has been solved by Patterson and Fourier methods and refined by a full-matrix least squares program using the three-dimensional diffractometer data. The intensities were corrected for absorption. The R-value is 0.08 at the present stage of refinement.

Some bond lengths and angles for both the orthorhombic and monoclinic form of *trans*-tetrachlorobis(tetramethylthiourea) tellurium(IV) are given in Table 1, while the coordination around the tellurium atom in the monoclinic crystals is shown in Fig. 1. In the orthorhombic structure, where the tellurium atoms lie in centers of symmetry, the octahedral configuration around the tel-

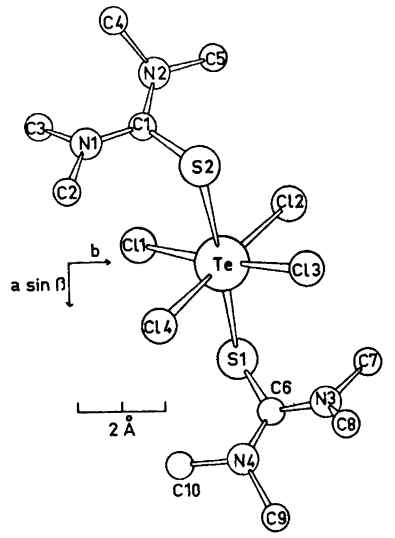

Fig. 1. The *trans*-tetrachlorobis(tetramethylthiourea)tellurium(IV) molecule seen along the *c*-axis.

Table 1. Some bond lengths (in Å) and bond angles (in degrees) found for the monoclinic structure (I) compared to the corresponding values for the centrosymmetric structure (II).

	I	II
Te–Cl1	2.457(3)	2.520(8)
Te–Cl2	2.528(3)	2.536(8)
Te–Cl3	2.598(3)	2.520(8)
Te–Cl4	2.542(3)	2.536(8)
Te–S1	2.725(3)	2.699(8)
Te–S2	2.649(3)	2.699(8)
S1–C6	1.745(9)	1.75(2)
S2–C1	1.740(9)	1.75(2)
∠Cl1–Te–Cl2	89.6(1)	89.1(2)
Cl1–Te–Cl3	172.0(1)	180.0
Cl1–Te–Cl4	91.3(1)	90.9(2)
Cl2–Te–Cl3	90.4(1)	90.9(2)
Cl2–Te–Cl4	177.2(1)	180.0
Cl3–Te–Cl4	89.1(1)	89.1(2)
Cl1–Te–S1	81.9(1)	81.5(2)
Cl1–Te–S2	92.3(1)	98.5(2)
Cl2–Te–S1	88.8(1)	91.1(2)
Cl2–Te–S2	89.7(1)	88.9(2)
Cl3–Te–S1	106.1(1)	98.5(2)
Cl3–Te–S2	79.8(1)	81.5(2)
Cl4–Te–S1	88.7(1)	88.9(2)
Cl4–Te–S2	92.9(1)	91.1(2)
S1–Te–S2	174.0(1)	180.0

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lurium atom is slightly distorted.[2] In the present, not centrosymmetric structure, the distortion is found to be larger (Table 1). It is not clear if this can be interpreted as resulting from lattice-packing effects or from a stereochemical activity of the lone pair of electrons. However, the lone pair is not stereochemically active in the sense that it occupies a position in the coordination polyhedron.

The tellurium-chlorine bond lengths are ranging from 2.457(3) Å to 2.598(3) Å, while the tellurium-sulphur distances are found to be 2.649(3) Å and 2.725(3) Å. These values show a much greater variation than the corresponding ones in the orthorhombic structure; however, the average Te–Cl and Te–S bond lengths of 2.53 Å and 2.69 Å found here are in good agreement with the corresponding values of 2.53 Å and 2.70 Å found for the orthorhombic form. The average Te–Cl distance is further in good agreement with reported bond lengths in hexachlorotellurate species,[3,4] *i.e.*, equal to the sum of the octahedral radius of Te(IV) [5] and the covalent radius of Cl, while the average Te–S distance is significantly larger than the sum of the octahedral radius of Te(IV) and the covalent radius of S, 2.59 Å. Similar Te–S bond lengths or even greater ones are found in other tellurium(IV) complexes.[6,7] An explanation of why the Te–Cl bond lengths are normal while the Te–S ones are so large can at present not be given.

The S–C bond lengths of 1.745(9) Å and 1.740(9) Å are in good agreement with the corresponding values found for the orthorhombic structure and for tetramethylthiourea complexes of tellurium(II).

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Synthesis of Tritium-labelled Tetrahydrocannabinol and Cannabidiol

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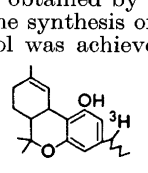
Several syntheses of ^{3}H-[1-5] and ^{14}C-labelled [1,6-8] tetrahydrocannabinols (THC's) have been reported. In distribution studies using autoradiography it is necessary to use compounds of high specific activity. For this purpose [9] tritium-labelled Δ^{1}-THC of specific activity 1.6 Ci/mmol has been prepared. This synthesis together with the preparation of tritium-labelled cannabidiol is here reported.

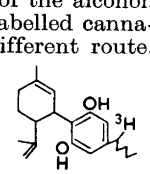
1-(3,5-Dimethoxyphenyl)-1-pentanone, synthesised according to the method of Baeckström and Sundström,[10] was reduced with sodium borohydride. The resulting alcohol,[4] dissolved in methanol, was tritiated with tritium gas over palladium supported on carbon. The reduction was then completed with hydrogen. The labelled dimethylolivetol was demethylated by heating with hydriodic acid.[11] The resulting olivetol was reacted with (+)-*trans*-*p*-menthadien-2,8-ol-1 to give (−)$\Delta^{1,6}$-THC,[12] which after purification on silica gel, was isomerised to (−)Δ^{1}-THC.[12]

1-(3,5-Dimethoxyphenyl)-1-pentanone could also be tritiated with tritium gas using the same condition as described above. The reduction was, however, slower than that of the corresponding alcohol and the exchange of tritium with the hydrogen atoms in the solvent occurred to such an extent that the resulting labelled dimethylolivetol had a specific activity only half of that obtained by tritiation of the alcohol.

The synthesis of tritium-labelled cannabidiol was achieved by a different route.



Δ¹-TETRAHYDROCANNABINOL



CANNABIDIOL