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Reaction of tellurium tetrachloride with cyclohexene and the crystal structure of racemic bis(*trans*-2-chlorocyclohexyl)tellurium dichloride

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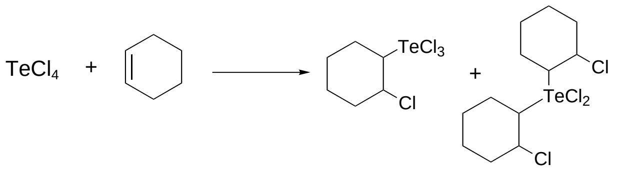
The confusing background literature concerning the reaction between tellurium tetrachloride and cyclohexene and the stereochemistry of the product has been surveyed. The crystal structure of racemic bis(*trans*-2-chlorocyclohexyl)tellurium dichloride was determined and compared with that of the previously reported *meso* isomer.

The reaction between cyclohexene and tellurium tetrachloride has been investigated by several groups of workers and both mono- and bis-adducts have been reported. (Scheme 1). In 1959 the monoadduct $TeCl_3(C_6H_{10}Cl\text{-}2)$ was described by de Moura Campos and Petragnani[1] who characterised it by tellurium analysis and reported the melting point to be 111–114 °C. A later report by Ogawa[2] described the bis adduct $TeCl_2(C_6H_{10}Cl\text{-}2)_2$ (m.p. 134–135.5 °C), although in a subsequent paper[3] he mentioned the contamination of the bis adduct of butene by monoadduct impurity. Unfortunately, none of these reports gives experimental details of the reaction, nor do they refer to the earlier work of Funk and Weiss,[4] who carried out the reaction by warming to 40 °C in carbon tetrachloride and obtained a m.p. of 132 °C for the bis adduct. The paper by Funk and Weiss does not appear to have been abstracted by *Chemical Abstracts*, and we were not aware of its contents when we started our work. In 1980 Cameron *et al.*[5] reported the crystal structure of the bis adduct, but the title of their paper is misleading concerning the configuration of the adduct and the provenance of the crystal is not given. In 1983 Engman and co-workers[6] published their NMR study of the stereochemistry of the addition of tellurium tetrachloride to alkenes. They found that the addition is predominantly *syn* when a radical inhibitor is present, but that cyclohexene has a marked tendency to give the *anti* product. Somewhat surprisingly, they do not cite the crystal structure[5] which confirms their NMR study, perhaps because they were only considering the formation of $TeCl_3(C_6H_{10}Cl\text{-}2)$, for which they quote a m.p. of 122–124 °C for the *threo* isomer. It was against this rather confusing background that we started our work. We have subsequently learnt[7] that the crystals studied by Cameron *et al.* were provided by Dr. B. C. Smith of Birkbeck College, London, and that the designation *cis* which was used in the original publication referred to the configuration at tellurium. The configuration of the 1,2-disubstituted cyclohexane ring is *trans*.

Results and Discussion

Our first attempts to carry out the reaction between cyclohexene and tellurium tetrachloride were based on the procedure of Engman and co-workers.[6] We found that when a suspension of $TeCl_4$ in chloroform is treated with 2.6 mol of cyclohexene at 0–5 °C the $TeCl_4$ quickly dissolves to give a clear solution. If the resulting mixture is stirred overnight and the solvent evaporated a solid is obtained which, on recrystallisation from acetonitrile, has a rather broad m.p. below 100 °C. It seems likely that this is a mixture of the mono- and bis-adducts, $TeCl_3(C_6H_{10}Cl\text{-}2)$ and $TeCl_2(C_6H_{10}Cl\text{-}2)_2$. Carrying out the reaction in chloroform under similar conditions, but with a 10 : 1 ratio of cyclohexene to $TeCl_4$, produced an increase in the m.p. of the product, but still substantially below that previously reported for the bis-adduct. We therefore changed our procedure to that implied by Ogawa,[2] that is using cyclohexene as solvent and reactant. Ogawa comments that the product of the reaction depends on the conditions, but does not give a detailed procedure. We carried out the reaction with a ten-fold excess of cyclohexene, bringing the reactants together at 0–5 °C and then allowing the mixture to react for 48 h. These conditions give the bis adduct, which we crystallised from glacial acetic acid to give the sample used in our crystallographic study. The melting point we obtained, 130–131 °C, agrees fairly well with that reported by Funk and Weiss[4] (132 °C), and is similar to that reported by Ogawa[2] (134–135.5 °C). After we had completed our work we learnt that the sample studied by Cameron *et al.* was obtained by refluxing $TeCl_4$ with an excess of cyclohexene (no solvent) and recrystallising the product from carbon tetrachloride–light petroleum (b.p. 40–60 °C).[8]



Racemate of diadduct **I**
meso Isomer of diadduct **II**

Scheme 1

The structure of the bis adduct which we prepared (**I**) is shown in Fig. 1, together with bond lengths and angles. The molecule consists of a roughly linear Cl–Te–Cl fragment with two substituted cyclohexane rings bonded at right angles to the Cl–Te–Cl vector. The cyclohexane rings are 1,2-disubstituted and have the *trans* configuration, with both the tellurium and chlorine substituents in equatorial positions as expected.[9a] The tellurium chloride has therefore added *anti* to the double bond of the cyclohexene as found in the formation of the monoadduct in the absence of a radical inhibitor. The addition of tellurium chloride to cyclohexene generates four chiral centres, and so leads to the possibility of diastereoisomers and enantiomers. It was therefore of interest to compare the earlier structure **II** of Cameron *et al.* (Fig. 2) with the present structure **I** (Fig. 1). The figures have been drawn so that the ring at the top left of each has the same stereochemistry and orientation. Hydrogen atoms have been shown to emphasise the stereochemistry at C(1), C(2), C(7) and C(8). It will be seen in Fig. 2, as noted by Cameron, that by appropriate rotation about the Te–C(7) bond the molecule has a mirror plane bisecting the C–Te–C angle. This is therefore the *meso* isomer. An alternative statement of this conclusion is to note that in Fig. 2 C(1) and C(2) have an *R*

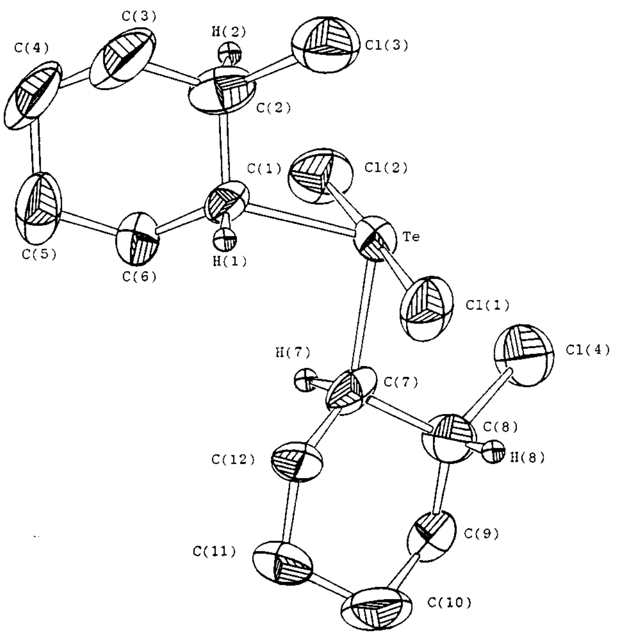


Fig. 1 Molecular structure of racemic bis(*trans*-2-chlorocyclohexyl)tellurium dichloride **I** with atomic numbering. Hydrogen atoms are shown only on C(1), C(2), C(7) and C(8) for clarity (ORTEP,[10], 50% probability ellipsoids for non-hydrogen atoms; arbitrary radii for hydrogen atoms). Selected bond lengths (Å) and angles (°): Te–Cl(1) 2.484(6), Te–Cl(2) 2.466(6), Te–C(1) 2.18(2), Te–C(7) 2.17(2), Cl(3)–C(2) 1.81(2), Cl(4)–C(8) 1.79(2), C(1)–C(2) 1.49(3) and C(7)–C(8) 1.49(3); Cl(1)–Te–Cl(2) 177.5(2), Cl(1)–Te–C(1) 90.2(6), Cl(1)–Te–C(7) 89.9(5), Cl(2)–Te–C(1) 89.4(6), Cl(2)–Te–C(7) 87.8(5) and C(1)–Te–C(7) 102.3(7)

configuration but C(7) and C(8) have an *S* configuration. In contrast all four stereocentres of the molecule depicted in Fig. 1 have the *R* configuration, and, as the space group is centrosymmetric, the crystal is a racemate. The average C–C–C angle in the cyclohexane rings is 109.8°, which is less than that in cyclohexane.[9b]

Recent reports of similar tellurium structures[11] have discussed the angles at tellurium in terms of the quadruple average angle of the lone pair.[12] As the position of the lone pair cannot be defined, it is assumed to bisect the angle between the relevant substituents. An idealised trigonal bipyramid with a lone pair in the equatorial plane would thus have a quadruple average angle of 105°, but observed angles are larger than this because lone pair–bond pair repulsions are greater than bond pair–bond pair ones. A typical[13] value is 112°. The quadruple average angles of **I** (110.1) and **II** (109.7°) are very similar, but slightly smaller than in related structures. Hargittai and Rozsondai[13] have pointed out that in **II** it is the low angles between the lone pair and chlorine rather than the alkyl groups which bring down the average. This is also the case in **I**. The average Te–Cl bond length of 2.475(6) Å is similar to that in related structures,[5,11,14] but larger than the sum of the covalent radii as is often found for trigonal-bipyramidal molecules.[14] There are no close intermolecular contacts.

We have studied the ^{1}H NMR spectrum of our bis adduct and find two well resolved multiplets at δ 4.03 and 4.52 for the hydrogen on the carbon atoms attached to Te and Cl respectively, as well as absorptions at δ 1.4–2.5 for the methylene hydrogens. Similar spectra have been reported for *trans*-2-alkoxy-cycloalkyltellurium trihalides.[15] The interesting question which arises is whether the racemic and *meso* forms are distinguishable from their NMR spectra. In the racemic case reported here the preparation appears to have given an uncontaminated sample, but three fractions were isolated from the preparation from which the *meso* crystal was taken. These fractions showed slightly different NMR spectra.[8] Larsson[16] has studied the NMR spectra of a number of *meso* and racemic forms of carboxylic acids and methyl esters, and found small differences in the chemical shift of corresponding hydrogen atoms. A comparison of the data available to us indicates that the sample from which the *meso* crystal was taken also contains some of the racemate. In retrospect, we were perhaps fortunate in not knowing the conditions used by earlier workers when we started our work. The reaction under refluxing conditions apparently gives a mixture, whereas mixing the reactant at 0–5 °C and allowing the mixture to warm to room temperature gives the pure racemate.

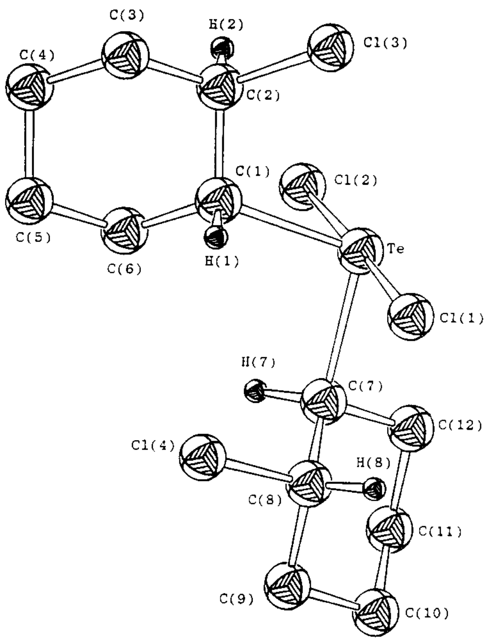


Fig. 2 Molecular structure of *meso* bis(*trans*-2-chlorocyclohexyl)tellurium dichloride **II** with atomic numbering using the coordinates given by Cameron *et al.*[5] Hydrogen atoms are shown only on C(1), C(2), C(7) and C(8) for clarity (ORTEP,[10] all atoms given arbitrary radii)

Experimental

Tellurium tetrachloride was sublimed before use. Cyclohexene (Aldrich) was used as received, and was stated to contain 0.01% 2,6-di-*tert*-butyl-4-methylphenol. Proton NMR spectra were measured at 20 °C in $CDCl_3$ solution at 360 MHz using a Bruker AM360 spectrometer.

Preparation of racemic bis(*trans*-2-chlorocyclohexyl)tellurium dichloride

Cyclohexene (7.05 g, 86 mmol) was stirred with finely powdered tellurium tetrachloride (2.19 g, 8.13 mmol) with ice cooling for 4 h. The cooling bath was removed and stirring continued at room temperature for 48 h. The mixture was evaporated to dryness *in vacuo*, and the residue recrystallised from glacial acetic acid to give colourless crystals (1.4 g, 40%), m.p. 130–131 °C (Found: C, 33.3; H, 4.4. Calc. for $C_{12}H_{20}Cl_4Te$: C, 33.2; H, 4.6%).

Crystallography

Crystal data. $C_{12}H_{20}Cl_4Te$, $M = 433.70$, monoclinic, space group $P2_1/c$, $a = 11.36(1)$, $b = 13.60(1)$, $c = 11.13(1)$ Å, $\beta = 111.28(7)$, $U = 1602(2)$ Å^3 (by least-squares refinement on diffractometer angles from 19 centred reflections $19 < 2\theta < 32°$), $T = 298$ K, Zr-filtered Mo-Kα radiation ($\lambda = 0.7107$ Å), $Z = 4$, $D_c = 1.80$ Mg m^{-3}, $F(000) = 848$, $R = 0.060$, $R' = 0.069$, goodness of fit = 2.39.

The crystal was multifaceted, roughly spherical and initially colourless, but orange at the end of the data collection. No correction was made for absorption. A standard reflection showed a 11% decrease in intensity during the data collection of 1488 reflections of which 1143 had $I_{net} > 2.5\sigma(I_{net})$; 2θ range 4–40°. The data were collected using a Picker four-circle diffractometer interfaced to a Turbo 286 IBM-compatible microcomputer. The structure was solved by direct methods and Fourier-difference techniques using the NRCVAX program package.[17] The hydrogen atoms were placed in calculated positions and fixed during refinement. The positions of all non-hydrogen atoms and their anisotropic thermal parameters were refined by full-matrix least squares with unit weighting of F.

CCDC reference number 186/726.

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