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Preliminary communication

THE X-RAY STRUCTURE AND MÖSSBAUER PARAMETERS OF THE DICHLORODIMETHYLTIN(IV) 1/1 SALICYLALDEHYDE ADDUCT

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Summary

X-ray structure analysis has confirmed that the dichlorodimethyltin(IV) 1/1 salicylaldehyde adduct is five-coordinate with a distorted trigonal bipyramidal geometry and the Mossbauer parameters are reported.

Many six-coordinate dichlorodimethyltin(IV) adducts with a range of donor groups are known. However, salicylaldehyde (salH) has been shown to form an apparently five-coordinate 1/1 adduct $Sn^{IV}Cl_2(CH_3)_2 \cdot salH$ and attempts to form the 1/2 adduct was unsuccessful [1].

The Mossbauer quadrupole splitting of $Sn^{IV}Cl_2(CH_3)_2 \cdot salH$ (Δ = 3.33 mm s^{-1}) [2] and the positive sign of the quadrupole coupling constant (e^2qQ, recorded in an external magnetic field with a powdered sample) are consistent with a CH_3—Sn—CH_3 angle greater than 109° [3]. From this a trigonal bipyramidal geometry for the adduct was proposed.

Pale yellow crystals of $SnCl_2(CH_3)_2 \cdot C_7H_6O_2$ are orthorhombic, spacegroup $P2_12_12_1$; a = 10.32, b = 17.44, c = 6.89 Å; D_o = 1.82, D_c = 1.83 g cm^{-3}, Z = 4. The structure determination was based on Patterson and Fourier methods. Full matrix least-squares refinement of the atomic positional and anisotropic thermal parameters has reduced the discrepancy index R to 0.047 for 981 independent visually estimated reflections (Mo-K_α radiation). The molecular geometry is shown in Fig. 1; estimated standard deviations in the bond lengths average Sn—Cl 0.006, Sn—C 0.018, Sn—O 0.013, C—O 0.02, and C—C 0.03 Å.

The tin atom is five-coordinate with a very distorted trigonal bipyramidal geometry. The nearest non-bonding contact is the phenolic oxygen of

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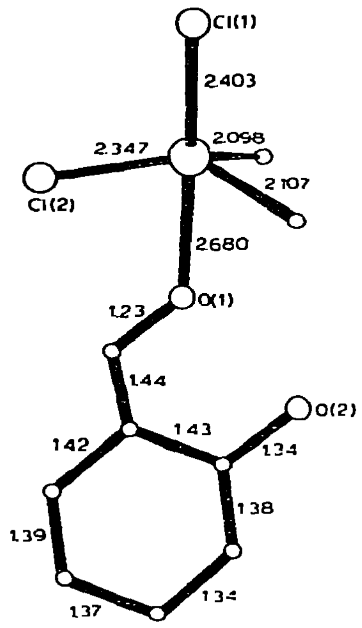

Fig.1. The structure of the dichlorodimethyltin(IV) 1/1 salicylaldehyde adduct; bond lengths in Å.

a neighbouring molecule, Sn—O(2)′ 3.37 Å. The axial Sn—Cl(1) bond is longer (0.056 Å, 8σ) than the equatorial Sn—Cl(2) bond, as expected for trigonal bipyramidal geometry. The aldehydic oxygen of the monodentate salicylaldehyde ligand forms the second axial bond, Sn—O(1) 2.680 Å. The distance between this oxygen atom and the uncoordinated phenolic oxygen atom, O(1)—O(2) 2.63 Å is consistent with the internal hydrogen bond proposed from infrared evidence [1]. The three equatorial ligands are slightly displaced from the equatorial plane towards the coordinated oxygen atom.

The two methyl—tin bonds are markedly displaced from regular trigonal bipyramidal geometry, the C—Sn—C angle being 131°. In the distorted tetrahedral molecule of dichlorodimethyltin(IV) itself the corresponding C—Sn—C angle (124°) is also very large, and this was attributed to weak intermolecular forces (two Sn—Cl contacts of 3.5 Å) [4]. However, there are no steric factors to account for the very large C—Sn—C angle in the $Sn^{IV}Cl_2(CH_3)_2\cdot$salH complex. This may be regarded as another example of the unusual CH_3—Sn—CH_3 angles, noted as a feature of organotin chemistry, which have been explained in terms of a large tin 5s orbital contribution to the tin—carbon bond [5].

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