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Preliminary communication

THE CRYSTAL STRUCTURE OF BIS(TRIMETHYLTIN)CARBONATE

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Summary

The crystal structure of bis(trimethyltin)carbonate, $(Me_3Sn)_2CO_3$ shows the presence of different tin-atom sites in a polymeric structure which arises as a result of a tridentate mode of coordination of the carbonate dianion.

Recent tin-119 NMR and Mössbauer studies on the bis(trialkyltin)carbonates, $(R_3Sn)_2CO_3$ (R = Me, Bu), indicated that in each of these polymeric compounds there are both 4- and 5-coordinate tin atoms [1]. The X-ray structure determination of the methyl derivative, $(Me_3Sn)_2CO_3$, reported herein, is in essential agreement with the spectroscopic results but the analysis indicates that the "4-coordinate" tin atom interacts weakly with a second oxygen atom.

Colourless crystals were obtained by slow evaporation of a CH_2Cl_2 solution of the compound. Intensity data were collected on an Enraf—Nonius CAD4-F diffractometer. Corrections were applied for Lorentz and polarization effects and for absorption. Of the 1763 reflections measured, 1375 satisfied the $I \geqslant 2.5\sigma(I)$ criterion.

Crystal data: $C_7H_{18}O_3Sn$, M = 387.6, orthorhombic, space group $P2_12_12_1$ (D_2^4, No 19), a 7.155(2), b 10.214(1), c 18.981(2) Å, U 1387.2 Å^3, D_x 1.856 g cm^{-3} for Z = 4, $F(000)$ = 736, Mo-K_α (graphite monochromator) radiation, λ 0.71073 Å, $1 \leqslant \theta \leqslant 25°$, μ 33.2 cm^{-1}, T 23°C, absorption correction applied, max/min transmission factors 0.8024 and 0.3418.

The structure was solved by direct-methods using the SHELX [2] system of programs. Anisotropic thermal parameters were introduced for all non-H atoms and H-atoms were included in the model at their calculated positions. A weighing scheme, $w = 0.16/[\sigma^2(F) + 0.008|F|^2]$, was introduced and the refinement converged with final R = 0.031 and R_w = 0.036. The maximum residual electron density peak was 0.84 eÅ^{-3} and the analysis of variance

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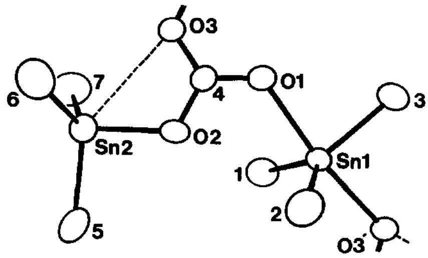

Fig. 1. The numbering scheme used for $(Me_3Sn)_2CO_3$. Important interatomic parameters: Sn(1)—O(1) 2.247(6), Sn(1)—O(3') 2.261(6), Sn(2)—O(2) 2.031(7), C(4)—O(1) 1.264(12), C(4)—O(2) 1.315(11), C(4)—O(3) 1.267(12) Å; O(3')—Sn(1)—O(1) 171.6(2), Sn(1)—O(1)—C(4) 124.7(6), O(1)—C(4)—O(2) 119.1(8), O(1)—C(4)—O(3) 122.9(8), O(2)—C(4)—O(3) 118.1(8), C(4)—O(2)—Sn(2) 116.1(6), C(4)—O(3)—Sn(1') 120.5(6)°.

showed no special features. The absolute structure could not be determined as there were no significant differences in the Friedel pairs included in the data set*.

The numbering scheme used for the structure is shown in Fig. 1 which illustrates the distinct tin-atom environments. The geometry about the five-coordinate tin atom is trigonal bipyramidal; the three methyl substituents define the trigonal plane and the apical positions are occupied by O(1) and the bridging O(3') atom. In contrast, an approximately tetrahedral environment, comprised of three methyl groups and O(2), is found for Sn(2). Distortion from an ideal tetrahedal geometry about Sn(2) may be due, in part, to an additional Sn(2). . .O(3) interaction of 2.896(6) Å, which is well within the sum of the Van der Waals radii for Sn and O of 3.7 Å [3].

The two Me_3Sn moieties are linked via a bridging carbonate dianion which forms dissimilar Sn—O bonds which probably reflects the *trans* influence of the bridging O(3) atom on the Sn—O(1) bond. The CO_3 fragment is essentially planar, as expected, and substantial delocalization of π-electrons in the CO_3^{2-} ligand is further indicated by the equivalence, within experimental errors, of the C—O bond distances. Additional O(3)—Sn(1) interactions lead to a polymeric structure, which has the consequence that the carbonate ligand is effectively tridentate. The polymeric structure is thus generated by —Sn(1)—O(1)—C(4)—O(3)—Sn(1')— bridges orientated along the crystallographic 2_1 screw-axis parallel to the *b*-axis direction.

The earlier spectroscopic study [1] showed that in the solid state two different tin-atom environments were present, but in solution a broad tin-119 NMR resonance was observed. This was explained in terms of a rapid exchange, on the NMR time scale, between 4- and 5-coordinate tin sites. A possible mechanism for this exchange, as indicated by the crystallographic results, would involve the weakening of the Sn(1)—O(3') bond with the commensurate increase in bond order of the Sn(2)—O(3) interaction. The effect of such a mechanism described would be to increase the coordination number of Sn(2)

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* The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

to five and concurrently decrease that of Sn(1) to four. The angle of approximately 157° found for Sn(1′)—O(3)—Sn(2) lends support to this hypothesis.

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