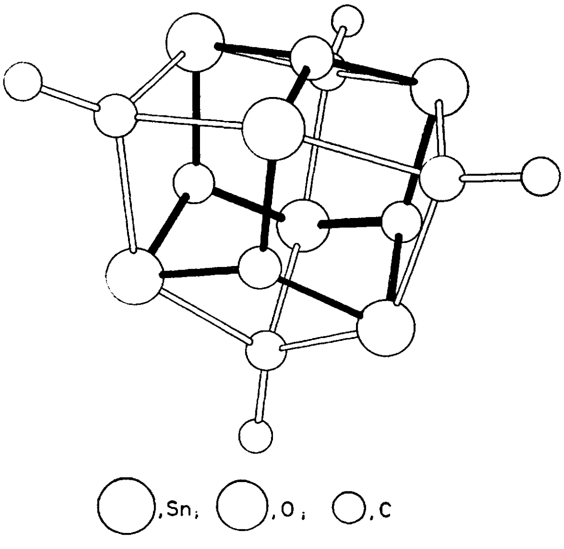
X-Ray Crystal Structure of $Sn_6O_4(OMe)_4$: an Intermediate in the Hydrolysis of Tin(II) Dimethoxide

By PHILIP G. HARRISON,* BERNARD J. HAYLETT, and TREVOR J. KING
(*Department of Chemistry, University of Nottingham, University Park, Nottingham* NG7 2RD)

Summary $Sn_6O_4(OMe)_4$, isolated from the controlled hydrolysis of $Sn(OMe)_2$, has an adamantane Sn_6O_4 skeleton with triply-bridging methoxy groups.

FEW intermediates in the hydrolysis of bivalent tin compounds have been characterised. Tin(II) chloride forms a dihydrate in which one water molecule is co-ordinated to the metal[1] prior to the formation of a basic chloride.[2] Two basic tin(II) sulphates have also been characterised[3] as well as a basic nitrate.[4] Exhaustive hydrolysis generally produces tin(II) oxide or hydrated oxide.

Tin(II) dimethoxide is an important synthetic intermediate in bivalent tin chemistry, and although its structure is unknown, its physical properties (infusibility, insolubility, *etc.*) suggest a polymeric structure in which methoxy groups bridge adjacent tin(II) atoms. Heating to reflux a suspension of this compound in benzene in the presence of a partial pressure of water in an argon atmosphere results in its dissolution. Filtration of the reaction mixture produces a colourless filtrate from which white needles form on standing. The ^{119m}Sn Mössbauer isomer shift of the product ($2{\cdot}78 \pm 0{\cdot}06$ mm s^{-1} relative to $BaSnO_3 = 0$) confirms the preservation of the lower valence state, and bands in the i.r. spectrum at 1027 and 570br cm^{-1} may be assigned to the C–O and Sn–O stretching vibrations, respectively, of a methoxytin compound. Complete



FIGURE

characterisation of the material was accomplished by an X-ray diffraction study, which showed its composition to be $Sn_6O_4(OMe)_4$, a hydrolysis product of tin(II) dimethoxide.

Crystal data: $C_4H_{12}O_8Sn_6$, monoclinic, space group $P2_1/c$ with $a = 18{\cdot}387(4)$, $b = 18{\cdot}519(4)$, $c = 10{\cdot}543(3)$ Å, $\beta = 104{\cdot}74(2)°$, $Z = 4$, Mo-K_α radiation ($\lambda = 0{\cdot}71069$ Å).†

The structure was solved using diffractometer data which were corrected for absorption and anomalous dispersion using the MULTAN programme to obtain the initial positions of the tin atoms. The positions of the remaining non-hydrogen light atoms were obtained by subsequent Fourier syntheses, and the refinement was completed by block-diagonal anisotropic least-squares to a final R-value of 7·25% for 4890 independent, non-zero reflections.

Crystals are composed of two crystallographically independent non-interacting $Sn_6O_4(OMe)_4$ units with a central Sn_6O_4 core possessing the adamantane structure, the whole approximating very closely to D_{2d} symmetry. The four methoxy groups triply-bridge in a symmetrical fashion the three metal atoms of the four faces of the adamantane skeleton (Figure). Bond distance and angle data for each of the two crystallographically independent molecules are very similar. The Sn–O bonds within the Sn_6O_4 skeleton [2·05(1)—2·08(1) Å] are amongst the shortest yet recorded, and are considerably shorter than those typically observed for bivalent tin–oxygen bonded compounds. The distances to the methoxy groups are more typical [2·35(1)—2·43(1) Å]. The resultant geometry at each tin atom is thus that of a distorted [angles O_{eq}–Sn–O_{eq} = 92·5(4)—94·6(4)°, O_{ax}–Sn–O_{ax} = 133·2(4)—135·0(4)°] pseudo-trigonal bipyramid similar to that observed in $Sn(O{\cdot}CPh{\cdot}CH{\cdot}COMe)_2$,[5] with oxygen atoms of the adamantane cage and the methoxy groups occupying equatorial and axial sites, respectively, and the tin lone pair of electrons being located in the remaining equatorial position.

In spite of the apparently quite strong bonding present in the Sn_6O_4 core, its preservation on reaction has not yet been observed. Thus, attempts preferentially to cleave the methoxy groups using hexafluoroacetylacetone or acetic acid results in the exclusive formation of $Sn(OC{\cdot}CF_3{\cdot}CH{\cdot}CO{\cdot}CF_3)_2$ and $Sn(O_2CMe)_2$, respectively.

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† The atomic co-ordinates 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.

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