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LETTER

Structures of dialkyltin hypophosphites and phosphites: comments on the paper 'Synthesis and IR study of some tin(IV) hypophosphito adducts and compounds'

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In a recent paper Sall and Diop reported the synthesis of some tin(IV) hypophosphito complexes, including the series $R_2Sn(H_2PO_2)_2$ (R = Me, Ph, Bu), which they claim to be new [1]. These authors also proposed structures for dialkyltin hypophosphites and for di-n-butyltin phosphite, n-Bu_2SnHPO_3, solely on the basis of infrared spectroscopic data [1]. The purpose of this letter is to point out that the synthesis and structures of dialkyltin hypophosphites and phosphites have been investigated extensively more than 15 years ago [2] and that the conclusions drawn by Sall and Diop concerning the structures of n-$Bu_2Sn(H_2PO_2)_2$ and Bu_2SnHPO_3 are inconsistent with the previously published ^{119}Sn Mössbauer data for these compounds [2].

In fact the synthesis of $Me_2Sn(H_2PO_2)_2 \cdot 2H_2O$ was first reported in 1959 [3]. Subsequently, the anhydrous compounds $R_2Sn(H_2PO_2)_2$ (R = Me, Et, ^{n}Bu) were assigned polymeric structures with hexacoordinate tin, bridging bidentate $H_2PO_2^-$ ligands and *trans*-methyl groups (Fig. 1) on the basis of ^{119}Sn Mössbauer and infrared spectroscopic data [2]. In particular, the positive value of the Mössbauer quadruple coupling constant ($\Delta E_Q = +4.36$ mm s^{-1}) and the value of the asymmetry parameter ($\eta = 0$) for $Me_2Sn(H_2PO_2)_2$ are consistent with a *trans*-octahedral structure. Similar structures have been proposed for $R_2Sn(O_2PF_2)_2$ [4] and $Me_2Sn(O_2PCl_2)$ [5].

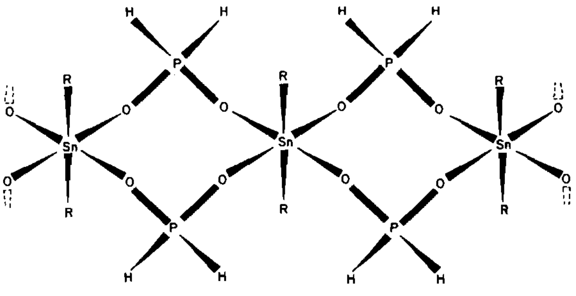

Fig. 1. Structure of $R_2Sn(H_2PO_2)_2$ (R = Me, Et, ^{n}Bu).

Sall and Diop also attribute this geometrical arrangement to $Me_2Sn(H_2PO_2)_2$ [1]. However, in the case of $^nBu_2Sn(H_2PO_2)_2$ they suggest a structure involving tetrahedral tin and a bent SnC_2 group on the basis of an infrared band at 530 cm^{-1} assigned to $\nu_s(SnC_2)$ [1]. This infrared band was not observed in the previous work [2] and, in disagreement with the suggestion of Sall and Diop, we point out that the ^{119}Sn Mössbauer parameters for $^nBu_2Sn(H_2PO_2)_2$ ($\Delta E_Q = 4.47$ mm s^{-1}) are essentially the same as those found for the methyl and ethyl derivatives [2] and leave little doubt that $^nBu_2Sn(H_2PO_2)_2$ has the *trans*-octahedral structure depicted in Fig. 1.

We also draw attention to an earlier paper by Ridenour and Flagg in which compounds of the type $^nBu_2Sn[O_2PR_2]_2$ ($R = C_5H_{11}$, C_6H_{13}) were found to be dimeric in solution [6]. The symmetric SnC_2 stretching frequency was *extremely weak* in the infrared spectrum, two signals were observed in the ^{31}P NMR spectrum and ^{119}Sn Mössbauer data were consistent with octahedral tin. Consequently, the authors proposed the structure illustrated in Fig. 2 [6].

Sall and Diop also describe the formation of $^nBu_2SnHPO_3$ from the reaction of $^nBu_3SnCl$ with $H_2PO_2^-$ in ethanol and they ascribe a tetrahedral structure to the product on the basis of infrared spectroscopic data [1]. The disproportionation of $(Me_3Sn)_2HPO_3$ into Me_2SnHPO_3 has been reported previously [7] and the structures of R_2SnHPO_3 (R = Me, Et, ^{n}Bu) and Me_2SnFPO_3 have been investigated in detail by ^{119}Sn Mössbauer as well as by infrared spectroscopy [2]. The ^{119}Sn Mössbauer quadruple splittings of 3.8–4.0 mm s^{-1} for R_2SnHPO_3 and 4.16 mm s^{-1} for Me_2SnFPO_3 are too large for a tetrahedral structure [8] and indicate a polymeric

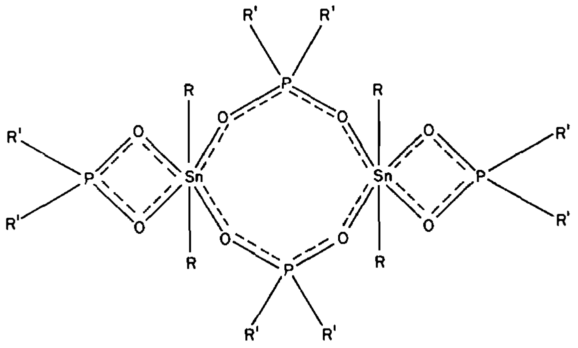

Fig. 2. Suggested structures of $R_2Sn(R'_2PO_2)$ (R = ^{n}Bu; $R' = C_5H_{11}$, C_6H_{13}).

penta- or hexa-coordinated structure with a non-linear C–Sn–C arrangement. The presence of a *weak* band for $\nu_s(SnC_2)$ in the infrared spectra of R_2SnHPO_3 also indicates a small distortion of the C–Sn–C group from linearity. The magnetic hyperfine Mössbauer spectrum of Me_2SnFPO_3 is consistent with either a distorted *trans*-octahedral (Fig. 3(a)) or a distorted trigonal bipyramidal structure (with both apical or both equatorial methyl groups, see Fig. 3(b) and (c) and, in view of the similarity of the ^{119}Sn Mössbauer parameters, these possibilities must also be considered for R_2SnHPO_3.

In summary, the analysis of structures of organotin derivatives of oxyacids on the basis of infrared spectroscopic data alone can often lead to erroneous conclusions. ^{119}Sn Mössbauer spectroscopy provides additional, more detailed structural information, but does not always lead to an unambiguous structural assignment. X-ray crystallography is necessary in most cases to define the structures with certainty. However, organotin derivatives of *inorganic* phosphorus oxyacids are usually polymeric, intractable powders unsuitable for X-ray crystallography. An exception is $(Me_2Sn)_3(PO_4)_2 \cdot 8H_2O$ which consists of a polymer ribbon with one tin atom in a regular octahedral environment and the other two tin atoms in highly distorted octahedral arrangements [9].

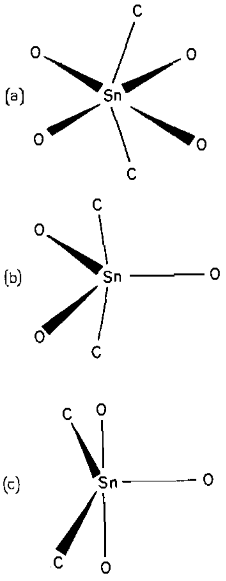

Fig. 3. Possible geometrical arrangements around the tin atom in R_2SnHPO_3.

Acknowledgement

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