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Infrared, Mössbauer and Lattice Dynamics Studies of (3-Mercaptopropionato)bis(trimethyltin(IV))

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The present work has been carried out in the context of an investigation of the interaction of triorganotin(IV) moieties with trifunctional aminoacids and related molecules, such as cysteine and penicillamine [1]. Such studies obviously require the knowledge of the bonding characteristics of derivatives of related monofunctional, as well as difunctional, ligands. Triorganotin(IV) carboxylates are either polymers, where the carboxyl group bridges five-coordinated metal atoms, or monomers with carboxyl–tin ester type bonds in a tetrahedral configuration, as function of steric hindrance, physical state and temperature; polymerisation usually occurs in the solid state and at low temperatures [2a–m]. Triorganotin(IV) alkyl- and phenyl-thiolates are generally four-coordinated compounds [3a–c]. Complexes with the difunctional ligands ω-mercaptocarboxylates exhibit both 1:1 and 2:1 triorganotin(IV): ligand stoichiometry [4]. In 1:1 derivatives the organotin moiety may be bonded to the carboxyl or to the thiol group, and the respective structural characteristics correspond to those of complexes with monofunctional ligands [4]. The 2:1 compounds insofar reported are bis(tri-n-propyltin)- and bis(tri-n-butyltin)-mercaptoacetate, which are liquid at room temperature and monomeric in solution; their Mössbauer spectra at liquid N_2 temperature consist of two doublets, the outer one being attributed to five-coordinated tin bound to carboxyl oxygen atoms, and the inner one to four-coordinated tin bound to thiol sulfur [4].

The work reported in this note extends the findings on 2:1 compounds; 3-mercaptopropionic acid, which is in some way a ‘precursor’ of both cysteine and penicillamine, has been selected as ligand, and the sterically non-hindering trimethyltin(IV) moiety has been used as acceptor. The complex $[(CH_3)_3Sn]_2$–$[SCH_2CH_2COO]$ has been synthesized by reacting 10^{-2} mol $(CH_3)_3SnOH$ with 5×10^{-3} mol $HSCH_2CH_2COOH$ in 35 ml dried $CHCl_3$, at 0 °C. Water formed during the reaction was removed by adding anhydrous Na_2SO_4. After filtering off the latter and partially evaporating the solution at 10 °C petroleum ether: diethylether (1:1) was added. On standing overnight at 0 °C, a white microcrystalline solid precipitated. This has been filtered off, washed with petroleum ether and dried under vacuum. *Anal.* Found: C %, 25.13; H %, 5.15; Sn %, 55.00. $C_9H_{22}O_2SSn_2$ requires: C %, 25.05; H %, 5.11; Sn %, 55.00). Yield 72%.

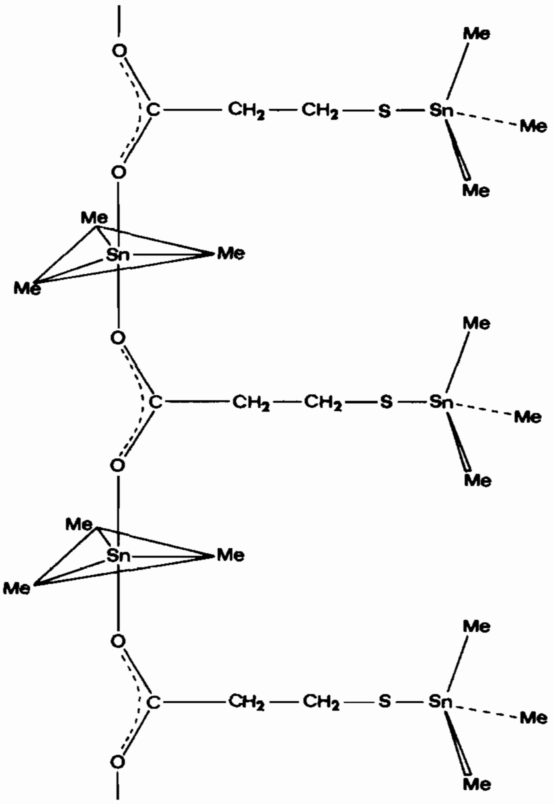

Fig. 1. The structure of *catena*-[3-mercaptopropionato-(2–)-*S*-*μ*-*O*,*O*′] bis(trimethyltin(IV)).

The infrared spectrum of the compound (measured in nujol mulls, as well as in CsBr disks) shows ν_{as} (COO) at 1582 cm^{-1}, ν_s (COO) at 1408 cm^{-1}, ν_{as} (SnC_3) at 560 and 542 cm^{-1}, ν_s (SnC_3) at 520 cm^{-1}, and ν(SnS) at 334 cm^{-1}. The frequencies of ν(COO) modes are typical of bridging carboxyl [2]. The SnC_3 skeletal modes are originated by both carboxyl- and thiol-bonded $(CH_3)_3Sn^{IV}$ moieties. In the derivative $(C_6H_5)_3SnSCH_2CH_2COOSn(CH_3)_3$, only $\nu_{as}(SnC_3)$ is detected at 560 cm^{-1} [5], which implies a planar SnC_3 (alk) skeleton at the –COO–Sn site; the values $\nu(SnC_3)$ of $[(CH_3)_3Sn]_2[SCH_2CH_2COO]$ are then interpreted in terms of

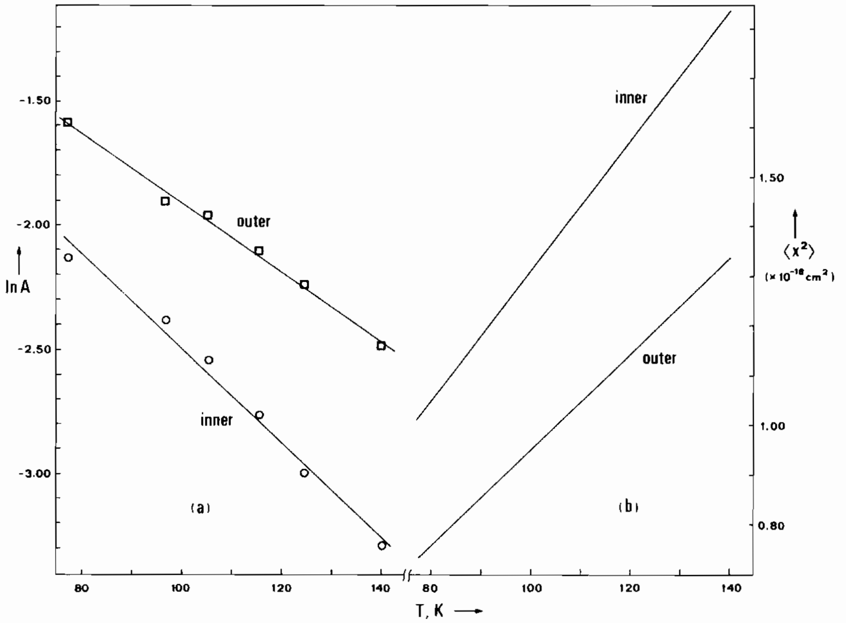

Fig. 2. Temperature dependent functions of the inner and outer pair of resonance maxima of $[(CH_3)_3Sn]_2[SCH_2CH_2COO]$. (a): the experimental data points, lnA (T), 'A' being the total Lorentzian area under the resonant peaks, and least squares fits (full lines); (b): the mean square displacements of the Mössbauer atom, $\langle x^2 \rangle$ (T), calculated from dlnA/dT.

TABLE I. Mössbauer and Lattice Dynamics Parameters of $[(CH_3)_3Sn]_2[SCH_2CH_2COO]$.[a]

Pair of resonance maxima	δ[b] (mm s^{-1})	ΔE[c] (mm s^{-1})	Γ_1[d] (mm s^{-1})	Γ_2[d] (mm s^{-1})
inner	1.326 ± 0.004	1.869 ± 0.011	0.838	0.854
outer	1.324 ± 0.002	3.580 ± 0.002	0.888	0.865
	dlnA/dT[e] (X 10^{-2}, K^{-1})	θ_D[f] (K)	$\bar{\nu}_D$[f] (cm^{-1})	$M\theta_D^2$[f] (u.m.a. X deg^2 X 10^{-6})
inner	−1.913(0.993)	50.8	35.3	1.11
outer	−1.391(0.997)	59.6	41.4	1.53

[a] Sample thickness 1.88 mg $^{119}Sn/cm^2$; this relatively high value has been employed in order to get well formed spectra even at the higher temperatures, the resonance effect, ϵ, being sensibly different for the two doublets (at 77.3 K, for the given thickness, ϵ_{inner} = 0.0426, ϵ_{outer} = 0.0674) [4]. [b] Isomer shift with respect to room temperature $CaSnO_3$, and [c] nuclear quadrupole splitting: average values (and standard errors) of data in the temperature range examined (see Fig. 2). The near constancy of the parameters excludes phase transitions. [d] Full widths at half height of the resonant peaks (Lorentzian fits): average values, at larger (Γ_1) and lesser (Γ_2) velocity than the spectrum centroid. [e] 'A' is the total Lorentzian area under the resonant peaks, A = $\pi/2 \times \epsilon \times \Gamma$, mm s^{-1}. Temperatures vary within ±0.5 °C with respect to nominal values of Fig. 2. Slopes are obtained from least-squares fits of data points shown in Fig. 2a. Correlation coefficients are in parentheses. [f] Debye-Mössbauer temperature θ_D, cutoff frequency, $\bar{\nu}_D$, and parameter of intermolecular force constant, $M\theta_D^2$, calculated by a computer program for dlnA/dT, the effective vibrating mass being the formula weight. See text.

a planar SnC_3 configuration occurring at the –COO–Sn site, and of a bent one at the –S–Sn site. The structure reported in Fig. 1 would then emerge from the infrared study for our compound at room temperature.

This hypothesis has been checked by Mössbauer spectroscopic investigations. The spectra, determined as usual [6], consist of two resonance doublets (as in the homologous compounds mentioned above [4]) in the whole temperature range examined (see Fig. 2); on fitting with Lorentzian lineshapes, the parameters δ, ΔE and Γ reported in Table 1 have been obtained. The values of δ and ΔE of the inner doublet are in excellent agreement with data of tetrahedral trialkyltin(IV) alkylthiolates (δ = 1.39, ΔE = 1.75, 1.80, mm s^{-1} [3a, b]), while values of the outer doublet correspond to those of polymeric trimethyltin(IV) acetate, with a trigonal bipyramidal environment of the tin atom (δ = 1.35, ΔE 3.68, mm s^{-1} [2e]). The ΔE data of the above mentioned thiolato and acetato compounds may be taken as point-charge model values, being employed as estimators of partial quadrupole splittings ([Alk-S]−[hal]), tetrahedral, and {$OCOCH_3$}, bridging, trigonal bipyramidal axial [3b, 7]. The environments of tin atoms extracted from the Mössbauer parameters δ and ΔE then fully agree with the configuration deduced from the infrared spectra (Fig. 1).

The structural feature of $[(CH_3)_3SN]_2[SCH_2CH_2COO]$ have been further studied by determining lattice dynamics parameters and functions through temperature dependent Mössbauer spectroscopy [8]. The experimental procedures and methods of treatment of data have been as described earlier [8]. The linearity of lnA(T) functions of both doublets of the spectra (Fig. 2a) allows the application of the thin absorber approximation and of the related equations in calculating $\langle x^2 \rangle$ (T), θ_D, $\bar{\nu}_D$, and $M\theta_D^2$ from slopes dlnA/dT (Fig. 2 and Table I) [8].

Tin atoms originating the outer doublet, with respect to atoms involved in the inner doublet, are characterized by: (i) a larger recoil free fraction f_a (indicated by larger A(T) and ϵ, and lower $\langle x^2 \rangle$ (T), values); (ii) lesser temperature dependence of ln A(T) and $\langle x^2 \rangle$ (T) functions; (iii) larger θ_D, $\bar{\nu}_D$ and $M\theta_D^2$ (Fig. 2 and Table I).

This implies that eventual intermolecular forces would act preferentially at –COO–Sn sites [2h, 8–11]. For these tin atoms, the values of the parameters d ln A/dT and $M\theta_D^2$, and the $\langle x^2 \rangle$ (T) function, are more consistent with the respective data of the bidimensional polymer $(CH_3)_2Sn(OCOH)_2$ rather than with those of the monodimensional, helical chain, polymers $(CH_3)_3SnOCOH$, $(C_6H_5)_3SnOCOCH_3$ and $(C_6H_5)_3Sn\ OCO(CH_2)_2COCH_3$* [2h, 10, 11]; besides, the $M\theta_D^2$ value (Table I) is typical of monodimensional polymers [11].

It follows clearly that $[(CH_3)_3Sn]_2$ $[SCH_2CH_2COO]$ is a solid state polymer, due to the occurrence of possibly non-helical $(OCOSn)_n$ chains. Tin atoms giving origin to the inner doublet cannot be treated into details, since no lattice dynamics investigations have been apparently carried out on triorganotin(IV) thiolates; anyhow, data dlnA/dT, $M\theta_D^2$ and $\langle x^2 \rangle$ (T) (Table I and Fig. 2b) are typical of monomeric species [10–12].

In conclusion, the structure reported in Fig. 1 clearly emerges from the present investigation, there being complete agreement between infrared spectroscopy, point-charge model rationalization of ΔE parameters, and lattice dynamics.

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*$dlnA/dT = dlnf_a/dT = \sim -2 \times 10^{-2}$ (K^{-1}), estimated from published $\langle x^2 \rangle$ (T) functions [2h], for the three R_3-SnOCOR compounds; $dlnA/dT = dlnf_a/dT = -1.05 \times 10^{-2}$ (K^{-1}) for $Me_2Sn(OCOH)_2$, calculated from $dlog_{10}f_a/dT = -4.56 \times 10^{-3}$ (K^{-1}) [12].