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Variable-Temperature Tin-119m Mössbauer Study of the Chlorodimethyltin(IV) Derivatives of L-Cysteine and DL-Penicillamine

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Introduction

Organotin compounds play an important role in biology and the environment [1, 2] and are themselves powerful biocides [3]. We have been pursuing studies in the synthesis [3–5] and structural characterization [7] of organotin(IV) derivatives of amino acids to help to elucidate their mode of action, and have extended these studies to some biologically relevant thio ligands [8–12]. We report in this paper the results from a variable-temperature tin-119m Mössbauer study of the L-cysteine monohydrate and DL-penicillamine derivatives of chlorodimethyltin(IV) which dinstinguishes between the several structural possibilities for these solids.

Experimental

Tin-119m Mössbauer spectra were recorded on a Ranger Engineering constant-acceleration spectrometer equipped with an NaI scintillation counter using Ca $^{119}SnO_3$ (New England Nuclear Corp.) as the source and $Ca^{119}SnO_3$ and β-tin as standard reference materials for velocity calibration at room temperature. Standard, nonlinear, least-squares techniques were used to fit the data to Lorentzian curves. The Ranger Engineering variable-temperature, liquid-nitrogen dewar and controller used in these studies are regulated by a variable-bridge, silicon-controlled-rectifier circuit and is accurate to ±1 K.

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Results and Discussion

The products from the reaction of L-cysteine hydrochloride hydrate and DL-penicillamine in dilute HCl with dimethyltin(IV) oxide contain sulfur–tin bonds:

$$(CH_3)_2SnO + HSCH_2\underset{\underset{NH_2}{|}}{CHC}(=O)OH\cdot HCl\cdot H_2O \rightarrow$$

$$\rightarrow (CH_3)_2\underset{\underset{Cl}{|}}{Sn}\underset{\underset{NH_2}{|}}{SCH_2CHC}(=O)OH\cdot H_2O \qquad (1)$$

$$(CH_3)_2SnO + HSC(CH_3)_2\underset{\underset{NH_2}{|}}{CHC}(=O)-OH\cdot HCl \rightarrow$$

$$\rightarrow (CH_3)_2\underset{\underset{Cl}{|}}{Sn}SC(CH_3)_2\underset{\underset{NH_2}{|}}{CHC}(=O)OH \qquad (2)$$

The former is obtained in quantitative yield as a monohydrate, the latter in 90% yield anhydrous. Titration of the cysteine derivative with sodium hydroxide removes the carboxylate and amino protons stepwise, and the absence of uv bands assignable to the cysteinate and chlorodimethyltin ions rules out a simple ionic formulation in aqueous solution. Infrared absorptions for the Sn–S bond near 400 cm^{-1} with the corresponding absence of the ν(SH) mode, together with mass spectral fragments such as $[Sn-SCH_2CHNH_2]^+$ lend corroborative evidence for the sulfur bonding [8–10].

The structures of the solids are of interest because of the possibilities for oligomeric or polymeric behavior, as found in the organotin derivatives of the simple amino acids [4–7]. In both products the ν(C=O) modes are reduced in frequency, presumably because of association to tin or strong hydrogen bonding. The $|^1J(^{119}Sn-^{13}C)|$ and $|^2J(^{119}Sn-C-^1H)|$ coupling constants in D_2O solution are indicative of higher coordinated tin atoms in that solvent [8–10].

Mössbauer spectroscopy can provide useful information in such cases. The Isomer Shift and Quadrupole Splitting data for these thiol derivatives [12] are consistent with five-coordinated structures, and the spectrum of the penicillamine derivative – being observable at ambient temperatures –

TABLE I. Variable Temperature Tin-119m Mössbauer Data for Chlorodimethyltin(IV) L-Cysteine Monohydrate and Chlorodimethyltin(IV) DL-Penicillamine.

T(K)	L-Cysteine		DL-Penicillamine	
	A(T)[a]	$\log_e$ [A(T)/A(77)]	A(T)[a]	$\log_e$ [A(T)/A(77)]
77	0.487	0.000	0.439	0.000
88	0.414	−0.162	0.346	−0.238
100	0.332	−0.383	0.287	−0.425
110	0.286	−0.532	0.244	−0.587
120	0.245	−0.687		
125			0.202	−0.776
130	0.214	−0.822		
135			0.172	−0.937
140	0.179	−1.001		
150			0.151	−1.067

[a]A(T) is the sum of the areas under the two wings of the doublet.

is suggestive of an associated lattice. Such association can arise either from intermolecular association through bridging amino groups, as in solid trimethyltin(IV) glycinate [7], bridging carboxylate groups as in the organotin acetates [13, 14], or through intermolecular hydrogen bonding which is also present in the structure of the solid glycinate where it stabilizes the lattice. Indeed, the crystal in that case propagates along the direction of the interchain hydrogen bonds and not along the propagation axis of the polymer chain, indicating that hydrogen bonding makes a more important contribution to the lattice energy than does the coordinate-covalent bonding to tin [7]. In contrast, the crystal structure of the ethyl ester of the cystein derivative contains a monomeric, five-coordinated, trigonal bipyramidal tin atom bonded to sulfur and chelated by the amino group [10, 11], which is also intramolecularly hydrogen bonded to the carbonyl. Thus the question of the lattice structure adopted in these species is a complex one and requires further investigation.

Variable temperature Mössbauer studies can distinguish these possibilities. The Mössbauer recoil-free fraction, f, reflects the mean square displacement of the tin atom $\langle\chi^2\rangle$ from its equilibrium position:

$$f = \exp\left[-\frac{\langle\chi^2\rangle}{\lambda\!\!\!^{-2}}\right] \quad (3)$$

where $\lambda\!\!\!^{-}$ is the wavelength of the tin-119m γ-ray divided by 2π. By the Debye model, for thin absorbers, f is linearly related to the area under the resonance, A_T, whose temperature dependence is given by:

$$A_T \left\{ f = \exp\left[-\frac{6E_R T}{k\theta_D{}^2}\right]\right\}; \text{ for } T \rangle \frac{\theta_D}{-2} \quad (4)$$

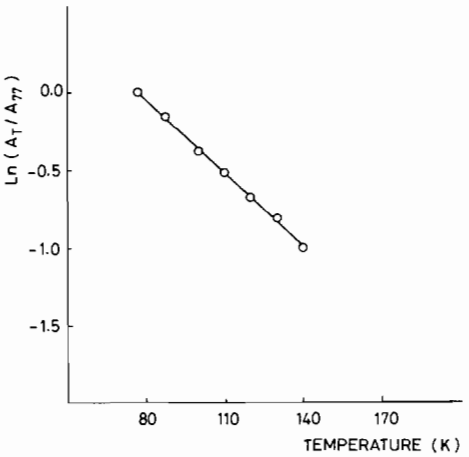

Fig. 1. Plot of lnA (normalized to the area under the resonance curve at 77 K) *vs.* temperature in K for chlorodimethyltin(IV) L-cysteine hydrate. The slope is −1.58 Å 10^{-2} K^{-1}.

where E_R is the recoil energy, and θ_D is a temperature which for an ideal monotomic solid is equivalent to the Debye temperature. The more tightly held are the tin atoms in a lattice, the slower will f – and hence A_T – decrease with increasing temperature. For methyltin derivatives, lattices of monomers exhibit slopes of $\log_e A_T$ *vs.* T of *ca.* -1.8×10^{-2} K^{-1}, regardless of the coordination number at tin. Weak hydrogen bonding reduces this value to *ca.* -1.7×10^{-2} K^{-1}, while complex networks of hydrogen bonding reduces it still more to *ca.* -1.2×10^{-2} K^{-1}. Strongly hydrogen bonded lattices and solids in which one- and higher dimension association is present exhibit slopes of *ca.* -0.9×10^{-2} K^{-1} [16, 17]. A particularly low value is given by tin(II) oxide at -0.23×10^{-2} K^{-1} [15, 17–19] and tetramethyl-

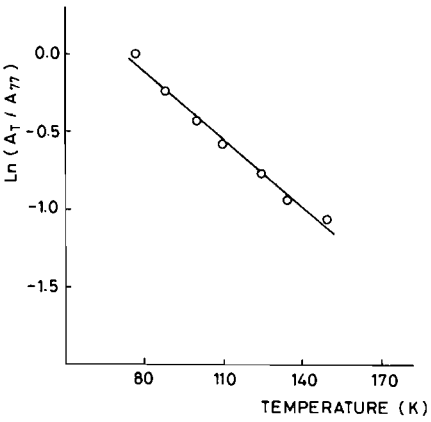

Fig. 2. Plot of lnA (normalized to the area under the resonance curve at 77 K) *vs.* temperature in K for chlorodimethyltin(IV) DL-penicillamine. The slope is -1.46×10^{-2} K^{-1}.

tin is at the other end of the methyltin scale at -2.76×10^{-2} K^{-1} [20].

Table I lists the slope data for chlorodimethyltin(IV) cysteine between 77 and 140 K which are plotted as ln A (normalized to the area under the resonance curve at 77 K) *vs.* temperature in K in Fig. 1. The analogous data for the DL-penicillamine derivatives between 77 and 150 K are given in Table I and plotted in Fig. 2. The slopes are found to be $-1.58 \pm 0.1 \times 10^{-2}$ K^{-1} (intercept at T = 0 K, 1.045, correlation coefficient 0.973 for 7 points) and $-1.46 \pm 0.1 \times 10^{-2}$ K^{-1} (intercept at T = 0 K, 1.215, correlation coefficient 0.999 for 7 points), respectively.

These values are higher than for trimethyltin(IV) glycinate (-1.15×10^{-2} K^{-1}) in which both hydrogen bonding and a one-dimensional association through bridging amino group nitrogen atoms are present [7], but considerably lower than those for monomeric lattices [15, 16, 20].

Against the background of these systematics for methyltin derivatives* the magnitudes of the slopes of the plots of A_T *vs.* temperature for the two chlorodimethyltin(IV) derivatives suggest a lattice in which small molecular or oligomeric units** are associated by a relatively extensive network of hydrogen bonds. The slope values serve to rule out an extended association through bridging amino nitrogen atoms as in the trimethyltin(IV) glycinate [7], or by carboxylate oxygen atoms as in the bridged acetates for which many examples are availabe [13, 14], and are consistent with the dimeric, hydrogen-bonded structure originally proposed on the basis of strong ditin fragments in the mass spectra [8]†.

The hydrogen bonding in the chlorodimethyltin(IV) cysteine monohydrate involves both the water of hydration and the $-NH_2$ group on the basis of the broad absorptions seen at 3450 ν(O–H) and 3000 cm^{-1} ν(N–H) in the infrared spectrum [8] and may involve the carbonyl group as in the ethyl ester [10, 11].

In the corresponding anhydrous DL-penicillamine derivative which exhibits an ambient temperature Mössbauer spectrum and a shallower slope, the hydrogen bonding can only involve the $-NH_2$ and carboxylate groups. The strongly lowered infrared ν(C=O) frequencies in these derivatives (1613 vs, br; 1620 s cm^{-1}, respectively [8]) compared with the monomeric ethyl ester [11, 12] (1733 vs cm^{-1} [8]), and the similarity of the $\nu(NH_2)$ frequencies (3450 s,br; 3450 s,br, respectively *vs.* 3309 s, 3243 s cm^{-1} [8]) specify that carboxylate rather than amino group bridging links the molecular units into the dimer or small oligomer. An alternative structure involving $Cl(CH_3)_2SnSCR_2CH(NH_3^+)COO^-$ units in which R = H, CH_3 can be ruled out by the presence of ν(OH) stretches in the infrared spectra of these compounds [8].

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*The effect of passing from the trimethyltin (whose slopes we are comparing) to our dimethyltin chlorides is not known, but the monomeric tetraphenyltin and diphenyltin dichloride solids [14, 15] have very similar slopes (−1.66 [20, 21] and -1.71×10^{-2} K^{-1} [20]).

**These data do not specify the molecularity of the unit. Attempts to determine the value of n in the formula $[Cl(CH_3)_2SnSCH_2CH(NH_2)COOH]^-$ by use of the effective vibrating mass model [24] proved inconclusive since no bands <200 cm^{-1} were found in the Raman spectrum which could be assigned to the intermolecular, intra-unit cell modes.

†Very weak (<1%) ditin fragments in the mass spectrum of the ethyl ester were shown from a thermogram to arise from decomposition at the probe temperature (160 °C) [9].

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