A MÖSSBAUER STUDY OF SOME TIN COMPLEXES WITH SULFOXIDES

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Abstract—Mössbauer spectrsocopy has been used to study six 1:1 triphenyltin chloride, four 1:2 dimethyltin dichloride and one 1:1 trimethyltin chloride sulfoxide complexes.

An increase in quadrupole splitting on complexation was found for all complexes, although it remains practically constant for each acceptor molecule. While the isomer shifts of the triphenyltin complexes are constant and, furthermore, are approximately the same as that for neat triphenyltin chloride, a significant decrease was observed on complexation of dimethyltin dichloride and trimethyltin chloride.

From the temperature dependence of the area under the Mössbauer lines it was possible to estimate the Debye temperatures for the dimethylsulfoxide-triphenyltin chloride and the di-*n*-propylsulfoxide-dimethyltin dichloride complexes.

There has been considerable interest in the chemical and physical properties of organotin compounds. In the present work, Mössbauer spectroscopy has been used to study some sulfoxide complexes of triphenyltin and trimethyltin chloride and dimethyltin dichloride. Although the Mössbauer parameters for some of these complexes have already been reported [1-5] we have remeasured them to obtain a uniform set of data.

EXPERIMENTAL

In general, the complexes were prepared by dissolving separately the acid and the base in either carbon tetrachloride or n-hexane, and the solutions mixed, with an excess of base. For the liquid sulfoxides the base was added directly to the Lewis acid solution. After slight heating, then cooling and addition of another solvent (usually water), changing the polarity of the medium, a white precipitate deposited. The precipitate was filtered, washed, dried under vacuum at room temperature, and finally recrystallized.

The complete characterization of the complexes was based on the elemental analysis, melting point, thermal stability and IR spectroscopy measurements[6].

Mössbauer spectra were obtained on a conventional constant acceleration spectrometer, moving a Ba^{119m}SnO₃ source at room temperature. The temperature of the absorbers could be varied continuously from 80 to 250 K, within ± 1 K, by means of a modified Ranger Engineering Corp. liquid nitrogen dewar equipped with a temperature controller. The velocity scale was calibrated periodically against an absorber of metallic iron, using a 5° Co-Pd source. All data were fitted to the sum of two independent Lorentzian lines with a nonlinear leastsquares fit computer program.

RESULTS AND DISCUSSION

The best values of the Mössbauer parameters for the complexes measured at 90 K, against a Ba^{119m}SO₃ source at room temperature, are summarized in Table 1, where we group the results according to the acceptor molecule. The spectra showed well resolved quadrupole splitting

⁺Present address: University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, England. with excellent quality of the Lorentzian line fitting and very acceptable linewidths.

(a) Isomer shift (δ)

Table 1 shows that, within the experimental errors, the values of δ for triphenyltin chloride and its complexes are essentially the same. Therefore, the complexation has no effect upon the *s*-electron density at the tin nucleus in the sulfoxide complexes of triphenyltin chloride, and the isomer shift is not sufficiently sensitive to study donor-acceptor effects. Similar conclusions have been reported by Wedd and Sams[2]. Our measured values of the isomer shifts and quadrupole splittings are in good agreement with earlier results [1-5].

On the other hand, the data (Table 1) show a significant decrease in the isomer shifts on complexation of Me_2SnCl_2 and Me_3SnCl . Although the differences are small, the following trend can be observed for the Lewis bases concerned:

$$\frac{\delta|(C_6H_5)_2SO| > \delta|(CH_3)_2SO| > \delta|(n-C_4H_9)_2SO|}{\simeq \delta|(n-C_3H_7)_2SO|}$$

The lower values of δ in the complexes could be caused by an increase in p and/or d-electron donation to tin, which would increase the shielding of the s-electrons. Whatever the mechanism is a decrease in the isomer shift reflects the extent of charge transfer from donor to acceptor for complexes having equal coordination numbers. Therefore, the sequence of Lewis bases quoted above may be considered as a measure of the relative donor activities of the bases with respect to dimethyltin dichloride.

It is interesting to note that Mössbauer studies carried out by Petrosyan *et al.*[3] on complexes of dimethyltin dichloride and trimethyltin chloride dissolved in various electron-donor solvents show no changes in the isomer shift.

For SnIV the electric field gradient arises mainly from

⁽b) Quadrupole splitting (Δ)

Table 1. Mössbauer parameters of some tin complexes at $(90 \pm 1)K$

First Group (C_cH_e)₇ SnCl. L

Base (L)	Isomer Shift ^a (mm/sec)	Quadrupole Splitting (mm/sec)	Linewidth ^C (mm/sec)	
			٢	Г _h
NEAT	1.30	2.52	0.93	0.97
(p-CH ₃ C ₆ H ₄) ₂ SO	1.28	3.03	0.91	0.93
(C6H5-CH2),50	1.28	3.16	0.88	0.92
(C ₆ H ₅) ₂ SO	1.29	3.09	1.02	1.07
(CH ₃) ₂ SO	1.30	3.13	0.83	0.84
$(n-C_4H_9)_2$ SO	1.27	3.16	0.92	0.97
(n-C ₃ H ₇) ₂ SO	1.26	3.07	0.94	0.98

Second Group (CH3) 2SnC12.2L

NEAT	1.55	3.53	1.20	1.19	
(C ₆ H ₅) ₂ SO	1.45	4.10	0.85	0,85	
(CH ₃) ₂ SO	1.40	4.09	1.00	0.97	
$(n-C_4H_9)_2$ SO	1.32	4.06	0.85	0.85	
$(n-C_{3}H_{7})_{2}S0$	1.31	4.05	0.83	0.85	

Third Group (CH₃)₃SnC1. L

NEAT	1.41	3.38	0.99	1.03
(n-C ₄ H ₉) ₂ SO	1.32	4.03	0.84	0.86

a) Isomer Shift relative to Ba^{119m}SO₃ at room temperature (errors:
 <u>*</u> 0.03mm/sec)

b) errors: + 0.06mm/sec

c) errors: <u>•</u> 0.02. The subscripts l and h refer to lower and higher energy lines, respectively.

ligand asymmetry. The values of Δ for all the complexes listed in Table 1 are larger than those for the corresponding parent compounds, but within the experimental errors, they are essentially the same for each acceptor compound family.

An increase in the quadrupole splitting on complexation has been obtained by Wedd and Sams [2] for some triphenyltin chloride complexes and by Petrosyan *et al.*[3] for some complexes of dimethyltin dichloride dissolved in various electron-donor solvents. As pointed out by Petrosyan *et al.*[3] the observed increase in the values of Δ may be explained by considering the increase in the ionic character of the Sn-Cl bonds and the change in the structure when the complex is formed.

Organotin halides such as $(C_6H_5)_3$ SnCl and $(CH_3)_3$ SnCl are pentacoordinate species in the solid state, forming chain polymers in which the tin atoms and the three organic groups lie in the equatorial plane of a trigonal bipyramidal unit, with the chlorine atoms occupying the axial positions [7]. When an adduct is formed the chlorine bridges are destroyed and monomeric species are produced, such as in $(CH_3)_3$ SnCl·py, with a corresponding decrease in molecular symmetry.

The structure of solid $(CH_3)_2SnCl_2$ approaches an octahedron. It consists of a chain of molecules having the tin atom and the four chlorines in one plane and the

methyl groups above and below that plane, with a C-Sn-C angle of $123^{\circ}30'[8]$. The adduct $(CH_3)_2SnCl_2 \cdot 2DMSO$, for which the structure has been determined, presents a trans-Me-cis-Cl₂-cis-(DMSO)₂Sn configuration and a C-Sn-C angle of 170° .

The likely decrease in symmetry which one expects upon adduct formation agrees with our quadrupole splitting data, which are always higher for the adducts. Moreover the per cent increase in Δ is greater for the adducts with $(C_6H_5)_3SnCl$ an $(CH_3)_3SnCl$ than for those with $(CH_3)_2SnCl_2$, indicating a more pronounced loss of symmetry in the former two cases.

(c) Debye temperature

It is well known that the Mössbauer recoil-free faction, f, for harmonic systems is given by $f = \exp(-k^2\langle x^2 \rangle)$, where $\langle x^2 \rangle$ is the mean-square displacement of the tin atom from its equilibrium position in the direction of the Mössbauer gamma wave vector **k**. For a harmonic system within the Debye approximation, the temperature dependence of the recoil-free fraction can be written as

$$f = \exp\left(-\frac{6RT}{k\theta_D^2}\right)$$
 for $T > \theta_D/2$,

where R is the Mössbauer recoil energy, k is the Boltz-

Temperature (<u>+</u> 1K)	Isomer Shift ^a (mm/sec)	Quadrupole Splitting (mm/sec)	Linewidth ^C (mm/sec) ^F l	[h	A(T)/A(90K) ^d
90	1.30	3.13	0.83+0.02	0.84+0.02	1,000+0,053
100	1.30	3.12	0.86+0.03	0.88+0.03	0,829+0,044
157	1.29	3.13	0.84+0.05	0.85+0.05	0.257+0.035
182	1.29	3.15	0.87+0.05	0.88+0.05	0.140+0.015
200	1.30	3.13	0.88+0.08	0.90 <u>+</u> 0.08	0.103+0.017
••••• •••••••••••••••••••••••••••••••	÷ ((CH ₃) ₂ SnC1 ₂ , 2(n-C ₃ H ₇) ₂ SO		- <u>-</u>
90	1.31	4.05	0.83+0.02	0.85+0.02	1.000+0.044
140	1.32	4.04	0.84+0.03	0.85+0.03	0.450+0.036
168	1.28	4.05	0.86+0.05	0.87+0.05	0.315+0.023
200	1.33	4.00	0.87+0.05	0.86+0.05	0.177+0.020
220	1.33	4.06	0.98+0.07	0.89+0.07	0.119+0.013
250	1 30	4 07	0 89+0 08	0.91+0.08	0 090+0 014

Table 2. Temperature dependence of Mössbauer parameters for the complexes

a) Isomer shift relative to $Ba^{119m}\text{SO}_3$ at room temperature (errors:

+ 0.03 mm/sec

- b) errors: + 0.06 mm/sec
- c) The subscripts $\boldsymbol{\epsilon}$ and \boldsymbol{h} refer to lower and higher energy lines, respectively.
- d) A(T)/A(90) area values normalized to the area under M8ssbauer absorption spectrum at 90 K.



Fig. 1. Plot of log_e (Mössbauer area normalized to area at 90 K) vs (T-90) in K.

mann constant and θ_D is the Debye temperature of the solid. Since for thin absorbers the recoil-free fraction is linearly related to the area under the Mössbauer absorption lines (A), plots of log A vs T should be linear, in the high temperature limit ($T > \theta_D/2$). It is found that smaller values of the slope of log A vs T correspond to more tightly bound tin atoms in a lattice. The Mössbauer parameters, as a function of the temperature, for two of the studied complexes are given in Table 2, where the last column lists the values of the area under the Mössbauer absorption lines normalized to the area at 90 K. First of all, it is interesting to note (Table 2) that for both complexes the isomer shift, the quadrupole splitting and the linewidth are, within the experimental errors, independent of the temperature.

The plots of $\log_{\epsilon} (A_T/A_{90})$ as a function of (T-90) for dimethylsulfoxide-triphenyltin chloride and di-*n*-propylsulfoxide-dimethyltin dichloride complexes are shown in Fig. 1, where the straight lines represent the best linear relation fitted to the experimental data. For the dimethylsulfoxide-triphenyltin chloride complex the slope is $-1.55 \times 10^{-2} \text{ K}^{-1}$ (correlation coefficient 1.002, number of points 6), which gives a Debye temperature of about 107 K. The di-*n*-propylsulfoxide-dimethyltin dichloride complex exhibits a slope of $-2.10 \times 10^{-2} \text{ K}^{-1}$ (correlation coefficient 0.999, number of points 5), giving a Debye temperature of about 92 K.

These values of the slopes indicate that tin atoms are more tightly bound in the lattice of the dimethylsulfoxide-triphenyltin chloride than in the lattice of the di-n-propylsulfoxide-dimethyltin dichloride complexes.

A similar procedure has been used by Ho et al. [9] to study the lattice dynamics of trimethyltin glycinate.

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