Abstract

Mossbauer measurements have been carried out on neat solid samples of diphenyltin (IV) dichloride at liquid nitrogen temperature, as well as on frozen solution samples of this solute in crystalline and glassy matrices. The isomer shift and quadrupole splitting observed for the neat solid - 1.359 ± 0.015 and 2.812 ± 0.015 mm/sec respectively - reflect in part the effect of crystal stacking forces which influence the metal-ligand bond angles and hence the Mossbauer parameters. The quadrupole splitting decreases by about 0.20 mm/sec in non-basic solvents and a value of 2.61 ± 0.04 mm/sec for this parameter is taken as characteristic of an isolated unrestrained molecule of the solute. The increase to 3.51 ± 0.09 mm/sec in basic solvents reflects the coordination of two solvent molecules, giving rise to a distorted trans octahedral complex in which the two aryl groups occupy axial positions. The temperature dependence of the recoil-free fraction in neat solid \( \phi_2\text{SnCl}_2 \) has been determined in the temperature range 83 < T < 170°K and can be used to estimate the importance of intermolecular bonding forces in comparable organotin (IV) compounds by a simple normalization procedure.
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Diphenyltin (IV) dichloride as a Model Compound in Mössbauer Spectroscopy

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Absolute parameter calculations in chemical Mössbauer spectroscopy have met with only very limited success, largely due to the assumptions made in various model calculations, and much of the chemical and solid state physics information which can be derived from such data is based on parameter systematics on large numbers of different but related samples. Such systematics have been especially useful in extracting meaningful information from isomer shift and quadrupole splitting systematics, and to a lesser extent in relating temperature dependence data on recoil-free fractions and intensity asymmetry to chemically meaningful structural descriptions. As is true in all molecular spectroscopic techniques, the most powerful arguments are based on a comparison of the parameters of the sample material to those of one or more model compounds, and the applicability of this kind of logical reasoning underlies most of the interpretations which have been advanced in this field.

The recent publication of the detailed crystallographic data on diphenyltin (IV) dichloride by Greene and Bryan has provided the Mossbauer spectroscopist with a useful model compound for a mono-
meric, distorted tetrahedral molecular solid, and the present paper concerns itself with the isomer shift (I.S.), quadrupole splitting (Q.S.) and temperature dependence of the recoil free fraction \([f(T)]\) for this compound determined from standard transmission geometry \(^{119}\) Sn Mossbauer effect experiments.

**Experimental**

Diphenyltin (IV) dichloride was obtained from Alfa Inorganics and purified by recrystallization. Samples of the corresponding ethyl, butyl and benzyl tin (IV) compounds were obtained from Alfa Inorganics and used as received. The solvents used in the solution studies were either spectrochemical grade (CCl\(_4\), CHCl\(_3\), benzene), or distilled from molecular sieves prior to use (MTHF, THF, EPA).

Mossbauer spectra were obtained at liquid nitrogen temperature using a constant acceleration spectrometer described earlier and a BaSnO\(_3\) source (New England Nuclear Corp.) at room temperature. The neat solid materials were mounted as thin layers of microcrystalline solid between layers of aluminum foil and clamped by means of a copper sample holder to the tail section of a liquid nitrogen dewar the temperature of which was monitored by calibrated thermocouple. Frozen solution samples were prepared by dissolving the sample in the solvent in question, injecting this by means of a hypodermic syringe into a copper sample holder fitted with windows of thermoplastic Mylar (G. T. Schjeldahl Corp), and immersing the assembly into liquid nitrogen, prior to mounting on the pre-cooled copper cold finger of the liquid nitrogen dewar.
For each sample at least 800K counts were scaled per channel so that the statistical uncertainty is less than 0.11%. Data reduction was effected using the Lorentzian fitting program described earlier.  

All isomer shifts in the present paper are reported with respect to the center of a BaSnO₃-BaSnO₃ room temperature spectrum, and are directly comparable to literature data reported with respect to SnO₂. Spectrometer velocity calibration was effected using NBS SRM 0.8 mil iron foil as detailed previously.  

When the spectrum of $\alpha_2$SnCl₂ is obtained using a BaSnO₃ source, one of the components of the doublet spectrum falls within 0.051 mm/sec of zero relative velocity. Because the line width at half maximum is -0.9 mm/sec and the position of the resonance maximum is essentially temperature independent in the range 78°K<200°K, it is possible to determine the temperature dependence of the recoil-free fraction by carrying out a zero-velocity transmission experiment. The advantage of this procedure is that since large numbers of counts can be accumulated in a short period of time - while the temperature is monitored over a short interval - very small resonance effects can be observed, extending the temperature range of the measurements very significantly. A necessary precaution in this procedure is to determine the change in the transmission rate due to thermal expansion (or contraction), if any, by carrying out a run with a dummy sample.  

Using this procedure, the transmission rate at zero relative
velocity was determined as a function of temperature, using a BaSnO$_3$
source rigidly clamped to an optical rail which also supports the
detector, for a sample of $\phi_2$SnCl$_2$ attached to the cold finger of a
liquid nitrogen dewar. The validity of the thin absorber approxima-
tion was checked by carrying out calibration runs at liquid nitrogen
and room temperature and comparing these results to a normal full
velocity range Mossbauer transmission experiment.

In carrying out the temperature dependent transmission intensi-
ity measurements it was observed that the time lag between the
temperature of the copper sample holder (as sensed by a calibrated
thermocouple) and the temperature of the powdered crystalline sample
sandwiched between two layers of aluminum foil (as sensed by the
change in the transmission rate) was less than 0.5 minutes. The
cooling rate from room temperature to liquid nitrogen temperature
was at the approximate rate of 36 degrees per minute. The warming
rate near 78°K was approximately 3.85° per minute. Since the count-
ing interval occupied 20 seconds during each minute interval, and
the temperature was recorded at the start of each counting interval,
the temperature uncertainty is approximately 0.65 degrees in this
region. At the upper end of the temperature range (~180°K), the
warming rate was approximately 2.27 degrees per minute and the tem-
perature uncertainty during the 20 second counting interval was
approximately 0.38 degrees.

The value of the magnitude of the resonance effect at temper-
ature $T$ is given by

$$\epsilon(T) = \frac{R(292°K) - R(T)}{R(292°K)}$$  \hspace{1cm} (1)

where $R(292°K)$ and $R(T)$ are the room temperature counting rate and
that at temperature T respectively and is calculated from the raw counting data uncorrected for background, scattering, and other gamma spectroscopic corrections. The value $\epsilon(84^\circ K) = 0.1251$ so calculated agrees reasonably well with the value of $-0.13$ calculated from the full Mössbauer spectrum data summarized in Fig. 1.

Results and Discussion

The I.S. and Q.S. parameters extracted from the present experiments are summarized in Table 1. The $78^\circ K$ values for the neat solid are in good agreement with those reported earlier and require no further comment. From an inspection of Table 1, it is seen that the frozen solution data for $\phi_2 SnCl_2$ can be grouped into two subsets, both distinct from the values obtained for the neat solid at liquid nitrogen temperature. The first of these comprises the values observed for carbon tetrachloride, chloroform, benzene and butylbenzene solutions for which the Q.S. parameter is $-0.17$ mm/sec smaller than for the neat solid. As the data of Greene and Bryan have shown, there is a considerable departure from regular tetrahedral geometry in the valence angles at the tin atom in the neat solid. The present data in contrast to interpretations offered earlier suggest that a significant part of this non-ideality arises from crystal stacking forces which contribute to the opening of the C-Sn-C bond angle to $\sim-126^\circ$ and the closing of the Cl-Sn-Cl bond angle to $\sim-100^\circ$. When the solid is dissolved in a non-polar solvent, these crystal stacking constraints are removed, and it may be inferred that the Q.S. value of $-2.61 \pm 0.04$ mm/sec reflects the geometry of an unconstrained $\phi_2 SnCl_2$ molecule. In this context it
may be argued that \( \text{CCl}_4 \), \( \text{CHCl}_3 \) and \( \text{C}_6\text{H}_6 \) all set to crystalline solids and that this may impose structural restraints on the solute molecule in such solvents. That this is not a significant effect, however, is shown by the data for the butylbenzene solution. This solvent, which glasses rather than setting to a crystalline solid at liquid nitrogen temperature, has a viscosity of \( 3.5 \times 10^{43} \) poise at 77.5°K, and it is clear that in this solvent, neither microcrystalline solute domains can be formed (the diffusional processes being too slow) nor is there a unique solvent constraint on the structure of the isolated solute molecules. Since the Q.S. observed for \( \phi_2\text{SnCl}_2 \) in butylbenzene is nearly the same as that observed in \( \text{CCl}_4 \), \( \text{CHCl}_3 \) and benzene solutions, it may be inferred that a Q.S. of \( -2.61 \pm 0.04 \) mm/sec is characteristic of an isolated solute molecule at liquid nitrogen temperature.

The second group of solvents [tetrahydrofuran (THF), methyl tetrahydrofuran (MTHF), and a mixture of ethanol, isopropanol and diethylether (EPA)] all have the property of setting to a glassy solid state at low temperatures, and hence, the influence of the solvent structure on the structure of the solute becomes unimportant. For this group of frozen solutions, the Q.S. parameter is seen to be \( 3.51 \pm 0.09 \), that is, 0.70 mm/second larger than the value observed for the neat solid, and 0.90 mm/sec larger than that observed for the non-basic solvent systems. Since all three of these solvents have considerable basicity (in the Lewis sense), it is probable that this increase in the Q.S. which is observed is due to a direct solvation effect. Although a completely unambiguous assign-
ment of the structure of the complex so formed will have to be based on X-ray crystallographic data, the Q.S. which is observed is indicative of a trans octahedral coordination for the stereochemistry of \( \phi_2 \text{SnCl}_2 \) in these basic solvents. In this context it may be noted that the 1,10 phenanthroline-, 2,2'-bipyridyl-, and bis pyridine adducts of \( \phi_2 \text{SnCl}_2 \) - to which a trans octahedral structure has been assigned - all have Q.S. values lying in the range 3.39 to 3.90 mm/sec, in good agreement with the values observed in the present studies for the THF, MTHF and EPA solution species.

This interpretation is also supported by the Mossbauer data and crystal structure results which have been reported for dimethyltin (IV) dichloride. In this molecule, the chlorine atoms act as bridging entities between adjacent dimethyltin units, with a bond length of 2.40 and 3.54 Å to the two adjacent metal atoms. The local symmetry around the metal atom is that of a deformed tetrahedron, strongly distorted toward an octahedral configuration, with a C-Sn-C bond angle of 123° and a Cl-Sn-Cl bond angle of 93°. The quadrupole splitting for this compound is about 3.55 mm/sec and is relatively insensitive to the substitution of longer chain length alkyl groups for the two methyl group ligands in the parent compound. The similarity in the Q.S. parameters for \((\text{CH}_3)_2\text{SnCl}_2\) and \((\text{C}_6\text{H}_5)_2\text{SnCl}_2\) in polar, basic solvents is consistent with the postulated distorted octahedral environment in each case, since the Q.S. parameter - in contrast to the I.S. parameter - is relatively insensitive to the substitution of an aryl for an alkyl group around the metal atom.

The results of the zero-velocity temperature dependent transmission rate experiment are summarized in Fig. 2. For a thin
absorber, the area under the resonance maximum of a Lorentzian curve is adequately given by

\[ A = \frac{\epsilon}{2\pi} \Gamma_{\text{exp}} \]  

where \( \epsilon \) is the resonance effect magnitude and \( \Gamma_{\text{exp}} \) is the full width at half maximum. In the thin absorber approximation\(^{11}\)

\[ \Gamma_{\text{exp}} = \Gamma_s + \Gamma_a \left( 1 + 0.027t + \ldots \right) \approx 2\Gamma \]  

and is essentially temperature independent. Moreover the effect magnitude, \( \epsilon \), for a thin absorber is directly proportional to the effective thickness parameter, \( t \), that is

\[ \epsilon = n \ a \ \sigma_0 f_a \]  

where \( n \) is the number of atoms of the element in question per unit area of absorber, \( a \) is the isotopic abundance of the Mossbauer nuclide, \( \sigma_0 \) is the cross section for resonant absorption and \( f_a \) is the temperature dependent recoil-free fraction in the absorber.

From the above it is seen that \( \ln A = \ln \left( \frac{\Gamma_{\text{exp}}}{2\pi} \right) + \ln \epsilon \), so that \( \frac{d \ln A}{dT} = \frac{d \ln \epsilon}{dT} = \text{constant} \ (\frac{d \ln f_a}{dT}) \) so that the temperature dependence of the resonance effect magnitude reflects the temperature dependence of the recoil-free fraction in the absorber. As has been pointed out previously,\(^2\) in the high temperature limit

\[ \frac{d \ln A}{dT} = -6 \ \frac{E_R}{kS_m^2} \]  

where \( E_R \) is the recoil energy of the Mossbauer nucleus \(\left( = \frac{EY^2}{2Mc^2}\right)\).
where $M$ is the effective mass of the recoiling species carrying the Mössbauer atom) and $\theta_M$ is a Mössbauer "temperature" which reflects the strength of the chemical bond binding the Mössbauer atom into the absorber lattice. The slope of the straight line function described by (5) is thus directly related to the strength of the intermolecular bonding forces in the solid, the larger the slope the "softer" is the bonding of adjacent molecular units in the material in question. In order to compare the strength of this intermolecular interaction between samples of different thickness, measured with different sources and under conditions of varying geometry, it is necessary to effect a normalization. This has been accomplished by using the 120°C data point (normally lying near the middle of the temperature range over which Mössbauer experiments for organotin compounds can be meaningfully carried out) as a standard reference point and to compare plots of $\frac{d \ln A(T)}{dT} / \ln A(120°C)$ to effect intersample comparison. The data summarized in Fig. 3 represents a comparison of the normalized temperature dependence of the recoil-free fraction for $\phi_2$SnCl$_2$ in the temperature range $85 < T < 170°C$, and related organotin (IV) compounds.

These results have been used to effect a model compound comparison with (CH$_3$)$_2$Sn(dtc)$_2$ (dtc = diethyldithiocarbamate), a molecule subjected to detailed study in this laboratory. Infra-red and nmr spectroscopic evidence has shown that the dithiocarbamate ligand acts as an anisobidentate moiety in this compound, with two distinct tin-sulfur interactions involved in each ligand-metal coupling. This obviously raises the possibility of a polymeric structure in
which the ligand fills a bridging function in bonding adjacent
(CH$_3$)$_2$Sn units to each other. The present data - using diphenyl-
tin (IV) dichloride as a model compound - suggests however that this
model is untenable. The temperature dependence of the recoil-free
fraction in the model compound (MW = 372) and in dimethyltin (IV)
bis (diethylidithiocarbamate) (MW = 445) are essentially identical
when appropriate molecular weight corrections are made, and hence
the presence of a significant intermolecular bonding in the latter -
which would lead to a distinctly smaller slope (d ln A/dT) - can be
ruled out. A similar conclusion concerning the absence of a poly-
meric structure for (CH$_3$)$_2$Sn(dtp)$_2$ (MW = 703) can be drawn from the
data summarized in Fig. 3, and is consistent with the infra-red and
molecular weight data for this compound. 13

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References


8. A. C. Ling and J. E. Willard, J. Phys. Chem. 72, 1918 (1968); ibid, 72, 3349 (1968) and references therein.


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a With respect to BaSnO₃ at 294°K
b + 0.030 mm/sec

Table 1 - Mossbauer Parameters for Diphenyltin (IV) dichloride and Related Compounds.
Figure Captions

Fig. 1 $^{119}$Sn Mossbauer spectrum of diphenyltin (IV) dichloride at 84°K. The reference point (zero velocity) of the horizontal scale is the centroid of a room temperature BaSnO$_3$ - BaSnO$_3$ spectrum obtained in the same geometry. The vertical scale is uncorrected for nonresonant contributions to the transmission intensity.

Fig. 2 Temperature dependence of the transmission rate of the $23.8$ keV gamma radiation of $^{119}$Sn through a thin absorber of diphenyltin (IV) dichloride at zero relative velocity. The uncorrected resonance effect magnitude is calculated directly from the difference in transmission rate at temperature $T$ and that observed in the high temperature ($T>200^\circ$K) limit, as discussed in the text.

Fig. 3 Temperature dependence of the Mossbauer effect magnitude ($\epsilon$) normalized to the 120°K data point. The data for diphenyltin (IV) bis (diethyl-dithiocarbamate) $[(\text{CH}_3)_2\text{Sn(dtc)}_2]$ and for dimethyltin (IV) bis (ditolyl thiophosphine dithiol) $[(\text{CH}_3)_2\text{Sn(dtp)}_2]$ are shown for comparison.
The graph shows a plot of $\frac{\text{In}e(T)}{\text{In}e(120)}$ versus temperature in Kelvin. The lines represent three different compounds: $(\text{CH}_3)_2\text{Sn(dtpp)}_2$, $(\text{CH}_3)_2\text{Sn(dtc)}_2$, and $\phi_2\text{SnCl}_2$. The temperature range is from 80 to 180 °K.