# Title
Variable-Temperature Tin-119m Mössbauer Study of Tin(II) and Tin(IV) Amines

# Authors
K.C. Molloy, M.P. Bigwood, R.H. Herber, and J.J. Zuckerman

# Abstract
The independence of the logarithm of the area under the tin-119m Mössbauer resonance (normalized to the area under the resonance at 77K), $\ln A$, on temperature in K is measured for two tin(IV) and three tin(II) amines containing the $\text{N(CH}_3\text{)}_2$, $\text{N(CH}_3\text{)}_2$, and the $\text{N(Si(CH}_3\text{)}_3\text{)}_2$ groups. The slopes of the plots of $\ln A$ vs. T are in increasing order of relative steepness, $\text{(CH}_3\text{)}_2\text{Sn[N(CH}_3\text{)}_2\text{]} -1.16 \times 10^{-9}K^{-1}$ for $T = 77-140K$, $\text{Sn[N(CN}_2\text{)}_2\text{]} -1.26 \times 10^{-9}K^{-1}$ for $T = 77-200K$ for the tin(IV) compounds, and, $\text{Sn[N(CH}_3\text{)}_2\text{]}_2$...
20. \([-1.05 \times 10^{-2} \text{K}^{-1} \text{ for } T = 77-1 \text{ K}], \text{Sn}[\text{N(CH}_3)_2]_2[-1.55 \times 10^{-2} \text{K}^{-1} \text{ for } T = 77-155 \text{K}] \text{ and Sn}[\text{N(Si(CH}_3)_3]_2][1.95 \times 10^{-2} \text{K}^{-1} \text{ for } T = 77-150 \text{K}]\) for the tin(II) compounds. Based on the systematics of the relation between the magnitudes of the slopes and known structures of tin solids, it is possible to assign bridged polymeric structures to the first four compounds and a structure composed of non-interacting molecular units to the last.
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ABSTRACT

The dependence of the logarithm of the area under the tin-119m Mössbauer resonance (normalized to the area under the resonance at 77K), \( \ln A_T \), on temperature in K is measured for two tin(IV) and three tin(II) amines containing the \( \text{N}(\text{CH}_3)_2 \), \( \text{N}(\text{CH}_2)_2 \) and the \( \text{N}[\text{Si}(\text{CH}_3)_3]_2 \) groups. The slopes of the plots of \( \ln A_T \) vs. \( T \) are in increasing order of relative steepness, \( \text{(CH}_3)_3\text{SnN}(\text{CH}_2)_2[-1.16 \times 10^{-2}\text{K}^{-1} \text{ for } T = 77-140\text{K}], \text{Sn}[\text{N}(\text{CN}_2)_2]_4[-1.26 \times 10^{-2}\text{K}^{-1} \text{ for } T = 77-200\text{K}] \) for the tin (IV) compounds and, \( \text{Sn}[\text{N}(\text{CH}_2)_2]_2[-1.05 \times 10^{-2}\text{K}^{-1} \text{ for } T = 77-1 \text{ K}], \text{Sn}[\text{N}(\text{CH}_3)_2)_2[-1.55 \times 10^{-2}\text{K}^{-1} \text{ for } T = 77-155\text{K}] \text{ and } \text{Sn}[\text{N}[\text{Si}(\text{CH}_3)_3]_2]_2[-1.95 \times 10^{-2}\text{K}^{-1} \text{ for } T = 77-150\text{K}] \) for the tin(II) compounds. Based on the systematics of the relation between the magnitudes of the slopes and known structures of tin solids, it is possible to assign bridged polymeric structures to the first four compounds and a structure composed of non-interacting molecular units to the last.
The systematics of tin structural chemistry are becoming increasingly well understood as data from X-ray diffraction studies accumulates. Single-atom bridges form in tin-halide solids, especially the fluorides. The hydroxides bridge through oxygen, but steric inhibition to association begins to manifest itself in the alkoxide derivatives. Amino nitrogen competes successfully with carboxylate oxygen as the base atom of choice in solid trimethyltin(IV) glycinate, but steric inhibition to coordination is generally more severe in the amine series since nitrogen holds two organic groups in Sn-NR₂ derivatives to oxygen's one in Sn-OR. In solid trimethyltin(IV) azide the α-nitrogen forms unique, single-atom bridges to adjacent, planar trimethyltin(IV) moieties, but the steric inhibition is at a minimum in this special case.

An example of low steric requirements is provided by the aziridine (ethyleneimino) ring, which also holds a special place among amines because of its exceptional electronic properties. The nitrogen lone pair interacts with the ring, diminishing its availability for further bonding interactions, and results in aziridine being a weaker base than dimethylamine. At the other end of the scale is the bis-(trimethylsilyl)amino group where great steric bulk is combined with a nitrogen atom having virtually no basic properties.

Another parameter determining whether association will occur is the oxidation state of the tin atom. Reducing tin(IV) to tin(II) increases atomic size, lengthens internuclear distances and relieves steric strain. However, Lewis acid strength would also be expected to diminish.

Variable temperature tin-119m Mössbauer data can yield information concerning the lattice dynamics of tin solids, and can be used to infer whether significant intermolecular association is present. For a thin absorber for which saturation effects can be neglected, the temperature dependence of the area under the resonance curve can be expressed in the form
\[ A = \exp \left( -6 \frac{E_R T}{k_B \theta_M^2} \right) \]  

(1)

where \( E_R \) is the recoil energy on gamma absorption and \( \theta_M \) is a Mössbauer atom-probed lattice temperature, similar to \( \theta_D \) for a Debye solid. One appropriate substitution in (1), the temperature dependence of \( \ln A \) is given by

\[ \frac{d \ln A}{dT} = -3 \frac{E}{M_{\text{eff}}} \frac{C^2 k_B \theta_M^2}{M_{\text{eff}}} \]

(2)

in which \( E \) is the Mössbauer transition gamma ray energy and \( M_{\text{eff}} \) is an effective lattice dynamical mass which reflects the relative inter- and intra-molecular bonding energies. Although for a detailed correlation between \( A(T) \) and the microscopic details of the bonding at the tin atom in the solid, independent data on \( \theta_M \) are needed to permit calculation of \( M_{\text{eff}} \), a number of broad generalizations can be made concerning the slope of the temperature dependence of \( A \) and the question of association (strong inter-molecular bonding) in the solid. In the simplest cases (where motional anharmonicity can be neglected), the plot of \( \ln A \) vs. \( T \) will be linear, and the slope of this plot will decrease with increasing association between the monomeric structure units.

The interpretation of temperature dependent recoil-free fraction data for particular molecular solids must be pursued with some caution since - as already noted above - independent data from vibrational spectroscopy or X-ray diffraction are frequently needed to permit an unambiguous evaluation of the magnitude of inter-molecular association effects. Nonetheless, a number of organotin systems have been studied in detail, and such investigations have shown that for monomeric species \( d \ln A/dT \) usually falls in the range (-1.6 to -2.6) \( \times 10^{-2} K^{-1} \), which for two- and three-dimensional polymers this value falls to \( -1 \times 10^{-2} K^{-1} \) or less. Values for representative organotin systems measured by us are listed in Table 1.

In this paper we report the application of variable temperature tin-119m Mössbauer measurements to five related tin amines.
Experimental Section

Trimethyltin(IV) aziridine, tin(IV) aziridine, bis-(dimethylamino)tin (II), and bis-[N,N-bis(trimethylsilyl)amino]tin(II) were prepared by literature methods and handled in a Vacuum/Atmospheres Dri-Lab glovebox.

Tin-119m Mössbauer spectra were recorded for all but the first-named amine on a Ranger Engineering constant acceleration spectrometer equipped with an NaI scintillation counter and using Ca$^{119m}$SnO$_3$ [New England Nuclear Corp.] as the source and CaSnO$_3$ as the standard reference material for zero velocity. Velocity calibration is based upon β-tin and natural iron. Standard, non-linear least squares techniques were used to fit the data to Lorentzian curves. The Ranger Engineering variable-temperatures liquid-nitrogen dewar and controller used in these studies is regulated by a variable-bridge, silicon-controlled rectifiers circuit and is accurate to ±1K. The best straight line through the data points was calculated by using standard least squares methods. The data for trimethyltin(IV) aziridine and tetrakis-(1-aziridinyl)tin(IV) were obtained using the system described earlier.

Results and Discussion.

The logarithmic plots of the areas under the Mössbauer resonances, $A_T$, (normalized to 77K for ease of comparison), vs. temperature are displayed for the two tin(IV) amines in Figure 1, and for the three tin(II) amines in Figure 2. The slopes, in order of relative steepness, are $(CH_3)_3SnN(CH_2)_2$ [-1.16 x $10^{-2}$K$^{-1}$ for $T = 77$-140K (regression analysis, $r = 0.994$, intercept = 0.900, 12 points)], Sn[N(CH$_3$)$_2$]$_2$ [-1.25 x $10^{-2}$K$^{-1}$ for $T = 77$-150K ($r = 0.998$, intercept = 0.95, 7 points)], for the tin(IV) compounds and Sn[N(CH$_2$)$_2$]$_2$ [-1.06 x $10^{-2}$K$^{-1}$ for $T = 77$-150K ($r = 0.998$, intercept = 0.802, 7 points)], Sn[N(CH$_3$)$_2$]$_2$ [-1.55 x $10^{-2}$K$^{-1}$ for $T = 77$-150K ($r = 0.998$, intercept = 0.802, 7 points)].
for $T = 77-150\text{K}$ ($r = 0.999$, intercept = 1.17, 9 points), and $\text{Sn}[\text{Si}(\text{CH}_3)_3]_2$ [-1.95 x $10^{-2}\text{K}^{-1}$ for $T = 77-150\text{K}$ ($r = 0.993$, intercept = 1.413, 8 points)] for the tin(II) compounds. Relevant Mössbauer data are listed in Table 2. We will discuss the tin(IV) compounds, followed by their tin(II) analogues in the above order.

Trimethyl(1-aziridinyl)stannane, $(\text{CH}_3)_3\text{SnN}$(CH$_2$)$_2$.\(^8\) This compound was originally reported as a liquid, bp 53-56°C (16 Torr),\(^{14}\) but sublimation at room temperature gives long, white needle crystals, mp 28.5°C.\(^8\) By contrast trimethyltin(IV) dimethylamine, which differs by only two units in molecular weight melts at -79°C.\(^{15}\) All other known trialkyltin(IV) amines are liquids at room temperature.\(^{16,17}\) The N-triorganotin derivatives in which nitrogen atoms are in 1,3-positions in a conjugated ring are exceptions, as in the imidazole, 1,2,3- and 1,2,4-triazole, benzimidazole and 1,2,3-benztriazole systems,\(^{18-21}\) in which association in the solid state can arise through intermolecular coordination by the second nitrogen atom in the heterocycle to give a one-dimensional polymer with planar triorganotin(IV) units axially bridged by the 1,3-dinitrogen heterocycles. The associated nature of these solids is reflected in their high Mössbauer quadrupole splitting (QS) values (2.5-3.0 mm s$^{-1}$)\(^{22-23}\) vs. only 1.0 mm s$^{-1}$ for the related open-chain diethylamino derivative,\(^{24}\) and in their chemical stability. Their viscous solutions in organic solvents contain oligomeric species,\(^{21-25}\) unlike the normal monomeric organotin(IV) amines.\(^{16-17,26}\) N-Trimethyltin aziridine is, on the other hand, dimeric in benzene by osmometry, and several fragments of both higher mass than the dimer, and containing two tin atoms, are seen in the mass spectrum. The tin-119m QS value of 2.27 mm s$^{-1}$\(^{18}\) is much above those of open-chain organotin(IV) amines,\(^{23}\) and rises to 3.03 mm s$^{-1}$ on complexation with BF$_3$ to give $(\text{CH}_3)_3\text{SnN}$(CH$_2$)$_2$$\rightarrow$BF$_3$.\(^8\) Infrared data rule out a precisely planar trimethyl-
tin group since a ν sym(SnC 3 ) absorption is clearly seen. N-trimethyltin(IV) aziridine is only moderately sensitive to hydrolysis in moist air, 8 while its liquid dimethylamino analogue fumes in the atmosphere. 16-17

Figure 1 is a plot of ln[A(T)/A(78)] for (CH 3 ) 3 SnAz in the range 78 ≤ T ≤ 140K, and these data are well-represented by a linear regression of the form ln[A(T)/A(78)] = 0.907 - 1.16 x 10⁻²⁻¹, with a correlation coefficient of 0.994 for the 16 data points. The data above 140K for this compound show a small but significant downward curvature (ln A smaller than that extrapolated from the low temperature data) which is assumed to arise out of motional anharmonicity which makes the mean square amplitude of vibration larger than that predicted by a harmonic oscillator potential. The data for T > 140K have not been used in the slope calculations reported in Table 1.

The lnA T va. temperature slope data help to distinguish between a dimeric form, A:

and a one-dimensional polymer, B:

The rather small dependence of A T on temperature (dlnA/dT = -1.16 x 10⁻²⁻¹) places N-trimethyltin(IV) aziridine among compounds which are intermolecularly associated, confirming the importance of the mass spectral fragments of higher mass than the dimer and the relative chemical stability 8 compared with other organotin amines as evidence for structure B. The association cannot be as strong, however, as in trimethyltin(IV) azide, where the trimethyltin group is precisely planar, 4,5 and the
absence of a strong, temperature-dependent doublet line asymmetry (Goldanskii-Karyagin effect)\(^{28}\) means no pronounced anisotropy of the Mössbauer recoil-free fraction, which is again corroboratory for weaker association. The slope of 

\[-1.16 \times 10^{-2} K^{-1}\]

is almost precisely equal to that for trimethyltin(IV) glycinate in which planar trimethyltin units are axially bridged by four-atom \(-O-C-CH_2-NH_2\) units through the terminal nitrogen donor. A closer comparison can probably be drawn, however, with the low melting (39.5°C), volatile (b. 154°C), trimethyltin(IV) chloride whose one-dimensional, polymeric structure contains non-planar trimethyltin groups bridged at very unequal distances by chlorine atoms to form badly distorted trigonal bipyramids in which the identity of the molecules engaging in the association is not lost.\(^{29}\) We believe that trimethyltin(IV) aziridine is likewise bridged by the sterically undemanding ethyleneimino groups in the solid.

**Tetrakis-(1-aziridinyl)tin(IV).** This white insoluble, involatile solid (mp 104-105°C.) exhibits a broad Mössbauer resonance with a near-zero IS (0.50 mm s\(^{-1}\))\(^{8}\) (see Table 2). These data are indicative of a highly coordinated tin(IV) atom, and the observation of a resolvable spectrum at ambient temperatures suggests a polymeric lattice\(^{30}\) formed by extensive bridging by the aziridine groups. The rather large linewidth could be interpreted in terms of a small QS and departure from perfect \(O_h\) or higher symmetry.

In the structure of tin(IV) fluoride two of the fluorines on each tin atom bridge at 2.12Å while two remain unassociated at 1.88Å. This arrangement produces infinite layers of octahedral \(SnF_6\) groups sharing edges.\(^{31}\) The Mössbauer IS is near zero, but a sizable QS is reported (1.16, \(1.80\) mm s\(^{-1}\)), no doubt generated by the differences in the two types of fluorine-tin bonds in the structure. In tin(IV) nitrate\(^{34}\) and acetate,\(^{35}\) on the other hand, each of the four ligand groups is utilized in chelation to produce a dodecahedral arrangement at the eight-coordinated tin atoms. The Mössbauer IS is again near zero for the nitrate\(^{36}\) and
acetate, but in these cases no QS is resolved. The tetrakis-dimethyl- and diethylamino derivatives of tin(IV) also exhibit low IS values (ca. 0.8 mm s⁻¹) and broad resonances suggesting some association in these cases, although the former is monomeric in the gas phase.

The data for SnAz₄ for the temperature range 78 ≤ T ≤ 200K show a small downward curvature over the entire range. A linear regression yields a slope of -1.287 x 10⁻² with a correlation coefficient of 0.998 for the seven data points, suggesting that motional anharmonicity is a very minor effect in the dynamical behavior of the tin atom in this compound over the indicated range.

The modest slope of lnAₜ with temperature for the tetrakis-aziridine (dlnA/JT -1.29 x 10⁻²K⁻¹) suggests that the monomeric units may be associated in the solid state. The small QS value requires some departure from perfect geometry, but it is not possible to tell whether octahedral or dodecahedral symmetry is being lowered. Bridging by one aziridine group in each molecule would produce five-coordination at tin, by two would give six-, three gives seven- and all four engaging in bridging would yield an eight-coordinated tin atom. For the intermediate five-, six- and seven-coordination choices, further questions of axial-, equational-, cis- or trans-bridging arise. The slope data suggest weak association through fewer than four unsymmetrically bridging aziridine units which would produce the low IS value and broad resonance line.

Bis-(1-aziridinyl)tin(II). This white, infusible (mp 205°C, decomp), sparingly soluble solid exhibits a Mössbauer resonance at ambient temperature (IS = 2.70; QS = 2.02 mm s⁻¹). The steric inhibition to association must be less here than in the tetrakis-analogue, but there are two fewer aziridine moieties to bridge, and the metal center is a weaker Lewis base. Variously bridging halide atoms and hydroxide groups characterize the SnX₂ and hydrous oxide structures,
but no structures of tin(II) alkoxide or amino solids have been reported so far as we are aware. In addition, the systematics of the slope data for tin(II) systems have not been worked out. Only two slopes for tin(II) materials have been reported: $\text{ca.} -3.5 \times 10^{-2} \text{K}^{-1}$ for bis-$(\text{h}^5\text{-C}_5\text{H}_5)\text{Sn(II)}$ and $-0.23 \times 10^{-2} \text{K}^{-1}$ for tin(II) oxide, which probably define the ends of the scale. It is very likely that the structure of stannocene is composed of non-interacting, monomeric molecules, and the structure of SnO contains four-coordinated tin atoms$^{(4-5)}$ sitting at the apex of a square pyramid.$^{41-42}$ Our slope of $1.05 \times 10^{-2} \text{K}^{-1}$ suggests a solid associated through one:

![Diagram](image)

or both aziridine group nitrogen atoms:

![Diagram](image)

to produce a three ($\psi - 4$)- or four ($\psi - 5$)-coordinated ion number at tin. More complex forms involving alternating double- and single-bridges are also possible.

**Bis-(dimethylamino)tin(II).** This white, crystalline, sublimable ($70^\circ\text{C}$ at $10^{-4}$ Torr) solid (mp $91-93^\circ\text{C}$) is soluble in cyclohexane to give solutions which yield cryoscopic molecular weight data of 1.80 to 2.64 depending upon the concentration. Nmr spectra at $-40^\circ\text{C}$ exhibit resonances potentially arising from higher coordinated species,$^{10}$ and the Mössbauer parameters$^{9}$ (IS = 2.72; QS = 2.07 mm s$^{-1})^{43}$ are virtually identical to those for the bis-(1-aziridinyl) analogue, except that
no ambient temperature spectrum can be resolved. Our slope \((\text{dln}A/\text{dT})\) of \(-1.55 \times 10^{-2}\text{K}^{-1}\) is, if the tin(IV) systematics can be taken as relevant to the three divalent examples discussed here, suggestive of a solid weakly associated through one or both dimethylamino groups to produce a three \((\psi = 4)\)– or four \((\psi = 5)\)-coordinated tin(II) atoms. Bridging by dimethylamino groups has been used to rationalize temperature-induced changes in the nmr spectra of organotin(IV)

\(^{44}\) and tin(II)

\(^{10}\) amines. Gas-phase electron diffraction shows a monomeric structure.

**Bis-[N,N-bis-(trimethylsilyl)amino]tin(II).** This intense red colored, distillable liquid (bp 104-110°C, at 0.75 Torr

\(^{11}\) or 84°C at 0.4 Torr

\(^{12}\) ) which is monomeric in cyclohexane, crystallizes to a thermochromic orange-yellow colored solid (mp 37-38°C.) on cooling.

\(^{12}\) The isoelectronic, isochromous \(\text{Sn}[\text{CH}[\text{Si}(\text{CH}_3)_2]^2]^2\) has a unique tin-tin bonded dimeric structure in the solid,\(^{46}\) and it is likely that the amino analogue does as well. The compound apparently lacks Lewis acid character, failing to form complexes with pyridine or bipyridyl,\(^{12}\) and hence the tendency for association through \(N \rightarrow \text{Sn}\) bridging would seem to be minimal, especially since the \(\text{SnNSi}_2\) system is planar in the gas phase,\(^{47}\) and presumably only weakly basic. Our slope of \(-1.95 \times 10^{-2}\text{K}^{-1}\) is, when compared with the tin(IV) compounds whose variable temperature Mössbauer data have been studied, completely within the range of magnitudes associated with solids composed of non-interacting molecular units (see Table 1),\(^{27,40,48}\) and we conclude that a non-associated, probably dimeric \((\text{vide supra})\) structure will be found for this solid.

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References and Notes

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(43) Reported as 2.80 and 3.17 mm s⁻¹, respectively, in ref. 10.


Table I. **Typical Slope Values for Organotin Compounds**

<table>
<thead>
<tr>
<th>Compound</th>
<th>dlnA/dT x 10^{-2}K^{-1}</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH₃)₄Sn</td>
<td>-2.15</td>
<td>a</td>
</tr>
<tr>
<td>(C₆H₅CH₂)₄Sn</td>
<td>-2.592</td>
<td>b</td>
</tr>
<tr>
<td>(C₆H₅)₄Sn</td>
<td>-1.659</td>
<td>c</td>
</tr>
<tr>
<td>(C₆H₅)₂SnCl₂</td>
<td>-1.705</td>
<td>c</td>
</tr>
<tr>
<td>SnI₄</td>
<td>-1.430</td>
<td>c</td>
</tr>
<tr>
<td>(CH₃)₂Sn(C₇H₅O₂)₂</td>
<td>-2.867</td>
<td>d</td>
</tr>
<tr>
<td>(C₆H₅)₂Sn(C₇H₅O₂)₂</td>
<td>-1.201</td>
<td>d</td>
</tr>
<tr>
<td>(C₆H₅)₂Sn[S₂P(O₅C₆H₅)₂]₂</td>
<td>-1.92</td>
<td>f</td>
</tr>
<tr>
<td>Aryltin(IV) Styrene Monomers</td>
<td>-2.06 to -2.14</td>
<td>g</td>
</tr>
</tbody>
</table>

**Trimer**

| [(CH₃)₂SnS]₃ | -2.464 | h |

**Polymers**

| [Sn(SCH₂CH₂S)₂]ₙ | -1.18 | h |
| [(CH₃)₃SnO₂CCH₂NH₂]ₙ | -1.15 | i |
| Aryltin(IV) Styrene Polymers | -1.80 to -1.95 | g |
The tin atoms in this solid are pendent to the polymer backbone.
<table>
<thead>
<tr>
<th>IS  $s^{-1}^a$</th>
<th>QS $s^{-1}^a$</th>
<th>d ln $A/dT \times 10^{-2} K^{-1}^b$</th>
<th>$k^c$</th>
<th>Intercept</th>
<th>Number of Points</th>
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<tbody>
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<td>1.209$^d$</td>
<td>2.244$^e$</td>
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<td>0.994</td>
<td>0.907</td>
<td>12</td>
<td>77-140</td>
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<tr>
<td>1.21$^f$</td>
<td>1.27$^f$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.552$^g$</td>
<td>0.747$^h$</td>
<td>-1.26</td>
<td>0.997</td>
<td>0.978</td>
<td>14</td>
<td>77-200</td>
</tr>
<tr>
<td>0.50$^f$</td>
<td>0$^f$</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>2.72$^i$</td>
<td>2.03$^j$</td>
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<td>0.998</td>
<td>0.802</td>
<td>7</td>
<td>77-150</td>
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<tr>
<td>2.72$^i$</td>
<td>2.07$^i$</td>
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<td>9</td>
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<td>3.17$^i$</td>
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<td>2.88$^k$</td>
<td>3.52$^k$</td>
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<td>0.993</td>
<td>1.41</td>
<td>8</td>
<td>77-150</td>
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For ease of comparison.

Ref. 9.

Ref. 10.

Ref. 11.
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<th>Amine Derivative</th>
<th>IS mm s$^{-1}$</th>
<th>QS mm s$^{-1}$</th>
<th>dln A/dT x10$^{-2}$K$^{-1}$</th>
<th>$\kappa$</th>
<th>Intercept</th>
<th>Number of Points</th>
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<tbody>
<tr>
<td>(CH$_3$)$_3$SnN(CH$_2$)$_2$</td>
<td>1.209$^d$</td>
<td>2.244$^a$</td>
<td>-1.16</td>
<td>0.994</td>
<td>0.907</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>1.21$^f$</td>
<td>1.27$^f$</td>
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<tr>
<td>Sn[N(CH$_2$)$_2$]$_4$</td>
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<td>0.747$^h$</td>
<td>-1.26</td>
<td>0.997</td>
<td>0.978</td>
<td>14</td>
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<tr>
<td></td>
<td>0.50$^f$</td>
<td>0$^f$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sn[N(CH$_2$)$_2$]$_2$</td>
<td>2.72$^i$</td>
<td>2.03$^i$</td>
<td>-1.06</td>
<td>0.998</td>
<td>0.802</td>
<td>7</td>
</tr>
<tr>
<td>Sn[N(CH$_3$)$_2$]$_2$</td>
<td>2.72$^i$</td>
<td>2.07$^i$</td>
<td>-1.55</td>
<td>0.999</td>
<td>1.17</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>2.80$^i$</td>
<td>3.17$^i$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sn[N(Si(CH$_3$)$_3$]$_2$</td>
<td>2.88$^k$</td>
<td>3.52$^k$</td>
<td>-1.95</td>
<td>0.993</td>
<td>1.41</td>
<td>8</td>
</tr>
</tbody>
</table>

$^a$At 77K.  
$^b$Normalized to 77K for ease of comparison.  
$^c$Correlation coefficient.  
$^d$Ref. 9.  
$^e$Ref. 10.  
$^f$Ref. 8.  
$^g$Ref. 11.  
$^h$0.010 mm s$^{-1}$.  
$^i$0.015 mm s$^{-1}$.  
$^k$0.027 mm s$^{-1}$.  
$^l$0.01 mm s$^{-1}$.  

**Figure Captions**

**Fig. 1.** Temperature dependence of the normalized area under the resonance curve for the two Sn(IV) compounds discussed in the text. The data for \([(\text{CH}_2)_2\text{N}]_4\text{Sn}\) (circles) reflect two different samples measured in separate experiments, and span the range from liquid nitrogen temperature to 200K. The data for \((\text{CH}_3)_3\text{Sn}((\text{CH}_2)_2\text{N})\) (diamonds) span the range from liquid nitrogen temperature to 140K. The straight lines are least-squares, linear regressions for which the numerical data are included in Table II.

**Fig. 2.** Temperature dependence of the normalized area under the resonance curve for the three Sn(II) compounds discussed in the text: \(\text{Sn}[(\text{CH}_2)_2\text{N}]_2\) (squares), \([(\text{CH}_3)_2\text{N}]_2\text{Sn}\) (circles), \([(\text{CH}_3)_3\text{SiN}]_2\) (diamonds). The straight lines are least-squares, linear regressions for which the numerical data are included in Table II.