

BONDING IN TRIORGANOTIN PYRIDINES

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Summary

A number of new compounds in which a 4-C-bonded pyridine group is attached to an organotin moiety, including $(C_6H_5)_3Sn$ -py, $(C_6H_5)_3Sn$ -py NO, and $(CH_3)_3Sn$ -py-Sn $(CH_3)_3Cl$, have been synthesized, and studied by variable temperature ^{119m}Sn Mössbauer spectroscopy, IR, and 1H NMR techniques. The bonding interaction between the metal and the heterocyclic ligand can be described without invoking a π -bonding mechanism to account for the resolvable quadrupole hyperfine interaction observed in the Mössbauer spectra of these compounds. The temperature dependence of the ^{119m}Sn recoil-free fraction in these covalent solids is characteristic of monomeric units, but the observed temperature dependence of the area ratio in $(CH_3)_3Sn$ -py-Sn $(CH_3)_3Cl$ is contrary to that expected from the theory of the Gol'danskii–Karyagin Effect.

Introduction

In an effort to prepare organometallic compounds which can be intercalated into transition metal layered lattices to form intercalation compounds, a number of new potential guest species have been prepared. Recent studies [1–3] have shown that these guest moieties have the common property of having unshared electron pairs and can function as electron donors [4] in the intercalation process. To extend the range of such guest molecules, a number of organotin compounds with pyridine and pyridine *N*-oxide, in which the heterocyclic ligand is C-bonded to the metal, have been prepared and characterized in the present study.

Experimental

Trimethyltin chloride, 4-bromopyridine hydrochloride, *n*-butyllithium (1.6 *M* in hexane), and 80–85% *m*-chloroperoxybenzoic acid were obtained from Aldrich Chemicals. Triphenyltin chloride and lithium (30% dispersion in mineral oil) were obtained from Alfa-Ventron Corp.

General comments. Due to the moisture and oxygen sensitivity of the starting materials involved in the present study, all manipulations were carried out under an inert atmosphere (argon or nitrogen) and strictly anhydrous conditions. Diethyl ether, hexane, and tetrahydrofuran were dried by refluxing with lithium aluminum hydride and distilled.

4-(Trimethyltin)pyridine (I). This compound was obtained in 50% yield by using the method of Weiner [5] and of Mitchell [6]. *N*-Butyllithium (74 ml of 1.54 *M* in hexane) was added to 18.00 g of 4-bromopyridine in 200 ml diethyl ether maintained at -40°C . The 4-bromopyridine was obtained from the hydrochloride [7]. $(\text{CH}_3)_3\text{SnCl}$ (22.72 g) in 100 ml ether was then added and the mixture was allowed to attain room temperature. After stirring for 1 h the mixture was treated with 100 ml of saturated aqueous ammonium chloride solution. The organic layer was dried over anhydrous magnesium sulfate and the solvents removed by flash evaporation. A side product of this reaction is an addition compound, VI, of 4-(trimethyltin)pyridine with $(\text{CH}_3)_3\text{SnCl}$, which will be discussed further below. The 4.98 g of crude solid side product (20% based on $(\text{CH}_3)_3\text{SnCl}$) was filtered off at 0°C . The liquid was distilled under reduced pressure to yield 14.3 g (52%) of colorless liquid, b.p. $55^{\circ}\text{C}/0.5$ mmHg (lit. $59^{\circ}\text{C}/0.3$ mmHg). An attempted synthesis of I via $(\text{CH}_3)_3\text{SnLi}$ and 4-bromopyridine in THF/ether at 0°C was shown by NMR to yield a mixture of hexamethylditin and 4,4'-bipyridine. This method was successful in the synthesis of the 2- and 3-isomers using $(\text{CH}_3)_3\text{SnNa}$ [8].

4-(Triphenyltin)pyridine (II) was obtained similarly in 60% yield from an ether/benzene solution of 4-Li-pyridine and $(\text{C}_6\text{H}_5)_3\text{SnCl}$ at -40°C . The product remained undissolved when the reaction mixture was treated with an aqueous saturated solution of ammonium chloride. The solid was filtered off and recrystallized twice from acetone to yield 8.4 g (60%) of colorless needles, m.p. 225°C . An analogous procedure has been used for the syntheses of the 2- and 3-isomers [9]. Anal. Found: C, 64.35; H, 4.60; N, 3.32. $\text{C}_{23}\text{H}_{19}\text{NSn}$ calcd.: C, 64.53; H, 4.47; N, 3.27%.

4-(Trimethyltin)pyridine *N*-oxide (III) was obtained by the reaction of 5.0 g of I with 4.3 g of 80–85% *m*-chloroperoxybenzoic acid in 100 ml of chloroform for 3 wks in the dark. The reaction product was treated with a stoichiometric amount of 1.0 *M* potassium hydroxide. The organic layer was separated and dried over magnesium sulfate. The mixture was filtered and the solvents removed by flash evaporation. The 4.8 g of crude product obtained were recrystallized from ligroine (b.p. 63 – 75°C) to yield 3.5 g (66%) of colorless flakes, m.p. 132°C (lit. 5 131 – 133°C). Anal. Found: C, 37.35; H, 5.20; N, 5.34; O, 6.26. $\text{C}_8\text{H}_{13}\text{NOSn}$ calcd.: C, 37.26; H, 5.08; N, 5.43; O, 6.20%.

4-(Triphenyltin)pyridine *N*-oxide (IV) was obtained similarly. The crude product was dissolved in hot ethanol, cooled, and filtered to remove the insoluble unreacted organotin. The solvents were removed under vacuum and the product was recrystallized from a 2/1 hexane/benzene mixture. It was then sublimed at 180°C under vacuum to yield 2.75 g (49%) of white powder, m.p. 194°C . Anal. Found: C, 62.21; H, 4.31; N, 3.15; O, 3.60. $\text{C}_{23}\text{H}_{19}\text{NOSn}$ calcd.: C, 62.47; H, 4.44; N, 3.12; O, 3.55%.

4-(Trimethyltin)pyridine(trimethyltin)chloride (VI). This compound was obtained as a side product in the synthesis of I. The compound was also synthesized by dissolving 0.77 g of I and 0.63 g of $(\text{CH}_3)_3\text{SnCl}$ in dry ether. The solvent was removed by flash evaporation and the crude product was recrystallized from

petroleum ether (b.p. 30–60°C) to yield 1.23 g (88%) of colorless needles, m.p. 119°C. Anal. Found: C, 29.81; H, 5.22; Cl, 8.20; N, 3.09. $C_{11}H_{22}ClNSn_2$ calcd.: C, 29.95; H, 5.03; Cl, 8.04; N, 3.18%.

The other organotin compounds used as model compounds in this study were either obtained commercially, or prepared by unmodified literature methods [10], and included $(CH_3)_4Sn$, $(C_6H_5)_4Sn$, $(CH_3)_3SnCl$, $(CH_3)_3SnCl \cdot py$ and $(CH_3)_3Sn(C_6H_5)$.

Characterization. All new compounds or syntheses used in this study were characterized by elemental analysis (Galbraith Laboratories, Inc. Knoxville, TN). Infrared studies were effected using a Perkin–Elmer Model 283 dispersion spectrometer. The solid compounds were examined in CsI pellets and the liquid compounds were studied as thin films between CsI plates. Proton NMR data were obtained with a Varian CFT 20 at 80 MHz with tetramethylsilane as an external reference.

^{119m}Sn Mössbauer effect studies. These were carried out as described earlier [11]. Spectrometer calibration was effected using the magnetic hyperfine spectrum of metallic iron at room temperature. All isomer shifts are reported with respect to an absorber spectrum of $BaSnO_3$ at room temperature. Data reduction was carried out on the Rutgers IBM 370/178 computer using a least-squares matrix inversion Lorentzian fitting routine in which line position, line width, and resonance effect magnitude are allowed to vary as free parameters. Temperature control over the time period required for data acquisition at a given temperature (typically 4 to 12 h) was better than ± 0.5 deg.

Results and discussion

The ^{119m}Sn Mössbauer, 1H NMR, and relevant infrared data are summarized in Table 1. The tabulated data are in good agreement with literature values for IR on III [6] and V [12] and for 1H NMR on I [5,6], III [5], and V [13] taking into account solvent effects. The isomer shifts at liquid nitrogen temperature fall into a rather narrow range (1.24 to 1.36 $mm\ s^{-1}$ with respect to $BaSnO_3$) and are characteristic of Sn^{IV} [11,14]. As has been noted in earlier studies [15], the isomer shift parameter is relatively insensitive to temperature variation in these organometallics, and is of little diagnostic value in the description of the bonding.

A particularly interesting observation related to the Mössbauer parameters of these compounds is that a significant quadrupole hyperfine interaction in I and III (as well as for one of the two tin atoms in IV) can be extracted from the resonance-effect data. A typical spectrum is shown in Fig. 1. The origin of this quadrupole interaction, which reflects the departure from cubic symmetry of the charge distribution about the metal atom, has been the subject of considerable speculation [16]. The key question to be answered concerns the necessity of invoking π -bonding between one (or more) of the ligands attached to the metal atom and empty acceptor orbitals of Sn, or whether the observed data can be accounted for solely by electronic effects in the σ -bonds.

It is, of course, clear from published data [14] that even in the absence of strict T_d symmetry around Sn, the quadrupole hyperfine interaction may be too small to be resolved from the ^{119m}Sn Mössbauer data. Thus, $(CH_3)_3SnH$, $[(CH_3)_3Sn]_2$, and $(C_6H_5)_3SnH$, inter alia, all give rise to what appear to be single line resonance spectra, and the rehybridization of the sp^3 tin orbitals is sufficiently complete to give

TABLE 1

^{119}mSn MOSSBAUER, ^1H NMR (δ in ppm) AND IR DATA (cm^{-1}) FOR THE COMPOUNDS DISCUSSED IN THE TEXT (^1H NMR data were obtained in acetone- d_6 except for values in brackets which are obtained in CDCl_3)

| | Mössbauer | | | | ^1H NMR | | | | |
|--|---------------------------------------|---------------------------------------|--|--|------------------|---------------|--------------|---|---|
| | IS (78 K) (mm s^{-1}) | QS (78 K) (mm s^{-1}) | $-\text{dln}A/\text{dT}$ ($\times 10^2 \text{ K}^{-1}$) | | methyl | α to N | β to N | $^2J(\text{H}-^{119}\text{Sn})$ (Hz) | $^2J(\text{H}-^{117}\text{Sn})$ (Hz) |
| $(\text{CH}_3)_3\text{Sn}(\text{C}_6\text{H}_5)$ (V) | 1.24 | 0 | — | | 0.30 | | (7.40 mlpt) | 55.5 | 53.3 |
| $(\text{CH}_3)_3\text{Sn-py}$ (I) | 1.29 | 0.61 | 3.40 | | 0.32 | 8.45 | 7.46 | 57.6 | 54.4 |
| $(\text{CH}_3)_3\text{Sn-py NO}$ (III) | 1.30 | 0.53 | 2.27 | | 0.34 | 8.06 | 7.48 | 57.8 | 55.4 |
| | | | | | [0.35] | [8.14] | [7.35] | [56.5] | [54.2] |
| $(\text{C}_6\text{H}_5)_3\text{Sn-py}^a$ (II) | 1.28 | 0 | 1.66 | | — | [8.60] | [7.50 mlpt.] | — | — |
| $(\text{C}_6\text{H}_5)_3\text{Sn-py NO}^a$ (IV) | 1.26 | 0 | 1.73 | | — | 8.18 | [7.50 mlpt.] | — | — |
| $(\text{CH}_3)_3\text{Sn}_a\text{-py-}$ (VI, Sn_a) | 1.29 | 0.86 | 2.70 | | 0.34 | 8.45 | 7.52 | 56.8 | 54.4 |
| $(\text{CH}_3)_3\text{Sn}_b\text{Cl}^a$ (VI, Sn_b) | 1.36 | 3.39 | 2.22 | | 0.65 | — | — | 65.6 | 63.2 |

| | IR Stretch | | |
|--|-------------------|----------------|-------------|
| | ν_{as} (Sn-C) | ν_s (Sn-C) | ν (N-O) |
| $(\text{CH}_3)_3\text{Sn}(\text{C}_6\text{H}_5)$ (V) | 528vs | 512s | — |
| $(\text{CH}_3)_3\text{Sn-py}$ (I) | 531vs | 512s | — |
| $(\text{CH}_3)_3\text{Sn-py NO}$ (III) | 536vs | 525vs | 1249vs |
| $(\text{C}_6\text{H}_5)_3\text{Sn-py}^a$ (II) | — | — | — |
| $(\text{C}_6\text{H}_5)_3\text{Sn-py NO}^a$ (IV) | — | — | — |
| $(\text{CH}_3)_3\text{Sn}_a\text{-py-}$ (VI, Sn_a) | 533vs | 512s | — |
| $(\text{CH}_3)_3\text{Sn}_b\text{Cl}^a$ (VI, Sn_b) | 543vs | 512w? | — |

^a New compound.

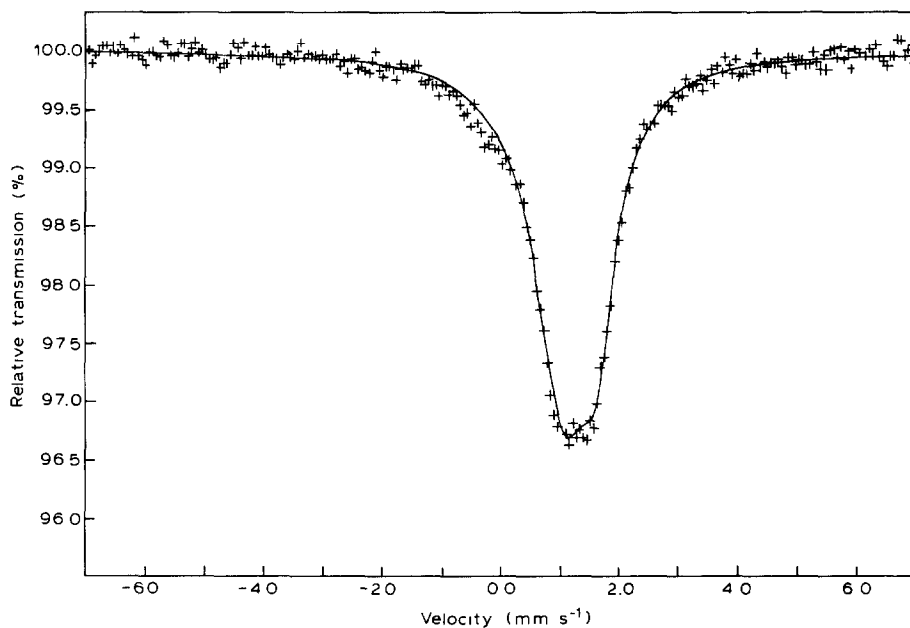


Fig. 1. ^{119m}Sn Mössbauer spectrum of $(\text{CH}_3)_3\text{Sn}(\text{C}_5\text{H}_4\text{N})$ (I) at 78 K. The isomer shift scale (abscissa) is with respect to BaSnO_3 at 78 K.

effectively a cubic charge distribution about the metal center. Moreover, in all cases where tin is bonded to four C atoms (whether these are of sp^3 , sp^2 , or sp hybridization is immaterial), and in which there is no possibility of electron donation by a ligand-atom lone pair into a fifth or sixth coordination site on the metal, there is no resolvable quadrupole interaction observable in the spectra. Thus, it is unexpected that the trimethyltin moiety bonded to C-4 of pyridine and pyridine *N*-oxide, gives rise to quadrupole splittings of 0.61 and 0.53 mm s^{-1} , respectively. On the other hand, no such splitting is observed when a triphenyltin moiety is bonded to these ligands instead (see Table 1).

If π -back donation into empty $5d$ orbitals of Sn were the major factor giving rise to the hyperfine splitting, such an effect should be observed in $(\text{CH}_3)_3\text{Sn}(\text{C}_6\text{H}_5)$, since the phenyl group is expected to be a better π -donor than the 4-pyridine group. As noted by Anderson et al. [17] in their study of amine group basicities by potentiometric titration in aqueous methanol, the greater electronegativity of nitrogen in the heterocyclic ring is expected to reduce the $(d-p)\pi$ -bonding [18] into the metal atom d orbitals of Sn relative to the phenyl group. It is clear from these considerations that $(d-p)\pi$ -back bonding effects alone cannot account for the observed data.

Turning next to the electronic effects transmitted through the σ overlap, these interactions can be considered in the framework of Bent's rule [19] which postulates that when a metal atom is bonded simultaneously to two ligands of differing electron withdrawing power, p density will concentrate in the bond to the more electronegative ligand, whereas the metal orbital directed toward the more electropositive ligand will be enriched in s -character. Because of the difficulties in assigning meaningful

electronegativities to polyatomic ligands, the question remains how large an electronegativity difference is required in $(\text{CH}_3)_3\text{SnX}$ and $(\text{C}_6\text{H}_5)_3\text{SnX}$ molecules between the organic group and the X ligand before a quadrupole splitting hyperfine interaction can be resolved from the data.

Thus, the present results suggest that the electron-withdrawing power of the ligands bonded to tin can be understood without invoking ligand metal π -back bonding. The electron withdrawing power in the $(\text{CH}_3)_3\text{SnX}$ series can be arranged in the order $\text{X} = \text{CH}_3 < \text{C}_6\text{H}_5 < \text{C}_5\text{H}_4\text{NO} \sim \text{C}_5\text{H}_4\text{N}$. The absence of a resolved quadrupole hyperfine interaction in $(\text{CH}_3)_3\text{SnC}_6\text{H}_5$, $(\text{C}_6\text{H}_5)_3\text{Sn-py}$, and $(\text{C}_6\text{H}_5)_3\text{Sn-py NO}$ must then be ascribed to an insufficiently large electronegativity (electron withdrawing ability) difference between the two kinds of ligands, compared to the situation in $(\text{CH}_3)_3\text{Sn-py}$ and $(\text{CH}_3)_3\text{Sn-py NO}$. In the latter two cases, metal orbital rehybridization into three $(5s^{1+\delta}5p^{3-\delta})$ and one $(5s^{1-\delta}5p^{3+\delta})$ orbitals gives rise to a non-spherical charge distribution about the metal atom sufficiently large for the quadrupole splitting to be observed in the Mössbauer spectra. Parenthetically it may be noted that the electron-withdrawing order suggested above accounts for the observed differences in quadrupole splitting in $(\text{CH}_3)_3\text{SnI}$ (QS 3.05 mm s^{-1}) and in $(\text{C}_6\text{H}_5)_3\text{SnI}$ (QS 2.05 mm s^{-1}) and related data for trimethyltin and triphenyltin monomers reported in the literature [14].

As will be noted from Table 1, the two tin atoms in $(\text{CH}_3)_3\text{Sn-py-Sn}(\text{CH}_3)_3\text{Cl}$ (VI) are readily distinguishable in terms of their ^{119}mSn Mössbauer parameters. A representative spectrum is shown in Fig. 2 in which the "outer" doublet is assigned to the 5-coordinate metal atom and the "inner" doublet to the 4-coordinate metal atom. In the context of the prior discussion, it is interesting to note that the

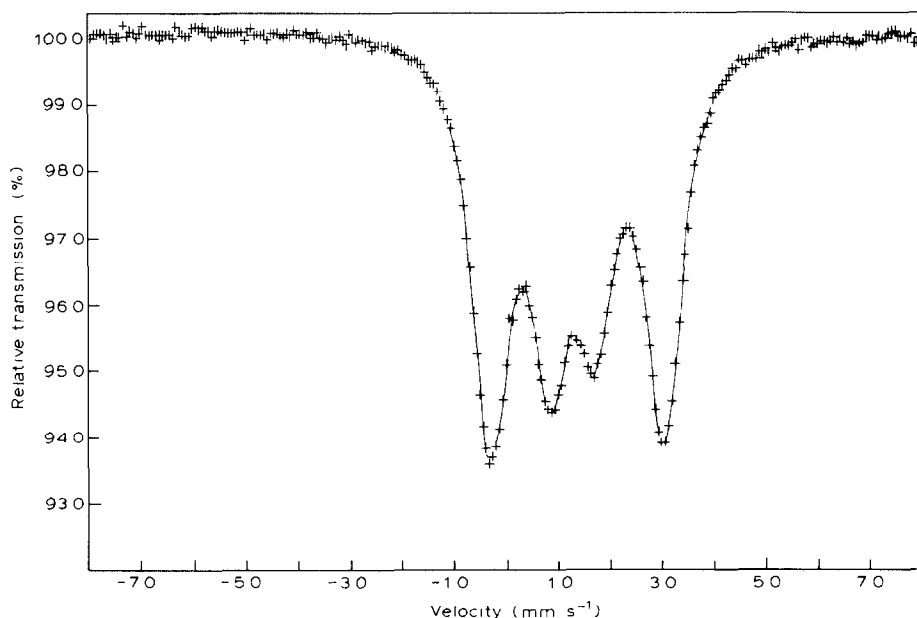


Fig. 2. ^{119}mSn Mössbauer spectrum of $(\text{CH}_3)_3\text{Sn}(\text{C}_5\text{H}_4\text{N})\text{Sn}(\text{CH}_3)_3\text{Cl}$ (VI) at 78 K. The "inner" doublet is assigned to the four-coordinate Sn atom, the "outer" doublet to the five-coordinate Sn atom. For a discussion of the intensity asymmetry, see text.

quadrupole splitting hyperfine interactions of the latter are increased by 0.27 mm s^{-1} (at 78 K) compared to the value observed in the spectrum of $(\text{CH}_3)_3\text{Sn-py}$. In the binuclear compound, electron density is donated by the lone pair of the bridging pyridine group into the fifth coordination site of the $(\text{CH}_3)_3\text{SnCl}$ moiety to give the latter a trigonal-bipyramidal configuration with an N–Sn–Cl bond angle near 180° . This effect makes the bridging pyridine atom a better electron withdrawing group than the pyridine group in which the N atom is uninvolved in bonding, leading to the larger quadrupole splitting which is observed. The quadrupole splitting of the doublet assigned to the 5-coordinate tin atom in this compound ($QS \text{ } 3.39 \text{ mm s}^{-1}$) is typical of the values associated with a planar trimethyltin group having electronegative ligands in the axial positions of the trigonal-bipyramidal environment. The infrared frequency assignments were made by comparison with I and $(\text{CH}_3)_3\text{SnCl} \cdot \text{py}$ ($\nu_{as} \text{ } 541s, \nu_s \text{ } 512vw$) [20].

Turning next to the temperature dependence of the ^{119m}Sn recoil-free fraction, this parameter is equal (for “thin” absorbers) to the temperature dependence of the area under the resonance curve. The normalized values of $-d[\ln A(T)/A(78)]/dT$ are summarized in Table 1. By comparison with literature values of this parameter it is inferred that all of the compounds considered in the present study are monomeric in the solid state. In this context it is interesting to note that $-d[\ln A(T)/A(78)]/dT$ for II is essentially equal to that observed [21] for $(\text{C}_6\text{H}_5)_4\text{Sn}$ ($1.630 \times 10^{-2} \text{ K}^{-1}$) in consonance with the assumptions of the effective-vibrating-mass model discussed earlier [22]. This model postulates that for covalent solids in which the inter-molecular vibrations occur at much lower frequencies than the intra-molecular (normal modes), the temperature dependence of the Mössbauer recoil-free fraction can be correlated with Raman active lattice modes and with the molecular weight of the covalent moiety [11]. Thus, it is expected in the present case, that the temperature dependence of the ^{119m}Sn recoil-free fraction for $(\text{C}_6\text{H}_5)_3\text{Sn-py}$ ($MW = 428$) and $(\text{C}_6\text{H}_5)_4\text{Sn}$ ($MW = 427$) should be nearly the same. The present results are in good agreement with these predictions. Moreover, the near identity of the $-d[\ln A(T)/A(78)]/dT$ for II and IV suggest very similar bonding interactions in the two solids.

The temperature dependences of the recoil-free fractions of the two tin atoms in VI are summarized graphically in Fig. 3 which also shows the comparable data for I. It is seen that in consonance with expectation, the temperature dependence is greater for the mononuclear tin compound than for either the 4-coordinate or the 5-coordinate tin atom in VI, and greater for the former than the latter in the binuclear compound.

There is, however, a puzzling feature of the temperature dependent ^{119m}Sn Mössbauer data for VI which is not yet adequately accounted for. A vibrational anisotropy of the metal atom relative to the molecular symmetry axis in organotin compounds is known to result in a temperature-dependent intensity asymmetry of the two components of the quadrupole split doublet. This phenomenon is commonly called the Gol'danskii–Karyagin Effect [23] and has been shown to occur in both octahedral (six-coordinate) compounds such as $(\text{CH}_3)_2\text{SnF}_2$ [24] and $(\text{CH}_3)_2\text{Sn}(\text{trop})_2$ [11] as well as in trigonal-bipyramidal (five-coordinate) compounds such as $(\text{CH}_3)_3\text{SnF}$ [25], $(\text{CH}_3)_3\text{SnN}_3$ [26], and $(\text{CH}_3)_3\text{SnCN}$ [27], inter alia. Consideration of the probable structure of VI inferred from the quadrupole splitting data led to the expectation that the vibrational anisotropy should be larger for the 5-coordinate tin

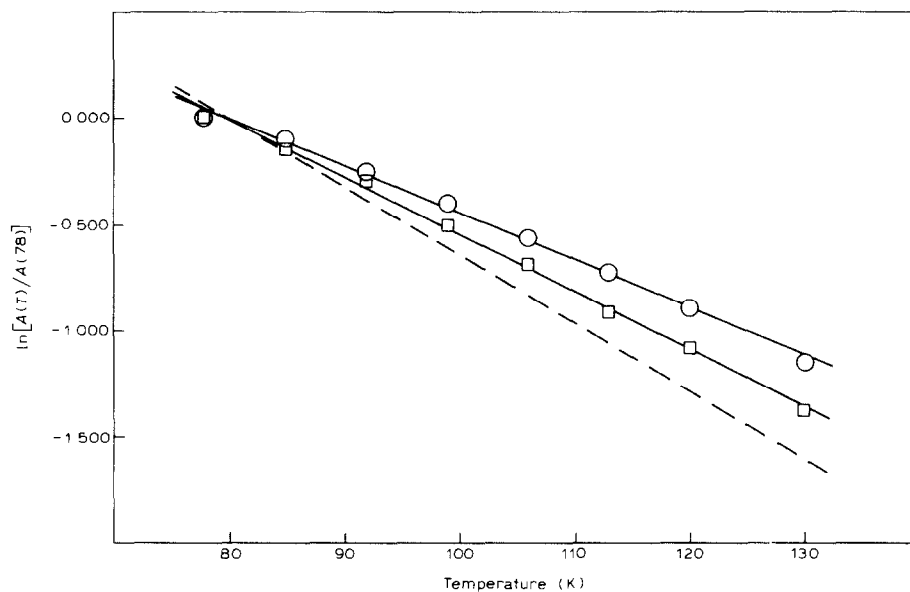


Fig. 3. Temperature dependence of the (normalized) area under the resonance curve for the four-coordinate Sn atom (squares) and five-coordinate Sn atom (circles) of VI. The dashed line shows the comparison data for $(\text{CH}_3)_3\text{Sn}(\text{C}_5\text{H}_4\text{N})$ (I).

atom (giving rise to the “outer” doublet) than for the 4-coordinate tin atom (“inner” doublet). The experimentally observed data are summarized in Fig. 4 in which the residual intensity asymmetry δ calculated from the intensity asymmetry difference at

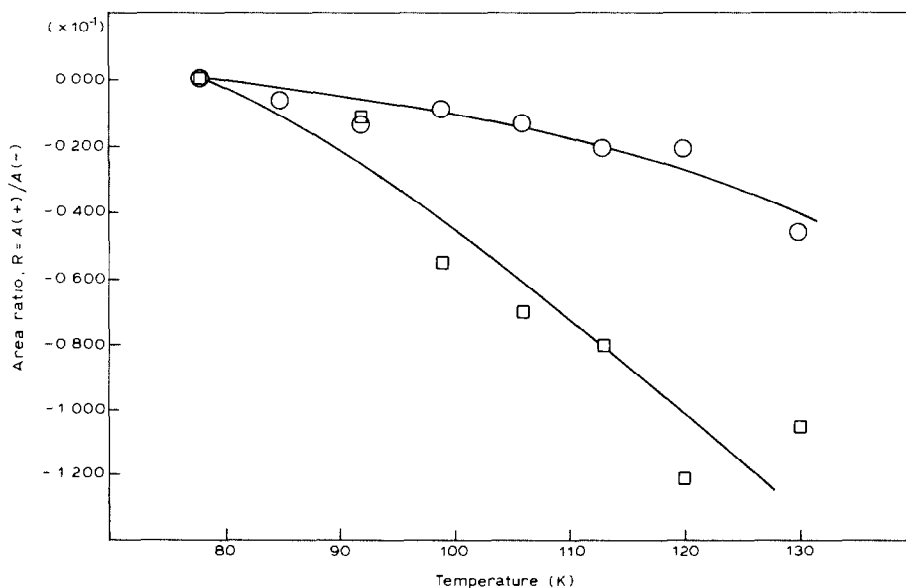


Fig. 4. Temperature dependence of the area ratio, R , for the two Sn atoms of VI. The ordinate shows the value $[R(T) - R(78)] \times 10^{-1}$, where the second term refers to the liquid nitrogen temperature datum.

temperature T and 78 K – is shown as a function of temperature. Contrary to expectation, the “inner” doublet shows the larger temperature dependent intensity asymmetry. The reasons for this apparent anomaly are not yet clearly understood at the present time, and are the subject of further study in this laboratory.

In conclusion it is appropriate to note that a number of the organotin complexes discussed in the present study, and similar compounds having lone-pair electron donor centers, have been successfully intercalated into host matrices, such as FeOCl. A more detailed description of the hyperfine interactions and lattice dynamical properties of such systems will be reported in greater detail elsewhere [28].

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