Registry No. ZnTPP, 14074-80-7; benzene, 71-43-2; ZnTPP–methyl acetate, 61483-53-2; ZnTPP–acetone, 61483-54-3; ZnTPP–ethyl acetate, 61477-51-8; ZnTPP–tetrahydrofuran, 61477-52-9; ZnTPP–bridge ether, 61484-37-5; ZnTPP–4-ethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane, 61477-53-0; ZnTPP–Me_2SO, 61483-89-4; ZnTPP–dimethylacetamide, 61477-54-1; ZnTPP–trimethyl phosphite, 61477-55-2; ZnTPP–pyridine, 24389-79-5; ZnTPP–triethylamine, 61484-36-4; ZnTPP–hexamethylphosphoramide, 61477-56-3; ZnTPP–1-azabicyclo[2.2.2]octane, 61477-57-4; ZnTPP–THTP, 61477-58-5; ZnTPP–diethyl sulfide, 61477-59-6; ZnTPP–pentamethylene sulfide, 61477-60-9.

Supplementary Material Available: Table I containing the spectroscopic data for the ZnTPP–donor systems (4 pages). Ordering information is given on any current masthead page.

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Lattice Dynamics, Vibrational Anisotropy, and Hyperfine Interactions in $Sn^{II}(C_5H_7O_2)_2$

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The synthesis and some properties of a number of tin(II) bis(1,3-diketonates) were reported a few years ago by Wakeshima and Kijima[1] and by Bos et al.,[2] and extensive information pertaining to these and related compounds has been published in the organometallic literature.[3] Among the properties which have been reported are the ^{119}Sn Mössbauer parameters at liquid nitrogen temperature[2,4,5] but these data have been considered only in a phenomenological manner to confirm the oxidation state assignment of the metal atom in these compounds.

Table I. ^{119}Sn Mössbauer Data for $Sn^{II}(C_5H_7O_2)_2$

Sample	Temp, K	IS, mm s^{-1}	QS, mm s^{-1}	ln [$A(T)$/ $A(78)$]	R
Neat solid	78	3.003	1.926	0	1.048
	90	3.028	1.928	−0.3391	1.087
	100	2.998	1.932	−0.7309	1.110
	110	2.982	1.936	−0.9087	1.123
	120	3.021	1.940	−1.248	1.138
	130	2.967	1.942	−1.459	(1.098)
	140	2.971	1.945	−1.766	1.176
	150	2.950	1.944	−1.991	1.183
30% v/v in butylbenzene	78	3.051	1.951		1.077

In a recent publication[6] from this laboratory the lattice dynamics and vibrational anisotropy of the related Sn(IV) compound $(CH_3)_2Sn(C_5H_7O_2)_2$ have been discussed in some detail, and in this context it was considered useful to examine related properties of $Sn^{II}(C_5H_7O_2)_2$ [$Sn^{II}(acac)_2$] in order to gain a clearer understanding concerning the geometry and bonding properties of the acetylacetonate ligand in these two species. In contrast to $(CH_3)_2Sn(acac)_2$, a solid at room temperature, for which an accurate single-crystal x-ray diffraction study[7] had provided detailed structural information and thermal parameters for the atomic motion at room temperature, the Sn(II) compound is an air- and moisture-sensitive liquid, and thus only indirect data concerning its structure have been published. In the present investigation, the lattice dynamical and hyperfine interaction parameters for this compound have been obtained over the temperature range $78 \leq T \leq 150$ K in order to elucidate the details of the bonding and intermolecular forces both in the neat (frozen) liquid and in glassy matrix samples of this material.

Experimental Section

$Sn^{II}(acac)_2$ was prepared by the method of Bos et al.[2] under dry nitrogen to yield a golden yellow oil which was freed of excess solvent by vacuum distillation. The reaction product was transferred to an anhydrous, N_2-filled glovebox and samples for Mössbauer effect studies were transferred in an inert atmosphere, using a hypodermic syringe, into Mylar window fitted copper cells and immediately cooled to 78 K before mounting in the spectrometer.

The Mössbauer data were acquired as described earlier.[8] Temperature control was maintained to better than ±1 K using an Artronix Model 5301 proportional temperature controller and a Pt resistance thermometer as sensor. Temperature measurement was effected using NBS-calibrated thermocouples having a sensitivity of $\sim 20\ \mu V$/deg. Spectrometer calibration was effected using the magnetic hyperfine splitting in NBS SRM 0.8-mil metallic iron foil.[9] All isomer shifts discussed in this paper are with reference to the resonance maximum observed using a high-purity $BaSnO_3$ absorber at 294 ± 1 K, employing the same $BaSn^*O_3$ source as used in the data runs.

Proton NMR spectra were obtained on $CDCl_3$ solutions in sealed tubes using a Varian T60 spectrometer with TMS as an internal standard, at room temperature, and the results were in good agreement with the values reported in the literature.[5]

Results and Discussion

The ^{119}Sn Mössbauer spectrum consists of a well-resolved doublet having an isomer shift of 3.015 ± 0.010 mm s^{-1} and a quadrupole splitting of 1.926 ± 0.015 mm s^{-1} at 78 K. These data are in reasonable agreement with those reported by Ewings et al.[5] and Bos et al.[2] (the latter corrected for the isomer shift of α-Sn). The resonance parameters over the temperature range $78 \leq T \leq 150$ K are summarized in Table I. Above 150 K the resonance effect magnitude becomes too small to permit accurate data reduction, even with an excess of 2×10^6 counts accumulated per velocity point in the spectrum.

The temperature dependence of the area under the resonance curve (normalized to the 78-K value) is summarized in the semilogarithmic plot shown in Figure 1. A linear

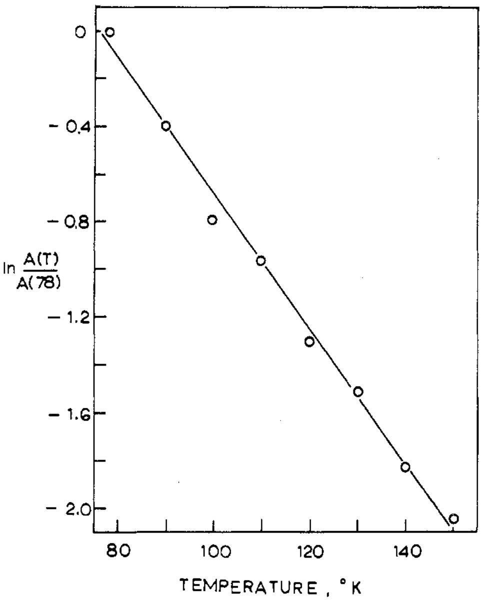

Figure 1. Temperature dependence of the normalized area under the resonance curve for $Sn^{II}(acac)_2$. The linear least-squares fit (full line) has a correlation coefficient of 0.997 over the temperature range $78 \le T \le 150$ K.

least-squares regression analysis yields d ln $[A(T)/A(78)]/dT$ of -2.81×10^{-2} K^{-1} with a correlation coefficient of 0.997. The temperature dependence of the quadrupole coupling parameter, e^2qQ (where Q is the ^{119}Sn nuclear quadrupole moment, $-0.064 \pm 0.005b$, and q is the electric field gradient tensor, V_{zz}), is also well fitted by a linear regression analysis and yields a value of d(QS)/dT of $+2.87 \times 10^{-4}$ mm s^{-1} K^{-1} with a correlation coefficient of 0.981.

The ratio of the area under the two components of the quadrupole-split doublet is temperature dependent, having a value of 1.06 at 78 K and 1.19 at 150 K (uncorrected for possible orientational effects resulting from quick freezing of the liquid sample in the sample cell). These data indicate the presence of a Gol'danskii–Karyagin effect[10,11] arising from anisotropic motional behavior of the metal atom in this compound, as summarized in Figure 2.

The temperature dependence of the isomer shift, d(IS)/dT, of -7.22×10^{-4} mm s^{-1} K^{-1} is moderately well fitted by a linear regression analysis and the small value of this parameter is typical of that observed for other organometallic compounds of tin,[8] in which isomer shift is an insensitive function of temperature, in contrast to the values observed in ionic or metallic tin containing matrices.

Finally, before discussing the significance of these data, it is necessary to establish the structural integrity of $Sn^{II}(acac)_2$ and the possible intermolecular interactions in the neat solid. In this context, the data pertaining to the Mössbauer results obtained on a frozen solution (~30% by volume) of $Sn^{II}(acac)_2$ in *n*-butylbenzene (Table I) can be directly related to the osmometric results of Ewings et al.[5] These authors have shown that in benzene solution the title compound is monomeric, with no evidence of significant intermolecular association, in consonance with the mass spectral data which show no tin-containing fragments larger than the polyisotopic parent ion.[4] From the data in Table I it is seen that both the IS and QS parameters (at 78 K) for the frozen-solution species are essentially identical with the values obtained for the neat frozen liquid and that the data obtained in the Mössbauer experiments on the neat (frozen) liquid pertain to essentially independent $Sn^{II}(acac)_2$ molecular species.

Moreover, these results may be contrasted to the observation[6] in the case of $(CH_3)_2Sn(acac)_2$ in which the considerable change in the ^{119}Sn Mössbauer parameters in going from the neat solid to a (frozen) *n*-butylbenzene solution was taken as indicative of a change from bidentate to monodentate of one (or possibly both) of the acac ligands in the species present in solution. No such structural change is evidenced in the case of $Sn^{II}(acac)_2$.

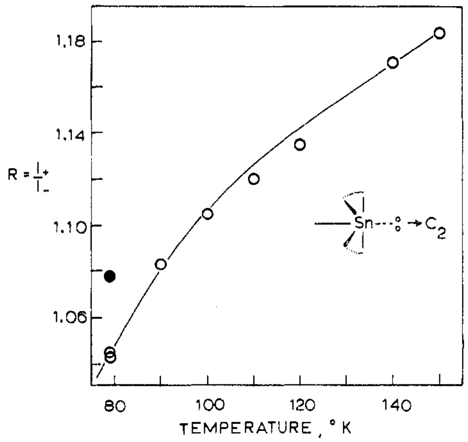

Figure 2. Gol'danskii–Karyagin asymmetry in the ^{119}Sn Mössbauer spectra of $Sn^{II}(acac)_2$. The presumed molecular symmetry, indicating the twofold axis passing through the metal atom and the lone pair, is shown on the figure. The full circle at 78 K indicates the value observed for a 30% (v/v) solution in *n*-butylbenzene.

The major contribution to the quadrupole splitting which is observed is expected to come from the lone-pair electrons on the metal atom. As Eriks et al.[12] have recently noted in connection with their crystallographic study of SnF_2, when stannous ion is bonded to light elements, including oxygen and fluorine, the preferred symmetry about the metal atom is that of a trigonal pyramid in consonance with the Gillespie–Nyholm rules[13,14] and extensive observations of related structures. Such a configuration in the case of $Sn^{II}(acac)_2$ can be achieved if the lone-pair electrons as well as one oxygen atom of each acac ligand are envisioned as occupying three bonding coordinates lying in the equatorial plane, while the two remaining oxygen atoms (one from each acac ligand) occupy the two axial positions. Assuming that the off-diagonal elements of the tensor describing the EFG are small and that $V_{xx} \approx V_{yy}$ (i.e., that near-cylindrical symmetry of the charge distribution obtains), the shape of that electrostatic charge distribution relative to the twofold symmetry axis passing through the metal atom and the lone pair will be prolate. Under this condition, the π transition $(\pm^1/_2 \rightarrow \pm^3/_2)$ in the Mössbauer absorption will move to higher energy relative to the σ transition $(\pm^1/_2 \rightarrow \pm^1/_2)$.[15] Thus, the observed intensity ratio, R, will be directly proportional to the A parameter ($A = I_\pi/I_\sigma$) of Gol'danskii and Makarov;[16] that is, the area ratio of the positive velocity peak to the negative velocity peak will yield A directly. Using the results of Flinn et al.,[17] it is seen that $A > 1$ implies that the mean-square amplitude parallel to the molecular symmetry (twofold) axis will be smaller than the mean-square amplitude perpendicular to this axis and the present data suggest that this condition is the one which describes the motional anisotropy of the tin atom in the title compound. Moreover, it is interesting to note that the observation that $R > 1$ obtained from the frozen *n*-butylbenzene solution spectrum leaves little doubt that the temperature-dependent intensity ratio of the two components of the quadrupole of doublet spectrum reflects an intrinsic molecular motional property of this molecule rather than an accidental crystal orientation caused by the sample-freezing process.

This unexpected result, that the mean-square vibrational amplitude is larger in the direction perpendicular to the metal atom–lone pair symmetry axis than parallel to this axis, should be reflected in a weaker interaction between Sn and the "axial" oxygen atoms compared to the Sn–"equatorial" oxygen atom interaction; thus the ligand is, in fact, anisobidentate[18] with two distinct Sn–O bond distances, the former being larger than the latter. Such anisobidentate bonding has been observed in bis(*N*,*N*-diethyldithiocarbamato)tin(II),[19,20] and similar bonding anisotropies have been reported for a number of other analogous stannous compounds, including tin(II) bis(benzoylacetonate)[21], Sn[SnEDTA][22] and sulfatobis(thiourea)-tin(II).[23]

Finally, it is worth noting that the thermal parameters reported by Eriks et al.[12] in their crystallographic study of SnF_2 yield a mean-square amplitude which is ~5% larger in the direction perpendicular to the axis containing the lone-pair electrons than in the parallel direction. Thus the ellipsoid of vibration is inferred to be qualitatively similar in this inorganic compound without bidentate ligands to that inferred for $Sn^{II}(acac)_2$ from the Mössbauer results and may, in fact, be a rather general property of trigonal-pyramidally bonded stannous compounds.

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Registry No. $Sn^{II}(acac)_2$, 16009-86-2; ^{119}Sn, 14314-35-3.

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Metal Ion Promoted Demethylation of *N*-Methyltetraphenylporphyrin by Nickel(II), Zinc(II), and Manganese(II)

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Reactions of metal complexes of *N*-methylporphyrins that result in demethylation have been observed to follow two very different mechanisms. Cobalt(I) and rhodium(I) *N*-methylporphyrin complexes can undergo an oxidative addition to give cobalt(III) and rhodium(III) organometallic porphyrin products.[1,2] The product analysis and presence of a term first order in nucleophile for demethylation of chloro-*N*-methyl-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatocopper(II) by di-*n*-butylamine, diethylamine, and pyridine, however, demonstrate simple abstraction of $-CH_3^+$.[3] The production of etioporphinatozinc(II) from chloro-*N*-methyletioporphinatozinc(II) in refluxing pyridine, observed by Hambright,[4] also likely involves dissociation of $-CH_3^+$. This reaction, in which a metal ion assists in the dissociation of an electrophile bound to one of the pyrrolic nitrogen atoms of the porphyrin, may be viewed as an analogue of the collapse of a "sitting-atop" complex.[5] Although the existence of such complexes as isolated species has been disputed,[6] such species are consistent with porphyrin metalation kinetics.[7] The very facile cleavage of a pyrrolic nitrogen–carbon bond in this reaction is also of interest.

In this report, it is shown that chloro-*N*-methyltetraphenylporphinatonickel(II) reacts similarly to the corresponding copper(II) complex, which shows a two-path mechanism in which each path involves removal of $-CH_3^+$ by a nucleophile. The reactions of the corresponding zinc(II) and manganese(II) complexes involve nucleophilic attack of the methyl group but the data only require postulation of a single-path mechanism.

Experimental Section

Preparation of the Complexes. The preparation and characterization of *N*-methyl-$\alpha,\beta,\gamma,\delta$-tetraphenylporphyrin ($N$-$CH_3TPP$)[8] and the chloromanganese(II) and chlorozinc(II) complexes[9] of this ligand have been described previously. The more reactive nickel and copper complexes were prepared in situ from the appropriate chloride salt, as reported previously for the copper complex.[3] Complexes prepared from the hydrated perchlorate salts behaved identically with complexes prepared from the chloride salts. The visible absorption spectra are very similar to those found for other N-CH_3TPP complexes of 2+ metal ions.[9]

Product Analysis and Stoichiometry. The products of demethylation reactions caused by di-*n*-butylamine are the planar porphyrin complexes and methyldi-*n*-butylamine. The planar porphyrin complexes were quantitatively identified from their visible absorption spectra.[10] The methylated amine product was identified quantitatively by gas chromatographic techniques for the nickel(II) and copper(II) reactions, as described previously.[3] The reactions of the manganese(II) and zinc(II) complexes were much too slow to employ concentrations of amine sufficiently low for relative GC peak height determination. The first-order dependence on amine concentration is taken as evidence of the similarity of the manganese(II) and zinc(II) reactions with the well-defined nickel(II) and copper(II) reactions. The NMR spectra of the diamagnetic planar porphyrins ZnTPP and NiTPP show that no methylation of the porphyrin ring system has occurred.

The stoichiometry of these reactions is given by

$$\begin{aligned} &M\text{-}N\text{-}CH_3TPP^+ + \text{di-}n\text{-butylamine} \rightarrow MTPP \\ &\qquad + \text{methyldi-}n\text{-butylamine} \end{aligned}$$

Kinetic Measurements. The measurements and results for the copper(II) reaction have been reported.[3] Similar conditions were used for obtaining kinetic information on the nickel(II) reaction. Stock solutions of the nickel(II) *N*-methyltetraphenylporphyrin complex varied in nickel(II) concentration from 10^{-4} to 10^{-3} M while the