

Metal Atom Dynamics in Sn(II) Phthalocyanin from Temperature-dependent ^{119}Sn Mössbauer Spectroscopy

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Dedicated to Prof. Hirotoishi Sano on the occasion of his 79th birthday

Temperature-dependent ^{119}Sn Mössbauer spectroscopy has been used to elucidate the root-mean-square-amplitude-of-vibration (rmsav) of the metal atom in Sn(II) phthalocyanin and to examine the (absence of) metal atom motional anisotropy in the temperature range $90 < T < 190$ K.

1. Introduction

Divalent tin phthalocyanin (SnPc) is an interesting compound due to its unusual structure and the presence of a non-bonding pair of electrons oriented along the four-fold axis perpendicular to the ring nitrogens. The crystal structure has been reported by several groups^{1,2} and it is well documented that the tin atom, having C_{4v} symmetry, is located 1.11 Å above the nitrogen atom plane. The lone pair of electrons is assumed to occupy the space above the metal atom. Due to this unique geometry, SnPc has been subjected to several ^{119}Sn Mössbauer studies³ and the hyperfine parameters – the isomer shift (IS) and quadrupole splitting (QS) – have been reported^{2,4} at or near liquid nitrogen temperature.

The focus of the present study is to relate the temperature-dependence of the recoil-free fraction, f , of the tin atom to the dynamics of the metal atom and to examine in detail the motional anisotropy of the metal center over a significant temperature range.

2. Experimental

The experimental details concerning the present studies have been detailed earlier.⁵

Spectrometer calibration was effected using an α -Fe absorber at room temperature in conjunction with a Rh(^{57}Co) source. The source used in the Sn experiments was $\text{Ca}^{119\text{m}}\text{SnO}_3$ and all isomer shifts are reported with reference to the centroid of a room temperature BaSnO_3 absorption spectrum.

The SnPc absorber used was commercially⁶ available material (despite the presence of a small impurity, *vide infra*), and temperature monitoring was effected using the Daswin program of Glaberson and Brettschneider.⁷ Temperature constancy to better than ± 0.2 K was achieved over the data collection times (up to 36 hours per temperature point).

3. Results and Discussion

As noted earlier by other investigators,^{3,4} the Mössbauer Effect (ME) spectra of SnPc consist of a well resolved doublet, and a typical spectrum is summarized graphically in Figure 1. The observed full line width a half maximum of 0.882 ± 0.010 mm s^{-1} is in reasonable agreement with the theoretical value of 0.642 ± 0.004 mm s^{-1} calculated from the lifetime of the first excited state. As will be noted, this spectrum also shows the presence of a small (10–15%) impurity with an IS of 0.178 ± 0.012 mm s^{-1} at 90 K which approaches zero at higher temperatures. This impurity is most likely SnO_2 and its contribution to the lattice dynamical data reported below has been corrected for in the data analysis. The IS and QS values for SnPc at 90 K are included in Table 1 and are in good agreement with values reported earlier and are not otherwise remarkable.

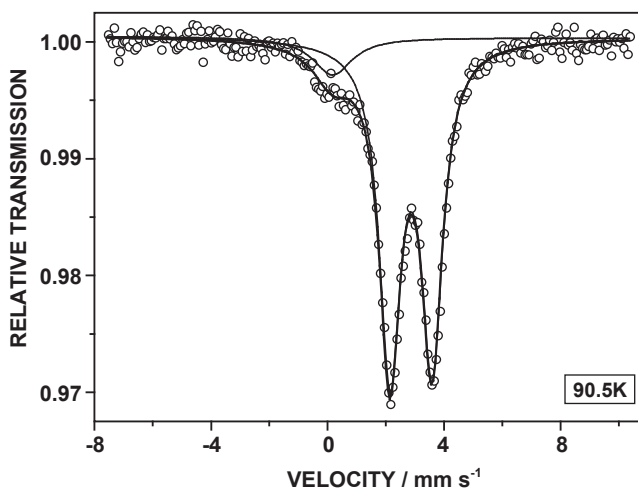


Figure 1. ^{119}Sn Mössbauer spectrum of SnPc at 90.5 K. The velocity scale is with respect to the centroid of a room temperature absorber spectrum of BaSnO_3 . The presence of a small impurity, assumed to be a Sn(IV) oxide at an IS of ~ 0 mm s^{-1} , has been corrected for in the subsequent data analysis.

TABLE 1: ^{119}Sn Mössbauer parameters for SnPc

IS(90) / mm s^{-1}	QS(90) / mm s^{-1}	Γ (90) / mm s^{-1}	$-d(\ln A)/dT$ / K^{-1}	$R=(A(+)/A(-))$
2.875 ± 0.018	1.455 ± 0.018	0.882 ± 0.010	$(19.5 \pm 0.30) \times 10^{-3}$	0.985 ± 0.015

The 4th and 5th columns pertain to the temperature range $90.5 < T < 189.9$ K.

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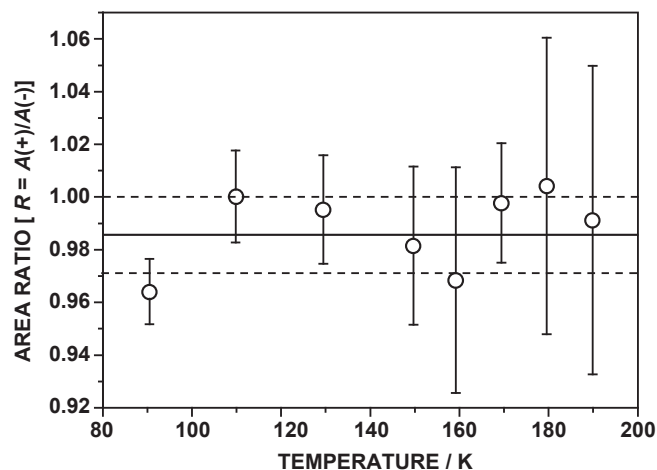


Figure 2. The area ratio of the two components of the doublet spectrum of SnPc. The difference between the mean value (0.986 ± 0.015) and unity is (presumed) due to a small residual temperature independent texture effect. The two dashed lines indicate \pm one standard deviation of the data.

Over the 90 to 190 K temperature range, neither of these parameters is strongly temperature dependent and it is not possible to extract a meaningful value⁸ for M_{eff} from $IS(T)$.

In numerous earlier studies^{9,10} of tin organometallics, it has been noted that the intensity ratio of the two components of the resonance doublet may be a temperature-dependent quantity, due to the Gol'danskii-Karyagin effect, and from such data it is possible to extract the vibrational anisotropy of the metal atom motion; that is, $\langle x_{\text{para}}^2 \rangle - \langle x_{\text{perp}}^2 \rangle$. Because in SnPc the metal atom is located 1.11 Å above the nitrogen atom plane and has a lone pair of electrons located on the four-fold symmetry axis,¹¹ it was expected that this motional anisotropy would be observable in the ME spectra here recorded. The observed area ratio, $R = [A(+)/A(-)]$, where + and - refer to the doublet components at greater and lesser velocity than the spectrum centroid, is summarized graphically in Figure 2. The mean value of $R = 0.986 \pm 0.015$ and is considered to be temperature independent over the indicated range. This observation is similar to that observed for a tricoordinate stannyl cation¹² (nominally tetravalent Sn) but has apparently not been reported in the literature for a nominally divalent Sn complex. Clearly, the metal atom motion up to 190 K appears to be equal in the two directions parallel and perpendicular to the C_{4v} axis.

The temperature dependence of the recoil-free fraction, f , extracted from the area under the resonance curve for an optically "thin" absorber, is summarized in Figure 3 in which the corrections for the small Sn(IV) impurity noted above, have been effected. The data in Figure 3 are well fit by a linear regression and yield $-d(\ln A) / dT = (19.5 \pm 0.3) \times 10^{-3} \text{ K}^{-1}$ with a correlation coefficient of 0.998 for seven data points. This value is significantly larger than the value of 14.0×10^{-3} reported

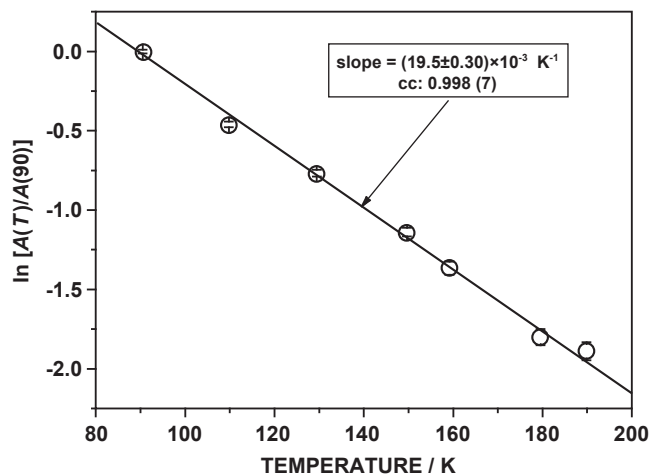


Figure 3. Temperature dependence of the recoil-free fraction for SnPc.

by Molloy and Quill⁴ in their 1986 study of Sn(II) and Sn(IV) phthalocyanins, but their reported line widths of 1.28 and 1.26 mm s^{-1} at 78 K make the assumption of an optically "thin" absorber somewhat uncertain. It is also interesting to note that $-d(\ln A) / dT$ for the (presumed) SnO_2 impurity is $(13.0 \pm 0.3) \times 10^{-3} \text{ K}^{-1}$, indicating, as expected, a somewhat "harder" lattice in this case.

As noted earlier in connection with other organometallic compounds investigated by the ME technique,^{13,14} making the assumption that the recoil-free fraction extrapolates to a value close to unity at absolute zero permits the calculation of a vibrational amplitude of the metal atom in these structures. Thus $\ln f = -k^2 \langle x_{\text{ave}}^2 \rangle$, where k is the wave vector of the Sn 23.9 keV radiation, $k^2 = 1.464 \times 10^{18} \text{ cm}^{-2}$, and $\langle x_{\text{ave}}^2 \rangle$ is the mean-square amplitude of vibration of the metal atom averaged over all directions. Using this simplified approach to the evaluation of the metal atom motion leads to the values of the root-mean-square-amplitude-of-vibration as a function of temperature summarized in Table 2 which also includes several other Sn(II) compounds recently studied by this technique.

4. Summary and Conclusions

Temperature-dependent ^{119}Sn Mössbauer effect spectroscopy of Sn(II) phthalocyanin over the temperature range 90 < T < 180 K has shown that there is no evidence of an anisotropy of the metal atom motion (Gol'danskii-Karyagin effect) parallel and perpendicular to the 4-fold symmetry axis running through the Sn atom, despite the fact that this atom is located 1.11 Å above the plane of the four indole nitrogens as well as the presence of the lone pair of electrons on this axis. The root-mean-square-amplitude-of-vibration of the metal atom in SnPc has been deduced from the recoil-free fraction data and compared to analogous values of related Sn(II) complexes.

TABLE 2: Root-mean-square-amplitudes of vibration of the Sn atom (in Å) in a number of related Sn(II) complexes

T / K	This work	Ref. 12	Ref. 5	$\text{Ar}^*\text{Sn}=\text{SnAr}^*$	$\text{Ar}^*\text{Sn}=\text{SnAr}^{*a}$
100	0.115	0.137	0.143	0.131	0.112
125	0.129				
150	0.141	0.168	0.176	0.160	0.137
175	0.153				
200	0.163	0.194	0.203	0.185	0.158

The errors are estimated to be $\sim \pm 10 \%$.

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