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Note

Static and dynamic disorder in organotin compounds: A bis(amido)stannylene coordinated by *N*,*N*′-diisopropyl-1,8-diamidonaphthalene

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Abstract

The root-mean-square amplitude of vibration of the tin atom in the bis(amido)stannylene $Sn[1,8\text{-}(N^{i}Pr)_2C_{10}H_6]$ has been determined from temperature-dependent ^{119}Sn Mössbauer effect measurements over the range $98 < T < 225$ K and compared with the $U_{i,j}$ value extracted from a single crystal X-ray diffraction study. The large difference in these values (at 238 K) is associated with the flexibility in the bonding between the Sn center and chelating diamido ligand in this complex.

Keywords: Stannylene; Mossbauer spectroscopy; Vibrational amplitude

1. Introduction

In a series of detailed studies of protein dynamics, Parak et al. [1] have discussed the differences in the mean-square displacements of atoms as probed by X-ray diffraction and by nuclear resonant scattering experiments. In these studies it has been noted that the mean square displacements derived from X-ray diffraction data are frequently significantly larger than those based on Mössbauer effect results at the same temperature and therefore provide complementary methods to examine the dynamics of these systems. In a number of recent temperature-dependent Mössbauer experiments (ME) of organometallics, using ^{57}Fe, it has been shown [2] that it is possible to correlate the root-mean-square-amplitude-of-vibration (rmsav) of the metal atom as detected by the nuclear resonance technique with the rmsav extracted from the $U_{i,j}$ values obtained from single crystal X-ray diffraction experiments. Especially in the case of ferrocene-based complexes it has been noted that the vibrational amplitudes extracted from the two techniques are in reasonably good agreement with each other. However when the two values are significantly different, additional chemical and structural information can be inferred from this observation.

In the present instance, this approach has been extended to organotin complexes, since both the ME technique (using the 23.8 keV line of ^{119m}Sn) and X-ray diffraction measurements are applicable to such systems. In particular, in the present study, we have examined the dynamical properties of a bis(amido)stannylene, $Sn[1,8\text{-}(N^{i}Pr)_2\text{-}C_{10}H_6]$, which has recently been described [3]. In this complex the Sn(II) center, which is part of a six-membered metalloheterocycle, is bonded not only to the two nitrogen atoms of the 1,8-diamidonaphthalene ligand, but also appears to exhibit a weak π-interaction between the Sn and an adjacent naphthyl group. This leads to an extended structure involving Sn and the centroid of the aromatic ring. It was also noted that the X-ray study carried out at 238 K displayed significant anisotropy in the metal atom motion relative to the twofold symmetry axis passing through the Sn center. The present study was undertaken

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to elucidate further the dynamical aspects of the tin atom in this compound.

2. Experimental

The moisture and air sensitive dark orange-red powder reported in Ref. [3] was transferred in an inert atmosphere glove-box to an O-ring sealed perspex sample holder and immediately cooled to liquid nitrogen temperature and maintained under N_2(l) until introduced into the pre-cooled cryostat for the ME studies.

ME spectroscopy was carried out in transmission geometry as described previously [4,5], using a 10 mCi Ba $^{119m}SnO_3$ source at room temperature. Spectrometer calibration was effected using a ^{57}Co (Rh) source in conjunction with a room temperature α-Fe absorber. All isomer shifts (IS) are reported with respect to the centroid of a $BaSnO_3$ absorption spectrum at room temperature. Constant temperature was maintained to better than ±0.5 K during the data acquisition times at each temperature (up to 24 h) and monitored using the DASWIN program described previously [6].

3. Results and discussion

The ME spectra at all temperatures consist of a principal doublet, with a small additional contribution from a second tin site. A representative spectrum at 98 K is shown in Fig. 1.

The IS of both the principal doublet, as well as of the minor contaminant clearly identify the metal atom as Sn(II), and the hyperfine parameters are summarized in Table 1, together with their derived temperature-dependent values. Over the accessible temperature range ($98 < T < 225$ K) neither the IS nor the quadrupole splitting (QS) are particularly temperature dependent, and are not otherwise remarkable except to note that the IS of the minor tin site is significantly smaller than that of the major site, while the QS is significantly larger. No further effort was made to identify the nature of the minor contaminant, but its contribution has been corrected for in the discussion (*vide infra*) of the dynamical properties of the major site Sn atom.

Table 1
^{119}Sn Mössbauer parameters for the bis(amido)stannylene discussed in the text

Component	Major	Minor	Units
I.S. (90 K)	2.913 ± 0.003	1.868 ± 0.015	mm s^{-1}
Q.S. (90 K)	2.813 ± 0.003	3.705 ± 0.015	mm s^{-1}
$-\mathrm{d}\ln A/\mathrm{d}T$	2.034 ± 0.020	1.230 ± 0.070	10^{-2} K^{-1}

Of particular interest in terms of the present discussion is the temperature dependence of the recoil-free fraction, *f*, as extracted from the ME data. The parameter *f*, in turn is related to the rmsav by the relationship $f = -k^2\langle x^2_{\text{ave}}\rangle$, where *k* is the wave vector of the 23.8 keV ^{119m}Sn gamma ray, and $\langle x^2_{\text{ave}}\rangle$ is the mean square amplitude of vibration of the Sn atom. For an optically "thin" absorber, the temperature dependence of *f* can be calculated from the temperature-dependence of the area (*A*) under the resonance curve, and a typical data set is summarized graphically in Fig. 2.

These data for the major constituent are well-fitted by a linear correlation, and yield a slope of $-(2.034 \pm 0.070) \times 10^{-2}$ K^{-1} with a correlation coefficient of 0.999 for the 12 data points. Making the assumption that the high-temperature data extrapolate to $f = 1$ as $T \to 0$ yields a value of $k^2\langle x^2_{\text{ave}}\rangle_M = 4.84$ at 238 K. In marked contrast, the value calculated for $k^2\langle x^2_{\text{ave}}\rangle_X$ at 238 K from the $U_{i,j}$ crystallographic parameters is 9.37 [3]. The explanation for this major difference in the two values is to be found in the differences in the two types of disorder which are probed by the ME and X-ray techniques, as discussed below.

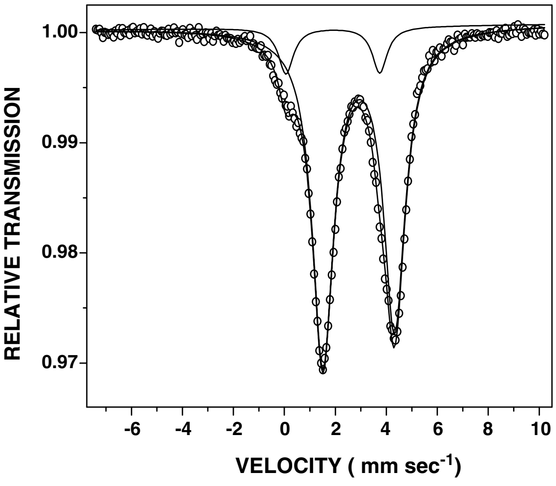

Fig. 1. Mössbauer spectrum of the bis(amido)stannylene, Sn[1,8-$(N^iPr)_2C_{10}H_6$], at 98 K. The velocity scale is with respect to the centroid of a room temperature $BaSnO_3$ absorber spectrum. The upper trace pertains to the minor constituent discussed in the text.

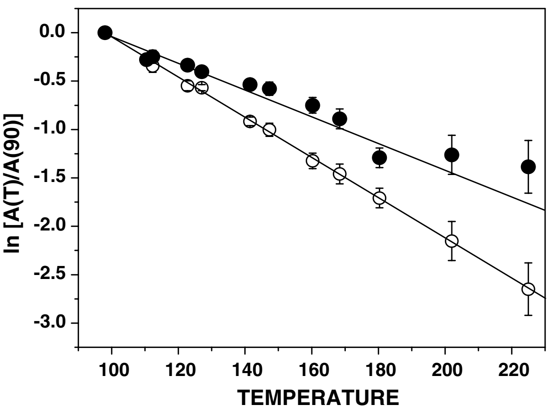

Fig. 2. Temperature dependence of the logarithms of the areas under the resonance curves (normalized to the 98 K data value). The open circles refer to the major spectral constituent, the filled circles to the minor constituent.

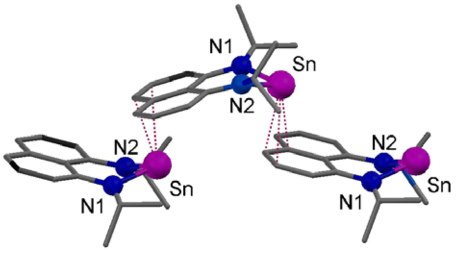

Fig. 3. A ball and stick representation of a portion of the extended structure showing the intermolecular interactions of Sn[1,8-($N^iPr)_2C_{10}H_6$]. The interaction between the Sn center and the naphthyl π-system is indicated in red. The chain interaction is along the crystallographic *b*-axis. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The time scale of a typical X-ray diffraction event is on the order of 10^{-15}–10^{-16} s. However, the much longer X-ray diffraction data collection time is on the order of minutes or more and, as a result, the diffraction data reflect the distribution in three-dimensional space of the atom positions over this data collection interval. This distribution, in turn, is sensitive to the low-frequency vibrational modes of the molecule as a whole. Such vibrational modes have characteristic time scales of 10^{-12}–10^{-13} s. In other words, the X-ray diffraction data reflect both the local vibrational amplitude of the scattering atom as well as the distribution in space of these atoms. In contrast, the characteristic time scale of a Mössbauer scattering event is on the order of 10^{-8}–10^{-7} s, but each scattering event samples only the local vibrational amplitude of the resonant atom, and is (as a first approximation) independent of the distribution in three-dimensional space of this atom.

As reported, the Sn(II) center in the diamidonaphthalene species Sn[1,8-($N^iPr)_2C_{10}H_6$] participates in an intermolecular π-interaction with the naphthyl ring in the adjacent molecule. This weak interaction results in a Sn-ring centroid distance of 3.23 Å and ultimately leads to formation of chains along the crystallographic b axis as shown in Fig. 3. It seems clear that the X-ray data reflect this interaction in the large $U_{i,j}$ values observed for this structure, while the ME data reflect only the local vibrational modes of the tin atom. Moreover, the ME data allow an approximate calculation of the rmsav of the Sn atom at various temperatures. In the case of the stannylene complex, the rmsav values are 0.118. 0.144, 0.167 and 0.186 Å at 100, 150, 200 and 250 K, respectively. These values are in reasonable agreement with those observed for the Sn atoms in the tetranuclear dirhenium ditin compound, $Re_2(CO)_8(\mu\text{-}SnPh_2)_2$, reported by Adams et al. [5] (0.133 and 0.171 Å at 150 and 250 K, respectively). In this latter compound, the Sn is in a distorted tetrahedral environment and is coordinated by two phenyl groups and two Re atoms. In this environment the tin atom is expected to be well localized in three-dimensional space, and the rmsav values reflect primarily the local dynamics of the metal center. Thus the modest agreement between the rmsav in these two instances and the differences noted in the present study would suggest the validity of the conclusion drawn above relative to the consequences of the weak bonding interaction in the bis(amido)stannylene complex here reported. Clearly the difference in the rmsav calculated from the X-ray $U_{i,j}$ value at 238 K and that derived from the ME $\ln f$ data reflect the weak bond ligation in the bis(amido) complex.

Further detailed comparisons of these two rmsav values (X-ray and ME) at various temperatures is expected to yield complementary information concerning bond flexibility in organotin complexes.

Finally, it is worth noting from Fig. 1 that there is a significant asymmetry in the area under the resonance curve of the two constituents of the major component spectrum. This asymmetry can have two major origins – a Gol'danskii–Karyagin effect which arises from true vibrational asymmetry with respect to the major symmetry axis involving the metal atom. This effect is temperature dependent. The second contribution may arise from preferred orientation of the crystallites with respect to the optical axis of the experiment. This latter texture effect is temperature independent. Because of the oxygen/moisture sensitivity of the present sample which has precluded grinding the sample to a fine powder, as well as the rather limited temperature range over which the resonance effect is observable, it has not been possible to separate these two contributions to the intensity asymmetry in the present series of experiments. Thus the local vibrational disorder reflected in the ME data represent an average over all vibrations of the Sn atom, irrespective of their orientation with respect to the major symmetry axis passing through the metal atom.

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