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The Unexpected Motional Isotropy of the Tin Atom in a Tricoordinate Stannylium Cation

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The dynamics of the metal atom in the recently isolated tricoordinate tin complex tris(2,4,6-triisopropylphenyl)stannylium tetrakis(pentafluorophenyl)borate was examined by temperature-dependent ^{119}Sn Mössbauer spectroscopy over the temperature range 90 K $< T <$ 170 K. Contrary to expectation, the metal atom motion in this temperature range is isotropic within experimental error of the Mössbauer data, and is only moderately anisotropic, even at 293 K, as evidenced by single crystal X-ray diffraction data. The hyperfine parameters at 90 K are completely consistent with trigonal coordination involving sp^2 hybridization of the 5s5p bonding orbitals of tin.

It has been well established since the seminal work of Gol'danskii and Karyagin[1] that temperature-dependent Mössbauer spectroscopy (MS) can elucidate the details of the motional anisotropy of the MS active atom by transmission scattering experiments. These early ideas were applied to organotin complexes in a series of studies, including those in which the metal atom was expected to evidence a large difference in the mean-square amplitude of vibration parallel and perpendicular to the highest local symmetry axis. In particular, a study[2] of trimethyltin cyanide, for which a detailed crystal structure had been published by Schlemper and Britton,[3] showed that the anisotropy parameter R, equal to the ratio of the resonance line area at higher and lower relative velocity than the spectrum centroid [$R = A(+)/A(-)$], was strongly temperature dependent in the range 9 K $< T <$ 204 K. This anisotropy arises out of the fact that the metal−ligand binding forces (Sn−C$_{CH3}$) in the trigonal plane of the pentacoordinated structure are very different from those operative along the orthogonal 2-fold axis (Sn−C$_{CN}$). In this structure,[3] the three equidistant methyl groups form a planar array around the tin and the latter is axially equally distant from the CN groups forming an infinite chain with a small amount of covalent character in the Sn−CN bond. An even more pronounced example of this anisotropy was subsequently demonstrated in pentacoordinated trimethyltin difluoride[4] for which a structure involving a disordered chain of fluorines joining the planar trimethyltin array was described by Clark et al.[5] In this context the recent publication[6] of the structure of a free, tricoordinate tin complex, tris(2,4,6-triisopropyl)stannylium cation (Tip$_3$Sn$^+$) as the tetrakis(pentafluorophenyl)borate (**I**), prompted a detailed Mössbauer study of this ion over the temperature range 90 K $< T <$ 170 K, in an effort to assess the motional anisotropy of the metal atom in this unusual environment. As far as has been possible to determine, the only other known trigonal planar tin center structure that has been reported is that of a "paddle wheel" array in which three aromatic cyclopentadienyl ligands are π-bonded to the metal center by η^5 interactions.[7]

The experimental details of MS as applied to the present study have been published previously.[8] Spectrometer calibration was effected by determining an α-Fe absorption spectrum at room temperature using a ^{57}Co(Rh) source. The isomer shifts are reported with respect to the centroid of a room temperature spectrum using a BaSnO$_3$ absorber. Temperature control was effected using a Cu−constantan thermocouple in a high-gain feedback control circuit. A powder sample of **I** was transferred to a Perspex sample holder inside a VAC model DLX-001-S.P inert atmosphere glovebox having a partial pressure of O$_2$ less than 0.5 ppm and of H$_2$O less than 1 ppm, and immediately quenched to

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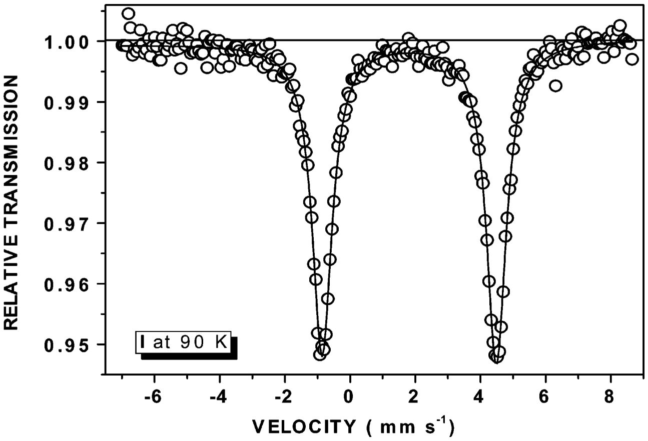

Figure 1. ^{119}Sn Mössbauer spectrum of **I** at 90 K. The velocity scale is with reference to a room temperature $BaSnO_3$ absorber spectrum as noted in the text.

Table 1. ^{119}Sn Mössbauer Parameters of **1**[a]

parameter	value	units	r^2
IS (90)	1.875 ± 0.011	mm s^{-1}	
QS (90)	5.534 ± 0.011	mm s^{-1}	
$-d(IS)/dT$	2.62 ± 0.75	10^{-4} mm s^{-1} K^{-1}	0.67
$-d(QS)/dT$	1.03 ± 0.08	10^{-3} mm s^{-1} K^{-1}	0.65
$-d(\ln A)/dT$	27.43 ± 0.66	10^{-3} K^{-1}	0.986
M_{eff}	159 ± 36	Da	
Θ_M	70	K	

[a] The temperature-dependent parameters are calculated from linear fits to the data over the interval 90 K $< T <$ 170 K.

78 K before being introduced into the precooled spectrometer cryostat.

The resonance spectra consist of well-resolved doublets at all temperatures, having a line width (fwhm), corrected for thickness broadening effects, of 0.66 to 0.74 mm s^{-1} over the entire temperature range. A representative spectrum at 90 K is shown in Figure 1.

The MS parameters of **I** at 90 K are summarized in Table 1. The isomer shift (IS) is 1.875 ± 0.011 mm s^{-1}, a value which is consistent with the presence of one 5s electron, as expected for a metal atom with sp^2 hybridization and predominant covalent metal−ligand bonding interaction. From the temperature dependence of the IS it is possible to calculate[9] an effective vibrating mass, M_{eff}, of 159 ± 36 Da, a value differing from that of the "bare atom" value of 119, due the covalency of the metal−ligand interaction. The quadrupole splitting (QS) of 5.534 ± 0.011 mm s^{-1} is among the largest such values yet reported for an organotin complex, but similar to a value of 5.54 and 5.51 mm s^{-1} reported by Aubke et al.[10] for dimethyltin compounds having two (SO_3X) ligands in a polymeric array. The QS has the usual negative temperature dependence due to thermal expansion, and is otherwise unremarkable.

The temperature dependence of the area under the resonance curve, related to the recoil-free fraction, and hence to the mean-square amplitude of vibration of the metal atom, is summarized graphically in Figure 2. The linear regression through the 8 data points has a correlation coefficient (r^2) of 0.986, and the data show complete reversibility of this parameter on heating and cooling. Due to the small sample size and the low lattice temperature (Θ_M) of 70 ± 5 K, it was not possible to extend the T range of the measurements beyond ~170 K since the resonance effect becomes too small to obtain statistically meaningful results. Θ_M was calculated from the temperature dependencies of the IS and ln A parameters as discussed previously.[8]

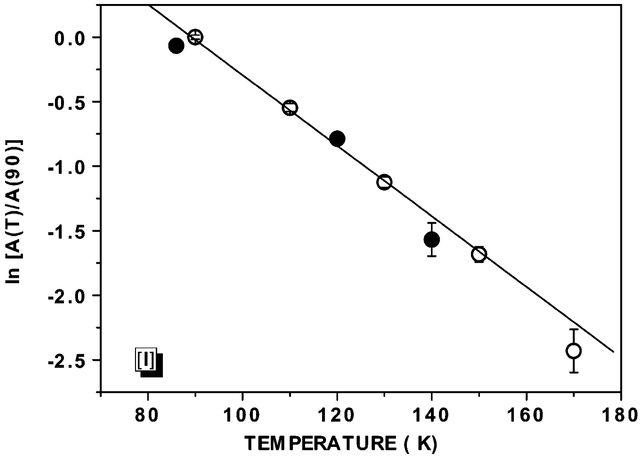

Figure 2. Temperature dependence of the logarithm of the spectral area (normalized to 90 K) for **I**. The open circles represent data acquired in a warming mode, the closed circles data acquired in a cooling mode after registering the 170 K measurement, showing the reversibility of the data.

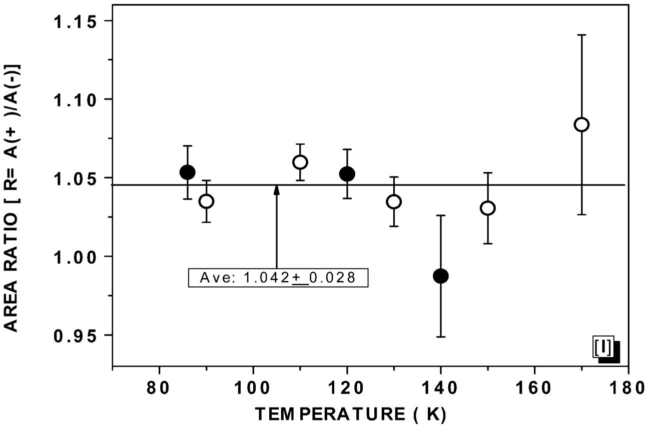

Figure 3. The area ratio R for **I**. The significance of the open and closed circles is as in Figure 2.The temperature independence in the interval 90 K $< T <$ 170 should be compared with the data reported in refs 2 and 4.

Turning now to the *raison d'etre* of the present study, the temperature dependence of R is summarized graphically in Figure 3. The observation that the average value is ~4% larger than unity is accounted for by a small preferential orientation of the crystallites in the absorber holder ("texture effect") and is temperature independent. From Figure 2 it is seen that—within experimental error—the R parameter is largely T-independent over the indicated range. This observation for the low temperature data, which indicates an essentially isotropic motion of the tin atom in its trigonal symmetry bonding environment is in qualitative agreement with the reported mean-square amplitudes of vibration at 293 K extracted from the $\mathbf{U}_{i,j}$ values of the single-crystal X-ray

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data,[6] and evident from an ORTEP representation of this structure projected parallel to the Sn−L_3 plane. These values are 0.0401, 0.0308, and 0.0241 Å^2 respectively. Thus, even at room temperature, the metal atom motion is only moderately nonisotropic despite the fact that the distance to the axial nearest neighbors is 3.259 Å compared with a covalent Sn−C bond distance of ∼2.14 Å. The origin of the near isotropy of the metal atom motion in **I**, even at room temperature, in the light of the presumed sp^2 hybridization of the tin 5s,5p orbitals, is not obvious from the presently available data.

There is, in addition, another puzzling feature relating the MS data of **I** to the single crystal X-ray data at 293 K. The temperature dependence of the recoil-free fraction (f) of the tin atom, over the range 90 K $< T <$ 170 K, is well represented by a linear regression as noted above as summarized in Figure 2. Making the reasonable assumption that the temperature dependence of $\mathbf{k}^2\langle x^2\rangle$ in the high-temperature limit is linear, with a zero intercept at $T = 0$, permits a calculation[11] of $\mathbf{k}^2\langle x^2\rangle$, where **k** is the wave vector of the 23.8 keV γ radiation of ^{119m}Sn. The value calculated from these MS data at 293 K is 8.01. It should be borne in mind that this calculation involves a linear extrapolation of the MS data from 170 K (the highest temperature at which meaningful MS data could be acquired) to room temperature. However, the same parameter calculated from the $\mathbf{U}_{i,j}$ values of the X-ray data is 4.51 at 293 K. An assumption made in this comparison is that the crystal structures at 170 and 293 K are identical, but this has not been verified experimentally. The origin of the large disagreement is, again, not evident from the presently available data, but might be accessible with a sample prepared with ^{57}Fe. Such studies are currently being planned.

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