Notes

Tin-119 and Nitrogen-14 Nuclear Magnetic Resonance and Tin-119 Variable-temperature Mössbauer Spectroscopic Study of Tricyclohexyltin Isothiocyanate including the First Observation of Resolved ^{117,119}Sn–^{14}N Coupling in an Organotin Compound

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Resolved ^{117,119}Sn–^{14}N coupling has been observed for the first time in an organotin compound in tricyclohexyltin isothiocyanate, with $^{1}J(^{119}\text{Sn}–^{14}\text{N})$ = 136 Hz. Variable-temperature Mössbauer spectroscopic data for $SnR_3(NCS)$ (R = C_6H_5 or C_6H_{11}) are interpreted in terms of the tertiary structure of the co-ordination polymer changing from an 'S' shape (R = C_6H_5, $a = -\text{dln} f/\text{d}T = 1.84 \times 10^{-2}$ K^{-1}) towards a more linear arrangement (R = C_6H_{11}, $a = 1.34 \times 10^{-2}$ K^{-1}).

Our interest in the biocidal chemistry of organotin compounds has (in part) centred upon derivatives of the tricyclohexyltin moiety, $Sn(C_6H_{11})_3X$.[1–5] These species show enhanced acaricidal activity, low mammalian toxicity, and a favourable environmental degradation pathway resulting ultimately in SnO_2,[6] and two representatives of this class, $Sn(C_6H_{11})_3(OH)$[7] and tricyclohexyl(1,2,4-triazol-1-yl)tin,[7,8] are currently in use as agrochemicals. Evaluation of the structural subtleties of tricyclohexyltin chemistry has failed to parallel this commercial exploitation.[9] As part of our studies designed to rectify this deficiency we have had cause to investigate the spectroscopic properties of $Sn(C_6H_{11})_3(NCS)$ and which we report herein, including the first observation of resolved ^{117,119}Sn–^{14}N magnetic coupling in an organotin compound.

Experimental

Tricyclohexyltin isothiocyanate was prepared by mixing equimolar quantities of tricyclohexyltin hydroxide and ammonium isothiocyanate in methylcyclohexane, as described previously.[10] Recrystallisation was from toluene (Found: C, 53.30; H, 7.90; N, 3.45. Calc. for $C_{19}H_{33}NSSn$: C, 53.55; H, 7.80; N, 3.30%), m.p. 119—121 °C (lit.,[10] 123 °C).

The ^{119}Sn and ^{14}N n.m.r. spectra were recorded in 10-mm tubes at 30 °C on a JEOL FX60Q spectrometer with field-frequency lock to external D_2O. The former spectra were recorded under nuclear Overhauser-suppressed conditions, with chemical shifts relative to $Sn(CH_3)_4$ and accurate to ± 0.1 p.p.m.; ^{14}N chemical shifts are relative to nitromethane and are accurate to ± 0.5 p.p.m. Details of our Mössbauer spectrometer, method of data acquisition and handling have been described elsewhere.[11] A finely powdered sample containing 1.5 mg ^{119}Sn per cm^2 was used for the collection of Mössbauer spectra in the temperature range 78—153 K; temperature stability was ± 0.1 K over the period of data collection (*ca.* 12 h). Despite the relative 'thickness' of our sample, the plot of ln A *vs.* T was linear over the range 78—135 K, with mild curvature at higher temperatures. This suggests that a Debye model is acceptable at least up to 135 K and the data have been fitted by a straight line with slope $a = -\text{dln}\, f/\text{d}T = 1.34 \times 10^{-2}$ K^{-1} (f = recoil-free fraction; correlation coefficient, $r = -0.998$ for eight points). No attempt was made to account for deviations from linearity of the plot in the high-temperature region ($T > 135$ K) in terms of a model incorporating anharmonic oscillators.

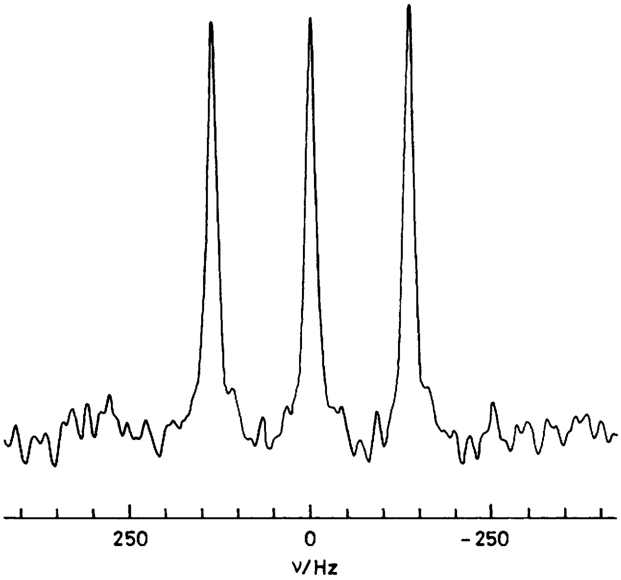

Figure 1. ^{119}Sn N.m.r. spectrum of $Sn(C_6H_{11})_3(NCS)$ (0.15 mol dm^{-3} in toluene)

Results and Discussion

^{119}Sn *and* ^{14}N *N.M.R. Spectra.*—Figure 1 shows the ^{119}Sn n.m.r. spectrum of a 0.15 mol dm^{-3} solution of $Sn(C_6H_{11})_3(NCS)$ in toluene. The chemical shift of −3.2 p.p.m. is consistent with a four-co-ordinate geometry about tin in solution, in accord with observations on related systems. For example, the ^{119}Sn chemical shift for $[(C_6H_{11})_3Sn]_2O$ is −7.9 p.p.m.[4] The fine structure of the spectrum consists of a triplet of (within experimental error) equal intensities and linewidths (*ca.* 14 Hz

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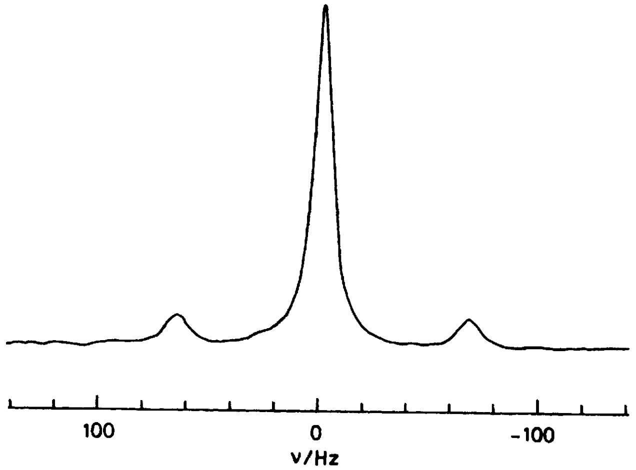

Figure 2. ^{14}N N.m.r. spectrum of $Sn(C_6H_{11})_3(NCS)$ (0.15 mol dm^{-3} in toluene)

after allowance for exponential broadening), and arises from coupling of ^{119}Sn and ^{14}N nuclei ($I = \frac{1}{2}$ and 1, respectively) with $^1J(^{119}Sn-^{14}N) = 136$ Hz. This is the first observation of resolved coupling between these two nuclei in an organotin compound, and can be compared directly only with one other report of such an interaction, namely in the anion $[Sn(NCS)_6]^{2-}$ (150 Hz).[12] In addition, indirect comparison can be drawn with about a dozen citings of $^1J(^{119}Sn-^{15}N)$ data (ref. 12 and refs. therein) using reduced coupling constants which normalise the effects of a different gyromagnetic ratio for each of the two nitrogen isotopes.* The reduced coupling constant for the title compound (42 nm^{-3}) is only exceeded by that for the above anion (46.3 nm^{-3}) and for $Sn(C_4H_9)_3(NCS)$ (68.5 nm^{-3}).[12]

The ^{14}N n.m.r. spectrum of the same solution (Figure 2) clearly shows $^{117,119}Sn$ satellites, and although the individual couplings to each tin isotope are not resolved the measured average $^1J(Sn-^{14}N)$ coupling of 133 Hz can be scaled up to a value of *ca.* 136 Hz for $^1J(^{119}Sn-^{14}N)$, and is entirely consistent with the ^{119}Sn spectrum. The ranges of ^{14}N chemical shifts for thiocyanate (M–SCN) and isothiocyanate (M–NCS) compounds are -100 to -150 and -200 to -300 p.p.m. respectively,[13] and on the basis of these schematics the direct linkage between tin and nitrogen is confirmed by the observed ^{14}N shift of -264.2 p.p.m. for $Sn(C_6H_{11})_3(NCS)$. The ^{14}N linewidth of 9 Hz (after correction for exponential broadening) implies a minimum spin–lattice relaxation time, T_1, of 0.035 s, a value which indicates a significant contribution to the observed ^{119}Sn linewidth from scalar coupling between the two nuclei.

Spectra in which coupling between $^{117,119}Sn$ and ^{14}N is not observed are generally attributed to the presence of one (or more) of the following phenomena: (*a*) ^{14}N quadrupole relaxation which is fast compared to the coupling constant, (*b*) fast tin relaxation, and (*c*) exchange. In the present case both conditions (*a*) and (*b*) must not be satisfied, while the observed ^{119}Sn and ^{14}N linewidths indicate that possible contributions from exchange mechanisms are, if at all, minimal. Nitrogen-14 n.m.r. spectra are usually most readily observed for compounds in which the electric field gradient at nitrogen is small or absent, *e.g.* NH_4^+, and it would appear that this is also fortuitously the case in $Sn(C_6H_{11})_3(NCS)$.

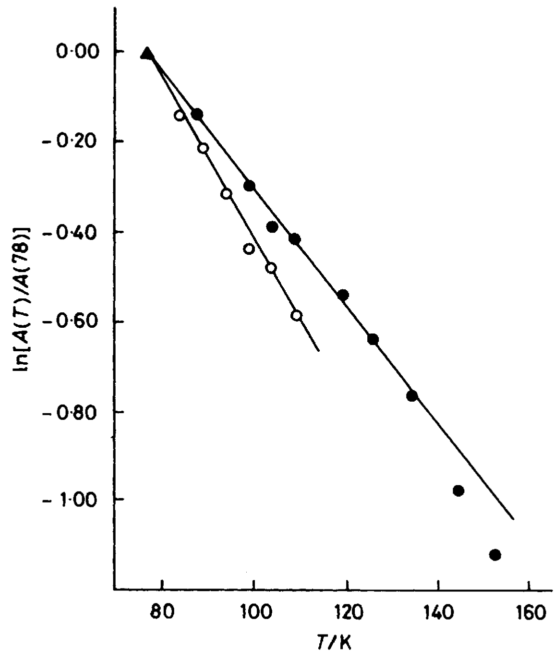

Figure 3. Plots of ln (reduced area) *vs.* T for $Sn(C_6H_{11})_3(NCS)$ (●) and $Sn(C_6H_5)_3(NCS)$ (○). The slopes of the lines, $a = -d\ln f/dT$, are 1.34×10^{-2} and 1.84×10^{-2} K^{-1} respectively. Data for $Sn(C_6H_5)_3(NCS)$ are taken from ref. 2

Mössbauer Spectroscopy.—While the ^{119}Sn n.m.r. shift data indicate a four-co-ordinate, tetrahedral geometry about the metal in solution, Mössbauer data [isomer shift (i.s.) = 1.66 mm s^{-1}, quadrupole splitting (q.s.) = 3.78 mm s^{-1} at 78 K] indicate a co-ordination number of five in the solid state. Furthermore, the magnitude of the q.s. specifies a *trans*-X_2SnR_3 trigonal-bipyramidal geometry at tin, which in this case can arise only from intermolecular association whereby isothiocyanate groups link adjacent tin atoms, with N and S atoms occupying axial sites on the polyhedron of ligands about the metal. It has been of interest to us to investigate the three-dimensional construction of such co-ordination polymers, and we have recently classified these species into four broad categories: (*i*) rod (class 1), (*ii*) zigzag (class 2), (*iii*) 'S' (class 3), and (*iv*) helical (class 4).[2] Preliminary results suggest that variable-temperature Mössbauer spectroscopy can play a significant part in distinguishing these classifications, on the basis of the rigidity with which they ascribe to the lattice as measured by the vibration of the Mössbauer atom. Briefly, plots of $\ln[A(T)/A(78)]$ *vs.* T are linear in the high-temperature limit ($T > \theta_D/2$; θ_D = Debye temperature of the lattice) assuming a Debye model for the lattice. The slope of these lines, a, is the temperature coefficient of the recoil-free fraction $a = -d\ln f/dT$. Class 3 and 4 polymers allow the tin a vibrational freedom akin to that of a monomer and $10^2a \approx 1.8$ K^{-1}, *e.g.* for $Sn(C_6H_{11})_3(O_2CCH_3)$, $10^2a = 1.59$ K^{-1}.[11] More linear polymers restrict the vibrations of the tin in the direction of polymer propagation, and a is reduced. Typical values for 10^2a for class 1 and 2 polymers are 0.91 [$Sn(C_6H_{11})_3F$] and 1.31 K^{-1} [tricyclohexyl(1,2,4-triazol-1-yl)tin] respectively.[2]

Variable-temperature Mössbauer spectroscopic data for both $Sn(C_6H_{11})_3(NCS)$ and $Sn(C_6H_5)_3(NCS)$ are illustrated in Figure 3 as $d\ln A$ *vs.* T plots, and values for 10^2a for the two compounds are 1.34 and 1.84 K^{-1}, respectively. The latter is a class 3 polymer with a local geometry identical to that inferred for $Sn(C_6H_{11})_3(NCS)$ described above,[14] and is illustrated in

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* The reduced coupling constant $K(Sn-N)$ is defined as $^1J(Sn-N)4\pi^2/h\gamma(Sn)\gamma(N)$.

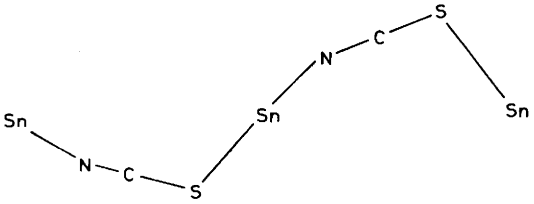

Figure 4. Schematic representation of the structure of $Sn(C_6H_5)_3(NCS)$, showing the class 3 nature of the co-ordination polymer (data from ref. 14)

Figure 4. The value of 10^2a is consistent with the schematics for this parameter suggested previously (see above), while that for the cyclohexyltin derivative indicates a rather more rigid lattice. Although other factors such as the strength of the intermolecular bond (Sn–S in this case) will also influence the value of a, the data suggest that polymeric $Sn(C_6H_{11})_3(NCS)$ is more linear in character and represents a transition from class 3 towards class 2 architecture. This is plausible since the bulk of a C_6H_{11} unit in the chair configuration is greater than that of a planar C_6H_5 ring, and under these circumstances a class 2 polymer more readily accommodates the steric requirements of hydrocarbons bonded to adjacent tin atoms along the polymer chain. We have recently observed a similar class 3 $\longrightarrow$ class 2 type conversion in the pair of carboxylates $Sn(C_6H_5)_3(O_2CR)$, $R = CH_3$ ($10^2a = 1.91\ K^{-1}$) and $R = H$ ($10^2a = 1.15\ K^{-1}$), which we will report more fully in a subsequent communication.[15]

Acknowledgements

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