

Motion in Solid Organotin(IV) Coordination Polymers: a Two-dimensional Exchange Magic Angle Spinning ^{13}C NMR Study

David C. Apperley,^a Nicola A. Davies,^a Robin K. Harris,^{*a} Stefan Eller,^b Peter Schwarz^b and R. Dieter Fischer^{*b}

^a Industrial Research Laboratory and Department of Chemistry, University of Durham, South Road, Durham, DH1 3LE, UK

^b Institut für Anorganische und Angewandte Chemie, Universität Hamburg, Martin-Luther-King Platz 6, Hamburg 13, W-2000, Germany

Solid-state ^{13}C CP MAS NMR studies of compounds $[(\text{Me}_3\text{Sn})_4\text{M}(\text{CN})_6]_\infty$ with M = Fe, Ru and Os, using variable temperature, show that the trigonal bipyramidal arrangements at Sn are undergoing internal rotation about the N–Sn–N axes with lifetimes of the order of 0.5 s at moderately lowered temperature.

Recently, a number of novel coordination polymers of the types $[(\text{Me}_3\text{E}^{\text{IV}})_3\text{M}^{\text{III}}(\text{CN})_6]_\infty$ (I; E = Pb or Sn, M = Co or Fe)^{1,2} and $[(\text{Me}_3\text{Sn}^{\text{IV}})_4\text{M}^{\text{II}}(\text{CN})_6]_\infty$ (II; M = Fe, Ru, Os)³ have been synthesized and characterised by various methods. In the case of the first type of compound X-ray diffraction work indicates a more complicated asymmetric unit than that suggested by high-resolution (magic angle spinning) NMR.^{2,4} For the compounds $[(\text{Me}_3\text{Sn}^{\text{IV}})_4\text{M}^{\text{II}}(\text{CN})_6]_\infty$, which are not

amenable to crystallographic studies, NMR at ambient probe temperature gives three cyanide signals for both ^{13}C and ^{15}N , two ^{119}Sn resonances and rather ill-defined ^{13}C bands for the methyl carbons, which have the appearance (for type II, M = Ru) of a 1 : 1 (by area) doublet. These observations prompted us to undertake a variable temperature ^{13}C NMR study to see if exchange processes of intermediate rate on the NMR time-scale are occurring.

Table 1 Methyl carbon chemical shifts^a for type II compounds, M = Fe, at -30 °C

	δ_C/ppm^b	$\delta_{\text{ave}}/\text{ppm}^b$	δ_C/ppm^c
SnMe ₃ unit A	8.8, 2.6, 1.3	4.2	4.3
SnMe ₃ unit B	3.6, 1.7, -2.6	0.9	1.2

^a Reported with respect to the resonance for solution-state tetramethylsilane. ^b At a nominal temperature of -30 °C (see Fig. 2). ^c At a nominal temperature of +40 °C.

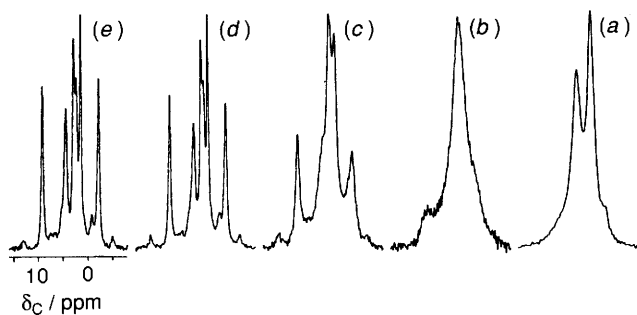


Fig. 1 ¹³C CP MAS spectra (methyl region only) of type II, M = Ru, at (a) 22, (b) 0, (c) -20, (d) -40 and (e) -60 °C. Minor peaks observable at low temperatures are tin satellites. Operating conditions: contact time 5 ms (2.5 ms at 22 °C); recycle delay 5 s (1 s at 22 °C); number of transients between 200 and 500; rotation rates between 3.60 and 4.53 kHz.

In each case the coordination around Sn or Pb may be expected to be essentially trigonal bipyramidal, with methyl groups occupying equatorial positions, as in the compounds of type I.² Since the structures are three-dimensional polymers, there are interconnecting M-C-N-E-N-C-M chains, of which there can be two or more types for a given compound (three in the case of type I²). The ratio of the number of Me₃Sn groups to the number of cyanide groups produces, in principle, a more complicated situation for type II compounds but room temperature NMR shows the existence of two types of Me₃Sn. Since room temperature NMR shows that the number of types of methyl groups is in general the same as the number of different E atoms, it is likely that either (i) there is an effective threefold axis of symmetry along the N-E-N axes, or (ii) there is rapid interchange of methyls in a given EMe₃ group by a novel type of internal rotation. Such an interchange as in (ii) need not affect X-ray diffraction patterns, and is therefore consistent with the X-ray evidence² for type I compounds.

Although lowering the temperature produced no substantial change in the CP MAS spectra of compounds of type I, dramatic differences were seen for all three compounds II. These were very similar in kind for M = Fe, Ru and Os, producing spectra below ca. -30 °C consisting of six lines of equal intensity, with some overlapping. The case of II, M = Ru, is illustrated in Fig. 1. These results suggest our hypothesis of internal rotation is correct, each methyl of the two SnMe₃ groups being in a different environment. The lifetime of a given rotational state is shown to be ca. 0.5 s at coalescence (ca. 0 °C), though clearly the exchange process causes complicated bandshape changes.

In order to confirm the motional process it is necessary to determine which methyl sites are interchanging. To do this we have employed the two-dimensional pulse sequence of Szeverenyi *et al.*⁵ The result is illustrated for type II, M = Fe, in Fig. 2, which clearly shows that the interchanges occur for two groups of Me signals independently, corresponding to the two SnMe₃ units. It allows assignments to be made as in Table 1 and confirms the timescale for the exchange process. The two-dimensional array is sufficiently good that it allows a distinction to be made between the peaks at $\delta_C = 1.7$ and 1.3 ppm, though these are not resolved in the normal one-

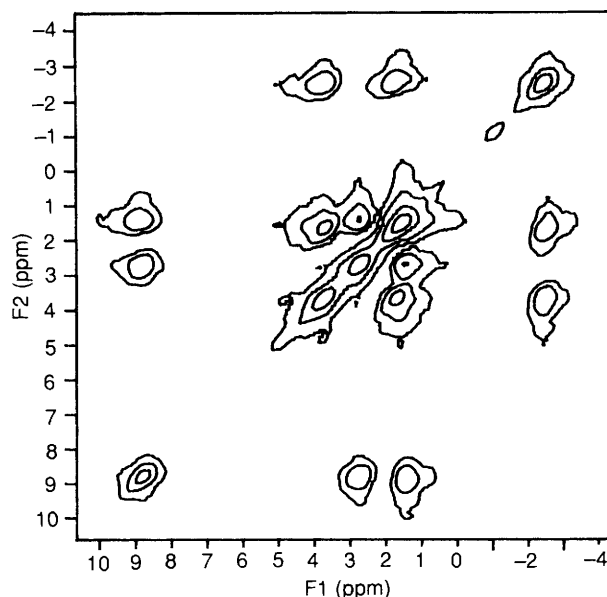


Fig. 2 Two-dimensional ¹³C CP MAS spectrum (methyl region only) of type II, R = Fe, at -30 °C, obtained using the pulse sequence of Szeverenyi *et al.*⁵ The mixing time was 0.5 s. Other operating conditions: contact time 1 ms; recycle delay 1 s; number of transients 198; rotation rate 2100 Hz.

dimensional spectrum. The average values for the two sets of three peaks are consistent with the data for ambient probe temperature (see Table 1). The chemical shifts given in Table 1 suggest that, for each SnMe₃ unit, one of the methyl groups is in a substantially different environment from the other two. We are currently undertaking further experimental work, plus calculations designed to simulate the one-dimensional bandshape changes and the two-dimensional cross-peak intensities, in order to obtain quantitative data on the exchange thermodynamics.

For compounds of type I it appears that internal rotation in the Me₃Sn groups is rapid on the NMR timescale down to -60 °C. This situation may reflect a less compact lattice packing in type I systems than in type II.

The ¹³C solid-state NMR spectra were obtained at 75.4 MHz using a Varian VXR 300 spectrometer in the cross-polarization mode with a Doty Scientific probe and a 7 mm o.d. sample rotor. Operating parameters are indicated in the figure captions. Temperatures quoted are nominal.

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