Journal of Organometallic Chemistry, 368 (1989) 31–33
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09737

Solid state 119-Sn NMR studies on some organotin compounds

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(Received September 30th, 1988)

Abstract

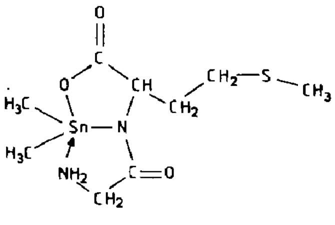
Tin-119 CP/MAS high resolution NMR spectra have been obtained for three solid diorganotin compounds of potential biochemical significance. The data are discussed in terms of their chemical structures, particularly the coordination about tin.

Organotin compounds have been known for a long time to exhibit marked biological properties [1]. Until now Mössbauer spectroscopy has been the technique of choice to study the structures of such compounds in the solid state, but, it often fails to give unambiguous results when lattice association is present. The advent of high resolution solid state NMR spectroscopy has made it possible to study compounds which can not be obtained in suitable form for X-ray crystallography. Harris et al. [2–4] have recently studied several organotin halides and oxides, and Molloy [5] has reported the 119-Sn chemical shifts for some carboxylates and thiophosphates.

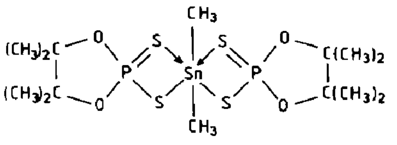
We report here the solid state tin chemical shifts for dimethyltinglycylmethionate (**1**), dimethylbis(4,4,5,5-tetramethyl-2-thioxo-1,3,2-dioxaphospholane-2-thiolato)tin (**2**) and dimethyltin inosinate (**3**).

Compound **1** gives a relatively sharp ^{119}Sn signal at $\delta - 79.9$ ppm which indicates the presence of five coordinate tin. The crystal structure of this compound clearly shows pentacoordination at tin with a very short equatorial Sn–N distance, indicating a strong bond and axial carboxylato oxygen and amino nitrogen bond distances which fall in the usual ranges [6].

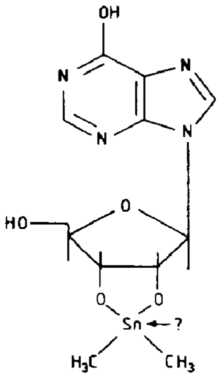
Tin NMR is particularly useful in the sense that even minor changes in geometry are reflected in chemical shifts. Compound **2** gives a signal at $\delta - 257.1$ ppm (the NMR spectrum is shown in Fig. 1), which can be attributed to six-fold coordination around the tin atom. The crystal structure of this compound demonstrates this



(1)



(2)



(3)

hexacoordination [7]. The tin atom is in a heavily distorted octahedral environment with two short Sn–S and two long Sn–S dative bonds. This compound shows a ^{119}Sn signal at $\delta - 209.7$ ppm in solution. It is monomeric in solution and in the solid state. The difference in the chemical shifts for the two phases is about 47 ppm, but this need not to be interpreted in terms of change in the coordination number. A slight change in the geometry or environment would suffice to cause such a shift.

A relatively sharp Sn signal is observed at $\delta - 211.5$ ppm for compound **3**. The ranges of ^{119}Sn chemical shifts for 5-fold and 6-fold coordination overlap, and it may be noted that there is not necessarily any precise definition of coordination in solids, even when full X-ray information is available, since as interatomic distances become long it may be debatable whether a "bond" exists or not. NMR, perforce, suffers from similar ambiguities. However, it is clear from the NMR data that the effective coordination at tin for **3** is indeed greater than 4.

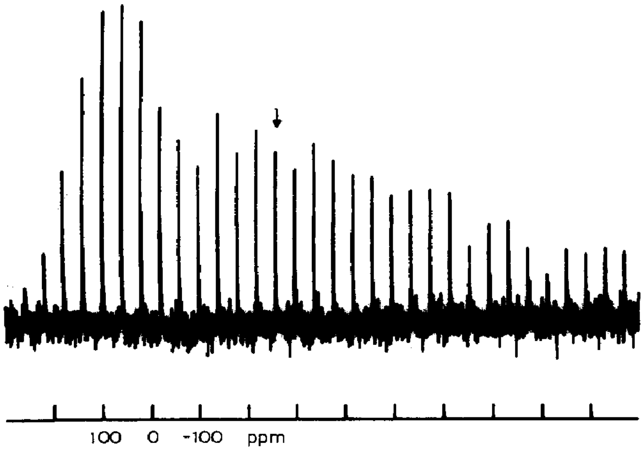


Fig. 1. 74.63 MHz CP/MAS 119-Sn NMR spectrum of dimethylbis(4,4,5,5-tetramethyl-2-thioxo-1,3,2-dioxaphospholane-2-thiolato)tin (**2**). Spectral parameters: contact time, 1 ms; recycle delay 10 s; number of transients, 4260. The vertical arrow indicates the centreband. There is evidence for some fold-back of spinning sidebands at the low-frequency end of the spectrum.

It has been suggested from the Mössbauer spectrum of the presumably analogous compound dimethyltin adenosinate that it might contain tin with a coordination number of 5 [8]. The observed value of $\delta - 211.5$ ppm for **3** is suggestive of 5–6 coordination and the coordination may be obtained in a similar way by intra- or inter-molecular association, with a possibility of oxygen being three coordinated. The Mössbauer data do not point to bonding by nitrogen atoms, but the possibility that the nitrogen atoms are involved in coordination cannot be ruled out on the basis of NMR data.

In all three cases there are extensive spinning sidebands, occupying ca. 700, 1300 and 1000 ppm for **1**, **2**, and **3**, respectively. These indicate substantial shielding anisotropy, which is not uncommon for ^{119}Sn. Surprisingly, the high-frequency limits of the side band manifolds seem to be approximately the same (ca. δ 250 ppm), in spite of the differences in coordination. None of the spectra show any evidence of crystallographic inequivalence for the tin atoms, but the linewidths are substantial (ca. 350, 150 and 500 Hz for **1**, **2** and **3**, respectively) so that any small splittings would be obscured.

For compound **2** the ^{31}P CP/MAS spectrum was also recorded. It showed the presence of only one type of phosphorus, in agreement with the X-ray structure. The chemical shift δ(p) is 106 ppm (reference: 85% H_3PO_4). Spinning sidebands cover the range from 220 to 0 ppm, and the line width is 90 Hz.

NMR experimental

All solid-state spectra were obtained with a Bruker CXP 200 spectrometer operating at 74.63 MHz for ^{119}Sn and 81.01 MHz for ^{31}P. The ^{119}Sn chemical shifts are quoted relative to external $SnMe_4$ with positive shifts to high-frequency. The cross-polarisation contact time used was 1 ms, and the recycle delay was either 10 s (compound **2**) or 20 s (compound **1** and **3**). Centrebands were located by varying the spinning speed, which was in the range 2 to 3.5 kHz. The number of transients varied between 200 and 6000, lower values being used when second spectra were acquired merely to locate centrebands. For further details of ^{119}Sn CP/MAS NMR see ref. 9. For the ^{31}P spectrum of the compound **2** only 90 transients were needed to achieve an excellent signal-to-noise ratio. The ^{119}Sn spectrum for compound **2** in solution was acquired at 93.3 MHz by use of a Bruker AC250 spectrometer, with CH_2Cl_2/C_6D_6 as solvent/lock. The line width was 55 Hz.

Acknowledgements. We thank the Alexander von Humboldt Foundation for the award of a research fellowship (to A.K.S.) and Deutsche Forschungsgemeinschaft and Fonds der Chemie for financial assistance.

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