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Short Communication

Solid-state and solution ^{117}Sn NMR study of $C_2O_4(SnPh_3)_2$: a revision

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Abstract

Solid-state and solution ^{117}Sn nuclear magnetic resonance studies of $C_2O_4(SnPh_3)_2$ have been carried out and found to be in good agreement with the tetrahedral environment of the tin (IV) atom as found from the solid state structure, previously determined by a single crystal X-ray diffraction analysis.

Keywords: monocoordinated $SnPh_3$ group; Mössbauer; oxalate; ^{117}Sn NMR spectra.

Based on the Mössbauer quadrupole splitting (QS) of -2.81 mm s^{-1}, similar to the QS value of $SnPh_3OH$, we recently suggested for C_2O_4 $(SnPh_3)_2$, a polymeric structure with the tin atoms to be pentacoordinated by bridging oxalate ligands in axial positions of the trigonal bipyramid Diop et al., 1997. However, a single crystal X-ray diffraction analysis Diop et al., 2003 revealed a tetrahedral environment around the tin (IV) atom. This apparent contradiction between the Mössbauer and X-ray data, reinforced by an aberrant value of the chemical shift of -503 ppm in the solution, raised questions and prompted us to carry out the solid state nuclear magnetic resonance (NMR) studies and to revisit the solution NMR data.

The synthesis of $C_2O_4(SnPh_3)_2$ has been described previously Diop et al., 1997; NMR data ^1H [δ(ppm)]: 7.45–7.35 ppm (m), d meta and para protons; 7.75–7.65 ppm (m), $^3J(^1H-^{119/117}Sn)$ coupling satellites of about 60 Hz, ortho protons. ^{13}C (δ in ppm, $^nJ(^{13}C-^{117/119}Sn)$ in Hz between brackets): 129.0 [63/66], meta carbon; 130.5 [14], para; 137.0 [49], ortho; 138.1, broad, ipso, no coupling satellites visible; 164.4, oxalate carbon. ^{119}Sn: -96 ppm.

The solution NMR spectra were recorded from a saturated $CDCl_3$ solution, at room temperature, using a Bruker Avance 250 spectrometer (Bruker Biospin, Rheinstetten, Germany), operating at 250.53, 63.00, and 89.27 MHz for ^1H, ^{13}C, and ^{117}Sn, respectively. ^1H, ^{13}C, and ^{117}Sn chemical shifts are given in ppm and are referred respectively to $SiMe_4$ and $SnMe_4$, all set to 0.00 ppm. The coupling constants are given in Hz. Cross/polarization-magic angle spinning (CP-MAS). ^{117}Sn solid-state spectra were recorded at 89.27 MHz on the same spectrometer, with a 4 MAS broad-band probe. Spinning frequencies are chosen between 5 and 9 kHz. A contact time of 1 ms and a recycling delay of 2 s were employed. The chemical shift reference was set with (*cyclo*-$C_6H_{11})_4Sn$ [~97.35 ppm relative to $(CH_3)_4Sn$].

The solid-state ^{117}Sn NMR displays a single isotropic chemical shift at ~87 ppm, consistent with a tetrahedral configuration for the tin atom. In the solution, the ^{119}Sn shift value of ~96 ppm is also consistent with a tetrahedrally configurated tin atom according to Holecek et al. (1983).

These ^{117}Sn NMR shift values found, well correlating with the tetrahedral environment of the tin center found by X-ray studies, allow to reject the anomalous value of -503 ppm reported earlier.

In conclusion, although in most cases, the value of the quadrupole splitting correlates well with the environment of the tin atom in $SnPh_3$-containing compounds, the situation appears to be more complex in $C_2O_4(SnPh_3)_2$. For the latter compound, a correct conclusion on the configuration of the tin atom can be drawn from the solid-state ^{117}Sn NMR chemical shift.

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