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^{119}Sn NMR and ^{119m}Sn Mössbauer Studies of Inorganic Tin(IV) Compounds with High Coordination Numbers

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Although ^{119}Sn NMR spectroscopic investigations of organotin compounds in solution are well established [1, 2], it is only within the last few years that their inorganic counterparts have attracted attention. For organotin compounds, it has been shown that the ^{119}Sn chemical shift, $\delta(^{119}\text{Sn})$, moves progressively to lower frequency as the coordination number of the metal increases from 4–7 [1–4]. The present communication reports a similar relationship for a series of inorganic tin(IV) complexes, in which the coordination number of the metal atom is varied from four to eight, these being to our knowledge, the first ^{119}Sn NMR data for hepta- and octa-coordinate inorganic tin derivatives.

The ^{119m}Sn Mössbauer parameters and ^{119}Sn NMR chemical shifts are listed in Tables I and II. The compounds tin(IV) tetraacetate, $Sn(O{\cdot}CO{\cdot}CH_3)_4$, tin(IV) tetranitrate, $Sn(NO_3)_4$, tin(IV) tetratropolonate monohydrate, $Sn(trop)_4{\cdot}H_2O$, tin(IV) tetraoxyquinolinate, $Sn(ox)_4$, monohydrotin(IV) diethylenetriaminepentaacetate trihydrate, HSn-(DTPA)$\cdot 3H_2O$, and tin(IV) ethylenediaminetetraacetate monohydrate, Sn(EDTA)$\cdot H_2O$, were chosen since their seven and eight coordinate structures have been established by X-ray crystallography or related techniques (see Table I). From Table I, it may be seen that the isomer shift (δ) values for the four neutral eight coordinate complexes, **1**–**4**, are all approximately equal to 0.0 mm s^{-1}, whereas the ionic compound, **5**, shows a value of 0.21 mm s^{-1}, consistent with the increase in s-electron density at the tin nucleus upon forming the anion. However, due to

TABLE I. ^{119m}Sn Mössbauer data

Compound	δ (mm s^{-1})[a, b]	ΔE_q (mm s^{-1})[a]	Coordination number
1 $Sn(O{\cdot}CO{\cdot}CH_3)_4$	0.08[c]	0.2[c]	8[d]
2 $Sn(NO_3)_4$	−0.04[e]	0.4[e]	8[d]
3 $Sn(trop)_4{\cdot}H_2O$	−0.02	0.0	8[g]
4 $Sn(ox)_4$	−0.05[h]	0.0[h]	8[h, i]
5 HSn(DTPA)$\cdot 3H_2O$	0.21	0.0	8[j]
6 Sn(EDTA)$\cdot H_2O$	0.16	0.0	7[k]

[a] For compounds 3, 5 and 6: error = ±0.05 mm s^{-1}. [b] Relative to $Ba^{119m}SnO_3$. [c] Ref. 5. [d] Ref. 6. [e] Ref. 7. [f] Ref. 8. [g] Ref. 9 (reported as anhydrous material). [h] Ref. 10. [i] Ref. 11. [j] Ref. 12. [k] Ref. 13.

TABLE II. ^{119}Sn NMR Chemical Shifts

Compound	Solvent	Concentration	$\delta(^{119}\text{Sn})$[a] (ppm)
1 $Sn(O{\cdot}CO{\cdot}CH_3)_4$	toluene/acetic acid	10% *w/v*	−858.2
2 $Sn(NO_3)_4$	CH_2Cl_2	1.1 M	−1033[b]
	CCl_4	1.1 M	−1033[b]
3 $Sn(trop)_4{\cdot}H_2O$	$CDCl_3$	~1% *w/v* (saturated)	−793
4 HSn(DTPA)$\cdot 3H_2O$	H_2O	1–2% *w/v* (saturated)	−783.5
5 Sn(EDTA)$\cdot H_2O$	H_2O	1–2% *w/v* (saturated)	−673.8
6 $Sn(O^nBu)_4$	$CDCl_3$	0.2 M	−612[c]
7 $Na_2Sn(OH)_6$	H_2O	saturated	−592[d]
8 $K_2Sn(OH)_6$	H_2O	saturated	−590[d]
9 $SnCl_4{\cdot}2CH_3OH$	CD_3OD	30% *v/v*	−600.5[e]
10 $Cl_2Sn(acac)_2$	$CDCl_3$	10% *w/v*	−646.2
11 $SnCl_4$	CCl_4	10% *w/v*	−149[f]
	neat		−150[d]

[a] $\delta(^{119}\text{Sn})$ values are relative to Me_4Sn and, for compounds **1**, **3**–**5** and **9**–**11**, are accurate to ±0.2 mm s^{-1}. [b] Ref. 16. [c] Ref. 17. [d] Ref. 18. [e] Ref. 19. [f] Ref. 20.

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the complex nature of the factors influencing the isomer shifts [14, 15], and to the limited number of compounds examined, comparison between the δ values of the 7- and 8-coordinate derivatives is not possible. All compounds studied showed Mössbauer spectra with essentially no quadrupole splitting (ΔE_q), indicating a symmetrical geometry about the tin atom.

With regard to the ^{119}Sn NMR chemical shifts, $\delta(^{119}\mathrm{Sn})$, the value shown by the four coordinate tin compound, $SnCl_4$, **11**, in non-donor solvents, moves to -600 ppm in methanol, where the species present is the 6-coordinate neutral adduct, $SnCl_4 \cdot 2CH_3OH$, **9**, (Table II). Additionally, a chemical shift of the order of -600 ppm is typical for six coordinate tin compounds containing at least four directly bound oxygen substituents, e.g. compounds **6–8** in Table II. As stated, an increase in coordination number of the tin atom generally results in $\delta(^{119}\mathrm{Sn})$ moving to low frequency, and, in accord with this, the 8-coordinate species studied show $\delta(^{119}\mathrm{Sn})$ values in the range -784 to -1033 ppm, whilst the seven coordinate complex, **5**, gives an intermediate chemical shift.

Further studies of complexes of this type are under way, in order to obtain a better understanding of the significance of the ^{119m}Sn Mössbauer and ^{119}Sn NMR data.

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