Solid-State ^{119}Sn NMR Studies of Poly(pyrazolyl)borate Complexes of Tin(II). Correlation of Solution- and Solid-State Structures

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Introduction

Some of us have recently reported[1] the synthesis and characterization of a series of complexes of tin(II) of the general formula $[H_nB(pz)_{4-n}]_mSnCl_{2-m}$ (n = 0, 1, 2; m = 1, 2; pz = pyrazolyl ring). It proved difficult to assign the number of nitrogen atoms coordinated to tin for complexes of the $[HB(pz)_3]^-$ and especially $[B(pz)_4]^-$ ligands. While previous work with transition metal complexes of these ligands generally demonstrated tridentate coordination,[2] a series of structures determined by X-ray crystallography of tin[1] and other main group metal complexes[3] has shown that the $[B(pz)_4]^-$ ligand and also possibly the $[HB(pz)_3]^-$ ligand frequently coordinate in a bidentate mode. Thus, $[B(pz)_4]_2Sn^1$ (**1**) and $[B(pz)_4]_2Pb^{3a}$ are four-coordinate at the metal in the solid state, adopting a pseudo-trigonal bipyramidal structure with two bidentate $[B(pz)_4]^-$ ligands each spanning an axial and equatorial site with the metal(II) lone pair in the remaining equatorial site. Also Cowley et al. have reported[4] that $[HB(3,5-Me_2pz)_3]_2Sn$ (**3**) is five-coordinate in the solid state, containing one noncoordinated pyrazolyl ring. Given these results,
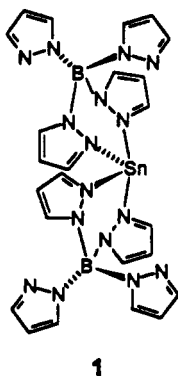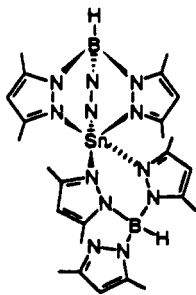
1   **3**

it was not possible to assign a coordination number to complexes such as $[HB(pz)_3]_2Sn$ (**2**) for which it has not proven possible to obtain crystals suitable for an X-ray investigation. Even for complexes whose solid-state structures are known, it is not clear whether the structures determined in the solid state are maintained in solution.

^{1}H NMR studies in solutions were not definitive in assigning coordination numbers. All of the tin(II) complexes prepared by

us show three resonances at ambient temperature, one for each of the three nonequivalent hydrogen atoms on the pyrazolyl rings. The spectrum of **2** does not change at low temperatures (–89 °C). For **1** at –80 °C, each resonance type has split into two resonances with 3/1 *integrated intensities*, and no additional line broadening was observed down to –89 °C. This pattern is not what is expected from the solid-state structure. While these data could be interpreted as indicating that **1** is six-coordinate in solution, the data were explained based on the four-coordinate structure observed in the solid.[1] In the structure, for each ligand, the boat orientation of the BN$_4$Sn six-membered ring places one of the noncoordinated pyrazolyl rings close to the tin while the other is distant from the tin atom. To explain the 3/1 pattern, it was proposed that the pyrazolyl ring in each ligand that is close to the tin equilibrates fast on the NMR time scale with the coordinated pyrazolyl rings, even at low temperatures. Such a process has also been proposed recently[5] to explain the low-temperature NMR spectra of $[HB(3,5-Me_2pz)_3]Rh(CNCMe_3)_2$.

To support the structural assignments, the ^{119}Sn solution-phase chemical shifts of the complexes were also reported and used to assign coordination numbers. It was assumed that **1** and **3** retained in solution the coordination numbers observed in the solid-state structures. From the result that the shift of complex **2** was closer to **3** than **1** (Table I), **2** was tentatively assigned a coordination number of five. Just after the appearance of our publication, a number of these complexes were reported by others,[6] and a different conclusion was reached on the coordination numbers in solution of **1–3**.

Given the ambiguities in these data, it was decided to measure the high-resolution *solid-state* ^{119}Sn chemical shifts of **1–3** using high-power proton decoupling and magic-angle spinning (MAS). Such techniques have had considerable success in the determination of structure and bonding (including coordination) for solid organotin compounds.[7–9] In fact, solid-state NMR can act as a bridge between X-ray diffraction and solution-state NMR. Therefore, with measured chemical shift values in both the solid and solution phases, we hoped to be able to correlate our solid-state structures determined by X-ray crystallography with the solution structures.

Results and Discussion

Table I shows the ^{119}Sn solution-phase chemical shifts for a series of poly(pyrazolyl)borate complexes of tin(II) as reported earlier,[1,6] along with the solid-state shifts and shielding tensor data for **1–4**. A general trend in the solution data is that higher coordination number complexes have chemical shifts that are more shielded.

The chemical shift of **1** is very similar in both the solid and solution phase. As it has been shown crystallographically that **1** is four-coordinate in the solid phase, these data argue strongly that four-coordination is retained is solution. The other three $[R_2B(pz)_2]_2Sn$ type complexes shown in Table I, complexes that are certainly four-coordinate in solution, show that the solution-phase chemical shifts for SnN$_4$ coordination with these ligands span a range of 91 ppm.

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Table I. Solid- and Solution-Phase Tin-119 NMR Data

	chem shift[c]		shielding tensor[d]	
compound	solution[e] δ_{iso}/ppm	solid δ_{iso}/ppm	anisotropy β/ppm	asymmetry η
[H$_2$B(3-Mepz)$_2$]SnCl[b]	−271			
[H$_2$B(pz)$_2$]SnCl[a] (4)	−307	−432	695	0.14[f]
[H$_2$B(pz)$_2$]$_2$Sn[a]	−652			
[H$_2$B(3-Mepz)$_2$]$_2$Sn[b]	−685			
[Ph$_2$B(pz)$_2$]$_2$Sn[b]	−728			
[B(pz)$_4$]$_2$Sn[a] (1)	−743	−738	608	0.30
[HB(pz)$_3$]$_2$Sn[a] (2)	−877	−841	587	0.30
[HB(3,5-Me$_2$pz)$_3$]$_2$Sn[a] (3)	−934	−943	320	∼0[f]

[a] Reference 1. [b] Reference 6. [c] Versus external Me$_4$Sn. [d] $\beta = \sigma_{33} - \sigma_{iso}$; $\eta = (\sigma_{22} - \sigma_{11})/\beta$. Note that the shielding convention used for the tensor is of opposite sign to the chemical shift (resonance frequency) convention. [e] In CDCl$_3$. [f] Values for η less than ca. 0.2 are notoriously subject to error.[10]

As with **1**, the chemical shift of **3** is very similar in both the solid and solution phase, indicating that the five-coordinate structure observed in the solid phase is retained in solution.

The chemical shift difference of **2** between the solid and solution phase is larger than those of **1** and **3**, but the values are within 36 ppm, indicating a similar coordination number in both phases. The solid-state shift of **2** is centered between four-coordinate **1** (difference of 103 ppm) and five-coordinate **3** (difference of 102 ppm). Even though the chemical shift range of ^{119}Sn is large and the complexes being studied here are similar, a definitive assignment on the coordination number of **2** cannot be made based on the chemical shift data. However, the shielding anisotropies and asymmetries, obtained by analysis of the spinning sideband patterns in the MAS spectra, show there is a very close similarity between the values for **1** and **2**, whereas those for **3** are substantially different (Table I). These results suggest that **2**, like **1**, has 4-fold coordination by nitrogen, with a similar distorted trigonal bipyramidal geometry (including the lone pair). The greater ability of the full shielding tensor data rather than the isotropic chemical shifts to indicate coordination has been remarked on previously.[8]

One other complex that was studied is [H$_2$B(pz)$_2$]SnCl (**4**). The structure of this complex in the solid phase is a weakly associated, centrosymmetric dimer with normal (2.485(3) Å) and very long (3.390(3) Å) Sn–Cl bond distances. Solution

4
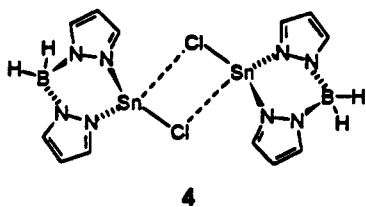
molecular weight studies (benzene) give values 20% higher than expected for the monomer, indicating partial association in solution. Low-temperature ^{119}Sn studies show that two species are present in solution.[11] The solid-phase chemical shift is 125 ppm more shielded than the ambient temperature solution value, and 93 ppm more shielded than the high-frequency resonance in

the low temperature spectrum. Clearly the solution structures are different from that observed in the solid phase. In this case, it is reasonable to assume that the different structure in the solid phase is caused by crystal packing forces associated with the centrosymmetric dimeric arrangement. As expected, the shielding anisotropy and asymmetry are significantly different for **4** than those for **1–3**.

In conclusion, we have been able to show using ^{119}Sn NMR that the solution- and solid-state structures of **1–3** are similar. The structure of **4** is different in the two phases. The chemical shift data do not allow a definitive assignment of the coordination number of **2**, but the shielding anisotropy and asymmetry parameters are suggestive of a similar environment about tin in both **1** and **2**.

Experimental Section

The complexes were prepared as reported earlier.[1] The solid-state NMR spectra were obtained at 111.9 MHz using a Varian VXR 300 spectrometer at ambient probe temperature. The powdered samples were packed into 5-mm-o.d. rotors and spun at 10–15 kHz in a Doty Scientific MAS probe. In each case two spinning speeds were used so as to locate the centerbands. Cross-polarization was used for **2** (contact time 5 ms; recyle delay 10 s) but not for the other three compounds (recycle delays of 60 s with pulse angles of 45 or 90°). Between 900 and 1600 transients were acquired for each spectrum. The spinning side-band manifolds were computer-fitted to yield shielding tensor data using a program written in-house.[12,13]

Note Added in Proof. Preliminary results from an X-ray crystallographic study on compound **2** indicate a highly distorted five-coordinate geometry about the tin atom. The similarity between the shielding tensor data for **1** and **2** is therefore fortuitous, but the X-ray results are consistent with the large shielding anisotropy and moderate asymmetry reported herein for **2**.

(11) At −58 °C, two resonances at −265 and −339 ppm with a ratio of ca. 1/7 are observed. This spectrum was observed by Niedenzu et al. and interpreted as arising from the two possible arrangements of the boat form of the six-membered BN$_4$Sn ring.[6] An alternative interpretation, given the molecular weight data, is that the two species in solution are a monomeric and oligomeric form of **4**.

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