Tin Porphyrins. 6. Tin-119 Chemical Shifts and Line Widths of Tin(IV) Complexes of Tetraphenyl-, Tetra-*p*-tolyl-, and Octaethylporphyrin

Dennis P. Arnold* and John P. Bartley

Center for Instrumental and Developmental Chemistry, Queensland University of Technology, G.P.O. Box 2434, Brisbane, Australia 4001

*Received September 17, 1993**

Tin-119 NMR spectra are reported for chloroform solutions of $PSnX_2$ [P = dianion of 5,10,15,20-tetraphenylporphyrin (TPP), X = $CF_3SO_3^-$, ClO_4^-, NO_3^-, $CF_3CO_2^-$, $Cl_2CHCO_2^-$, (*o*-OH)$C_6H_4CO_2^-$, HCO_2^-, $C_6H_5CO_2^-$, $CH_3CO_2^-$, (*p*-NO_2)$C_6H_4O^-$, (*p*-Br)$C_6H_4O^-$, (*p*-CH_3)$C_6H_4O^-$, HO^-, CH_3O^-, F^-, Cl^-, Br^-, I^-; P = dianion of 5,10,15,20-tetra-*p*-tolylporphyrin (TTP), X = HCO_2^-, HO^-, Cl^-; P = dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin (OEP), X = HO^-, Cl^-]. For the complexes of O-bound axial ligands, stronger donors generally shift the ^{119}Sn resonance downfield, while for the carboxylates (apart from HCO_2^-) the reverse is the case. The nature of the porphyrin ligand has little effect on δ_{Sn} for the same axial ligands. For the TPP series, and excluding the halides, the widths at half-height of the ^{119}Sn signals are dependent on the nature of the axial anions. These line widths correlate (r = 0.968) with the coupling constants between the tin nucleus and protons on the pyrrole β carbons, suggesting that these parameters are reflecting the *cis*-influences of the axial ligands on the Sn–N bonds. The spectra of the halide complexes display more complex behavior.

Introduction

The six-coordinate complexes of porphyrins and related aromatic macrocycles with tin(IV) have been of interest in recent years, mainly for their potential medical applications. Most studies have concentrated on the ability of tin(IV) complexes of protoporphyrin (and other similar ligands) to inhibit the enzyme heme oxygenase, which is responsible for hyperbilirubinemia in neonates.[1] While these results were initially encouraging, concern has been expressed about the deleterious side effects of such agents, since they are also potent photosensitizers.[2] Indeed, the use of tin(IV) complexes of porphyrins and purpurins for photodynamic cancer therapy has also been reported.[3] Some of these complexes have also been shown to have immunostimulatory effects.[4] Meyerhoff and co-workers[5,6] have discovered that salicylate levels in serum can be determined using an ion-selective electrode based on a polymer membrane doped with (TPP)$SnCl_2$ ($TPPH_2$ = 5,10,15,20-tetraphenylporphyrin).

It is therefore of some importance to study and understand the static and dynamic coordination chemistry of tin(IV) complexed to porphyrins. Ligands occupying the axial sites are clearly of vital importance in the electrode mechanisms and may be relevant when the complexes are employed in cellular systems. We have studied the spectroscopic properties of TPP complexes of tin(IV) by ^1H NMR, UV–visible, and FT-Raman spectroscopy and have generated *cis*- and *trans*-influence series for oxygen-bound anions and the halides.[7–9] Some electrochemical results have been presented for a limited series of (tetraarylporphyrinato)tin(IV) complexes.[10] We also reported the crystal structures of a series of five (TPP)SnX_2 complexes of relevance to the ion-selective-electrode application.[11] Interestingly, none of these techniques showed any specific differences between salicylate and other ligand types, which might account for the selective electrode responses.

We have now extended our studies of these systems by recording the ^{119}Sn NMR spectra of an extensive series of (TPP)SnX_2 complexes and some complexes of other porphyrins. Our initial postulate was that, because the complexes are very similar, the ^{119}Sn chemical shifts would depend in a simple manner on the properties of the axial ligands and directly reflect electron density at the tin nucleus. This would complement the other spectroscopic techniques and might reveal some specific effects of certain ligands. In any case, patterns might emerge which would allow assignments of structures of species in biological systems. Indeed, there was already one report of the observation of ^{119}Sn signals from tin protoporphyrin complexed with equine myoglobin,[12] although the lack of a chemical shift reference makes this work of limited comparative value. As we began this work, Meyerhoff and co-workers published the results of further studies into the salicylate problem, as part of which they recorded the ^{119}Sn NMR spectra of (TPP)$SnCl_2$, (TPP)SnCl(salicylate), and (TPP)Sn(salicylate)$_2$.[6] They interpreted the respective upfield shifts of these complexes as a reflection of an increase in electron density around the tin nucleus.

There have been rather few reports of NMR studies in which spectra of the metal nuclei in metalloporphyrins have been directly observed. Of the readily accessible nuclei, ^{113}Cd,[13] ^{31}P,[14–16] and ^{195}Pt[17] have been studied to a limited extent, and there are presently

* Abstract published in *Advance ACS Abstracts,* March 1, 1994.

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0020-1669/94/1333-1486$04.50/0

too few data for use in structural studies. The data reported by Milgrom *et al.* on ^{195}Pt chemical shifts in four-coordinate Pt(II) porphyrin complexes revealed *downfield* shifts of the ^{195}Pt resonance with more electron-rich porphyrins and rather broad lines (*ca.* 300–800 Hz).[17] While it is possible that some of this broadening was due to chemical shift anisotropy, the authors concluded that ^{195}Pt–^{14}N coupling was the major contributor. The data in a recent report of ^{31}P chemical shifts in (tetraarylporphyrinato)phosphorus(V) complexes revealed variations with axial ligand properties, but a simple dependence on factors such as pK_a was not evident.[15] On the other hand, Kunimoto *et al.*, in their brief report on unsymmetrical $[(TPP)P(OR)_2]X$ complexes, state that such a dependence was observed in their series.[16] The results described herein indicate that the ^{119}Sn spectra of the tin(IV) complexes should be a useful tool for structural, chemical, and possibly *in situ* biochemical studies. This report covers a survey of chemical shifts and line widths for a series of $(TPP)SnX_2$ complexes, where X = O-bound anions and the halides, as well as some complexes of the more electron-rich porphyrins, 5,10,15,20-tetra-*p*-tolylporphyrin ($TTPH_2$) and 2,3,7,8,12,13,17,18-octaethylporphyrin ($OEPH_2$).

Experimental Section

Synthesis of Complexes. Most of the TPP complexes were available from our earlier work.[7,8,11] Where this was not the case, the species were prepared by adding the appropriate acid to a solution of $(TPP)Sn(OH)_2$ (2.5:1 molar ratio) in chloroform in the NMR tube. All complexes except those of dichloroacetic acid, *p*-bromophenol, and *p*-nitrophenol have been reported previously.[7,8,11] These last three complexes were isolated by evaporation of the solvent and trituration with ether to remove the organic acids. Respective ^1H NMR data are as follows. $TPPSn(Cl_2CHCO_2)_2$: δ 9.27 [$^4J(Sn-H)$ = 16.1 Hz] (pyrrole β), 2.88 (Cl_2CH). $(TPP)Sn(p\text{-}BrC_6H_4O)_2$: δ 9.10 (12.6 Hz), 5.73 (2,6-H of phenolate), 1.68 (3,5-H) (AA'BB'). $(TPP)Sn(p\text{-}NO_2C_6H_4O)_2$: δ 9.19 (13.8 Hz), 6.62, 1.86. The protons of the TPP phenyl groups appeared in all compounds in the normal range of 7.8–8.3 ppm. In some cases, the mixed hydroxo acido complexes were observed by ^{119}Sn NMR; in such cases, the solutions were also examined by ^1H NMR to confirm this assignment. Complexes of other porphyrins were prepared as for those of TPP[18,19] using $SnCl_2{\cdot}2H_2O$ in pyridine (for $PSnCl_2$), followed by aqueous ammonia [for $PSn(OH)_2$], and were purified by recrystallization from chloroform/methanol and dichloromethane/hexane, respectively.

NMR Measurements. ^1H NMR spectra were recorded on a Varian Unity 300 spectrometer and are referenced to residual $CHCl_3$ in $CDCl_3$ (7.25 ppm). ^{119}Sn spectra were obtained on the same instrument, at 111.862 MHz. Most of the porphyrin complexes were dissolved in analytical reagent grade chloroform or $CDCl_3$ at 0.01 M in 10-mm tubes. For $(TPP)Sn(OCH_3)_2$, $CDCl_3$ was distilled from phosphorus pentoxide directly into the tube containing the freshly prepared complex (some hydrolysis was still observed as usual[7,20]). Complexes with low solubility in chloroform [$(TPP)Sn(CF_3SO_3)_2$ and $(TPP)Sn(ClO_4)_2$] were also examined in acetone (see Results and Discussion). The reference standard was a 4 mg mL^{-1} solution of tetramethyltin in $CDCl_3$ contained in a concentric 4-mm inner tube. The spectra were accumulated using the following parameters: spectral width 70–100 kHz, pulse width 10 μs (*ca.* 45°), data points 64K with zero filling to 128K, relaxation delay 1.0 s, ^1H WALTZ decoupling during acquisition only, number of transients 20 000–60 000 (depending on line width). For the spectrum without ^1H decoupling (see below), a saturated solution of $(TPP)SnBr_2$ was used (*ca.* 0.025 M). The complex $(TPP)SnI_2$ was examined using a spectrometer frequency of 111.800 MHz with $(TPP)Sn(OH)_2$ in $CDCl_3$ as a secondary reference in the inner concentric tube. The complex $(TPP)Sn(HCO_2)_2$ was also examined under higher resolution conditions (spectral width 2000 Hz, data points 16K, zero-filled to 32K, exponential line broadening 1 Hz), using a concentration of 0.04 M. For line width estimation, FIDs were transformed using an exponential line broadening of 5 Hz. The transformed and phased data were imported as binary files from the NMR spectrometer into the application Igor, running on an Apple Macintosh IIsi computer. The ^{119}Sn lines were fitted to a Lorentzian function using a macro written by Dr. P. A. Duckworth.

Table 1. ^{119}Sn Chemical Shifts and Line Widths for Sn(IV) Porphyrin Complexes

no.[a]	porphyrin	axial ligand	δ_{Sn}[b]	$\nu_{1/2}$[c]
1	TPP	CF_3SO_3	–630.9	99
1a[d]		CF_3SO_3	–600.3	~180
2a[d]		ClO_4	–600.2	~180
3		NO_3	–623.3	90
4		CF_3CO_2	–625.9	87
5		Cl_2CHCO_2	–625.9	73
6		$o\text{-}(OH)C_6H_4CO_2$	–630.3	68
7		HCO_2	–618.1	56
8		$C_6H_5CO_2$	–631.1[e]	63
9		CH_3CO_2	–635.7[f]	67
10		$p\text{-}(NO_2)C_6H_4O$	–612.8	49
11		$p\text{-}BrC_6H_4O$	–605.0	40
12		$p\text{-}(CH_3)C_6H_4O$	–602.0	41
13		HO	–569.6	31
14		CH_3O	–561.7[g]	27
15		F	–621.1[h]	78
16		Cl	–589.7	50
17		Br	–711.7	37
18		I	–977.6	192
19	TTP	HCO_2	–617.1	47
20		HO	–569.9	28
21		Cl	–589.9	46
22	OEP	HO	–570.9	48
23		Cl	–591.2	78

[a] Point number in figures and text. [b] In ppm from Me_4Sn; negative shifts to low frequency. [c] Width at half-height, in Hz, derived from Lorentzian curve fitting. [d] In acetone solution. [e] $(TPP)Sn(OH)(C_6H_5CO_2)$ also observed, δ = –601.3. [f] $(TPP)Sn(OH)(CH_3CO_2)$ also observed, δ = –602.3. [g] $(TPP)Sn(OH)(OCH_3)$ also observed, δ = –565.1. [h] A 1:2:1 triplet, $^1J(Sn-F)$ = 1879 Hz.

Results and Discussion

Chemical Shifts. The ^{119}Sn resonances of the complexes appeared in the expected range, to very high field of tetramethyltin. The data are collected in Table 1. The values found by us for $(TPP)SnCl_2$ and $(TPP)Sn(salicylate)_2$ compare closely with those already reported,[6] namely δ –589.7 (–587) and –630.3 (–628), respectively. We recorded the spectra using rather dilute solutions (0.01 M), in order to allow for the limited solubility of some of the complexes and still maintain the same concentrations across the series. This meant long accumulation times, especially for those species with broad lines (see below). For complexes with narrow lines and high solubility, good spectra were readily obtainable in 2 h or less.

For the same axial anions, changing the porphyrin causes remarkably small changes in chemical shifts [Table 1, numbers 7 and 19 (formates), 13, 20, and 22 (hydroxides), and 16, 21, and 23 (chlorides)]. While TTP and TPP are perhaps expected to be very similar, it is unusual that a change to the more electron-rich OEP makes so little difference to δ_{Sn}. This can be contrasted with the behavior of δ_{Pt} in square planar Pt(II) complexes examined by Milgrom and co-workers.[17] In their spectra, the ^{195}Pt resonance in the TPP complex appeared some 80 ppm upfield of that of the OEP complex. Generally, ^{195}Pt chemical shifts do occupy a larger range than those of ^{119}Sn.[21]

The lack of sensitivity of δ_{Sn} to the nature of the porphyrin can be contrasted with the large variation due to changes to the axial ligands. The O-bound ligands will be discussed first. In view of

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some of the data trends (see below), we have included more ligands than in our earlier studies, by preparing the dichloroacetate, *p*-nitrophenolate, and *p*-bromophenolate complexes. We were unable to obtain a ^{119}Sn signal for (TPP)Sn$(ClO_4)_2$ in chloroform solution, because of the very low solubility of this complex.[7] When we tried to prepare this complex by adding aqueous perchloric acid to a $CDCl_3$ solution of (TPP)Sn$(OH)_2$, a species was observed at δ_{Sn} −582 ppm. The ^{1}H spectrum of this solution showed a major compound with δ_H = 9.20 and ^4J(Sn–H) = 16.1 Hz and a minor component with δ_H = 9.39 and ^4J(Sn–H) = 19.6 Hz. Both species showed phenyl resonances which indicated that they were symmetrical through the porphyrin plane or were undergoing rapid axial ligand exchange. We have previously reported the detection of unsymmetrical axial ligation in (tetraarylporphyrinato)tin(IV) complexes by the observation of nonequivalence of the ortho protons of the *meso*-aryl groups.[22] This is possible only if the rates of aryl ring rotation are slow on the 300-MHz NMR time scale and the proton environments are sufficiently different. The appearance of a broad ^{1}H resonance at 0.5 ppm (for coordinated water in exchange with dissolved water) suggested that the major component was [(TPP)Sn$(H_2O)_2$]$(ClO_4)_2$. Kadish *et al.* reported the dissociation of the perchlorate anions in tin(IV) porphyrins in the presence of donor solvents such as THF and were also able to detect facial nonequivalence of the ortho protons in complexes with unlike axial ligands.[10] The minor species in our solution had ^{1}H NMR parameters almost identical to those described for the complex with coordinated perchlorates.[7] Removal of water from a $CDCl_3$ solution containing (TPP)Sn$(OH)_2$ and excess aqueous $HClO_4$ caused complete precipitation of the porphyrin, presumably as the covalent species. Similar behavior was exhibited by the triflate complex, but despite some precipitation, we were able to measure its ^{119}Sn spectrum. A spectrum of a solution of (TPP)Sn$(OH)_2$ and excess CF_3SO_3H in $CDCl_3$, without water removal, showed a broad ^{119}Sn peak at −586 ppm, suggesting the predominance of an aquo cationic complex. Both the perchlorate and triflate were also examined in acetone, in which they are quite soluble,[7,11,23] and the very broad ($\nu_{1/2}$ *ca.* 180 Hz) ^{119}Sn resonances appeared at −600 ppm for both anions, suggesting that a common species [(TPP)Sn(acetone)$_2$]X_2 was present. This behavior, and solvent effects in general, warrant further study but are beyond the scope of this survey.

In our earlier studies, various parameters [pyrrole δ_H, ^4J(Sn–H) in (TPP)SnX_2,[7] ^3J(Sn–O–C(O)–H) in (TPP)SnX(O_2CH),[8] and Raman shifts[9]] were related to the pK_a of the conjugate acids HX, as a measure of the σ-donor capacity of the O-bound anions. The fair to good correlations for these parameters led us to expect a similar trend in the δ_{Sn} values. Figure 1 shows that this expectation is only partially met. First, the *overall* trend from weak to strong σ-donors is in the direction of greater deshielding; i.e., increased electron donation from the axial ligand results in a *downfield* shift. This is contrary to arguments based simply on electron density at the tin atom. It should also be noted that, where both (TPP)SnX_2 and (TPP)Sn(OH)X were observed, the chemical shift changes from (TPP)Sn$(OH)_2$ were additive within *ca.* 1 ppm. Even the overall trend in Figure 1 shows pronounced curvature, suggesting the possible existence of two opposing influences. The most striking point to emerge from Figure 1 is the cluster of data for the carboxylate ligands, which appear to be in opposition to the general trend, especially for the benzoate, salicylate, and acetate. This behavior has been observed before, in the above-mentioned series (TPP)Sn(X)(O_2CH), where the various carboxylate anions exerted rather different influences on the attached *trans*-formate ligand, despite their similar pK_a values. In particular, formate and acetate appeared to have very different *trans*-influences, as measured by ^3J(Sn–O–C(O)–H).[8]

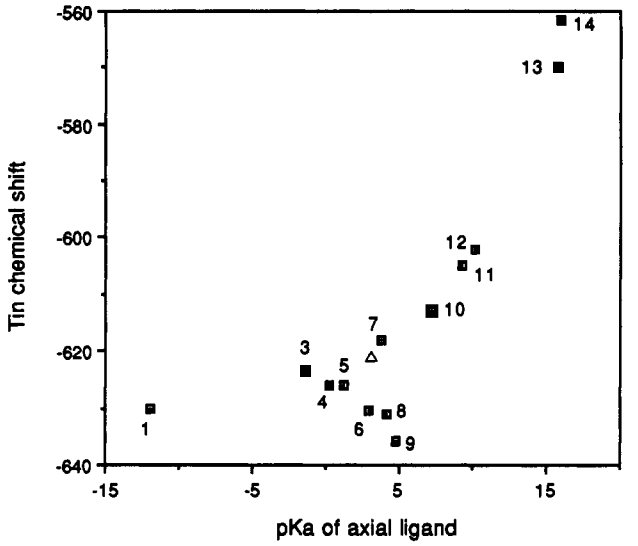

Figure 1. Plot of ^{119}Sn chemical shift for (TPP)SnX_2 vs pK_a of conjugate oxoacid HX (△ = datum for (TPP)SnF_2). Points are labeled according to Table 1.

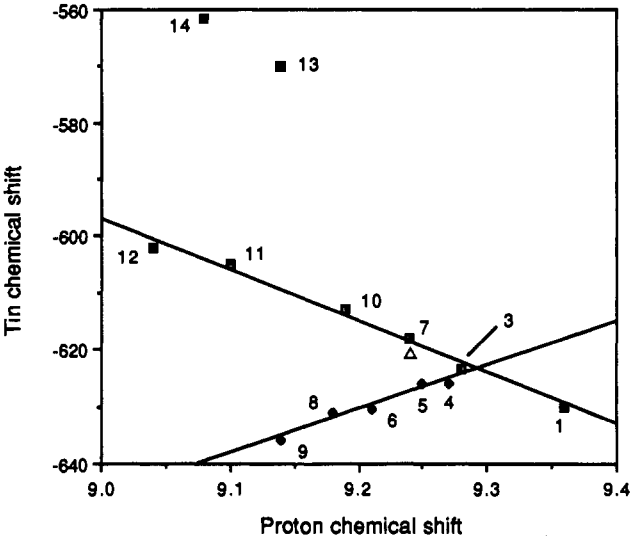

Figure 2. Plot of ^{119}Sn chemical shift for (TPP)SnX_2 vs ^{1}H chemical shift of pyrrole β protons (△ = datum for (TPP)SnF_2). Points are labeled according to Table 1.

Comparison of the ^{119}Sn chemical shifts and the ^{1}H chemical shifts of the pyrrole β protons for the complexes (TPP)SnX_2 produces the remarkable results shown in Figure 2. This plot emphasizes the unusual deviation of the carboxylate complexes. Correlation coefficients for the two lines shown in Figure 2 are 0.980 (for the five carboxylates, excluding formate) and −0.995 (for the other ligands, excluding hydroxide and methoxide). The last two ligands were previously noted to have anomalous σ_H values,[7] for which we cannot presently see a simple explanation. Tin chemical shift data have been collected for many organic and inorganic derivatives.[21,24,25] The chemical shifts of many nuclei, including ^{119}Sn, have previously been discussed in terms of the equation given by Jameson and Gutowsky,[26] which has been discussed by the authors of the above-mentioned reviews. In general, it is said that the paramagnetic term is the dominant influence on the overall shielding constant for heavy nuclei with wide chemical shift ranges. The three contributors to the paramagnetic term are ΔE, an average singlet–triplet excitation energy, the p and d electron imbalance, and the effective nuclear

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charge.[21,24-26] These terms cannot usually be separated, even for fairly closely related compounds, so approximations based simply on predicted electron density at the tin nucleus often break down.[21]

An increase in the electron-withdrawing ability of groups bound to tin generally leads to a downfield shift, especially in related molecules where the point of variation is remote from the tin atom, e.g. in triphenyltin carboxylates, for which the downfield shift is approximately linear with decreasing pK_a of the carboxylic acid.[27] This is consistent with our data for the carboxylates, with the notable exception of formate. When changes are made to the coordinated atoms closer to the tin nucleus, e.g. changing from carboxylates to the other series of anions, or even from –O–C(O)–R to –O–C(O)–H, it is not unexpected that exceptions should arise.[21] However, the complete *reversal* of the "normal" trend is notable. Although the nature of the axial ligands has a pronounced influence on the electronic spectra of tin(IV) porphyrin complexes,[7,10,28] π–π^* transitions are noncontributors to the ΔE term.[21] Further speculation is probably not warranted, but one should clearly take care in assigning structures of tin porphyrin complexes in, e.g., biological systems, solely on the basis of ^{119}Sn chemical shifts.

In the other comparative studies,[7-11] the halides behaved differently from the O-bound ligands, and this is again the case here. The trend in chemical shifts is not monotonic, with a downfield shift from F to Cl and then a very large upfield shift to Br and I. The latter effect is the normal behavior for ^{119}Sn chemical shifts in tetrahedral Sn(IV) species containing the three heavier halides and is expected on the basis of electronegativities.[21] In other data sets for TPP complexes, such as ^4J(Sn–H) in (TPP)SnX_2[7] and ^3J(Sn–H) in (TPP)Sn(X)(O_2CH),[8] the values for X = F fit in well with those of the O-bound ligands, e.g. in correlations with σ-bonding ability of X^-. This has previously been attributed to the dominance of σ-donation for first-row elements.[7,8] At least for these δ_{Sn} correlations (Figures 1 and 2), the point for X = F is located among those of the O-bound ligands. The reasons for the apparent reversal of the normal trend from F to Cl are obscure, with the inclusion of π-bonding effects further complicating the factors mentioned above.

Line Widths. We have found that, for the O-bound ligands, in contrast to the chemical shift changes, some consistent trends emerge when ^{119}Sn line widths are compared. The width at half-height data in Table 1 were obtained by simulating the spectral data as single Lorentzian functions. Despite the low signal-to-noise ratios in many of the spectra, good to excellent fits were seen. It should be noted that we first checked that there was no residual ^{1}H coupling present, by measuring the same signal [in (TPP)$SnBr_2$] without ^{1}H decoupling and with single frequency on-resonance ^{1}H decoupling. In the former case, the line width increased from 37 to 78 Hz, which is expected for a nine-line signal with ^4J(Sn–H) = 15.2 Hz[7] and a proton-decoupled line width of 37 Hz. In the latter case the spectrum was identical to that observed with broad band decoupling.

The obvious explanation for the line width differences is change in the coupling constant between ^{119}Sn and ^{14}N, or a convolution of coupling and quadrupolar relaxation variations. The line width of the tetramethyltin resonance varied between *ca.* 8 and 20 Hz (when transformed under the same conditions as in Table 1), so that "natural" line width in the absence of ^{14}N effects would be expected to be of that order. We examined one of the more soluble complexes, (TPP)Sn(O_2CH)$_2$, under high digital resolution and discerned no fine structure; we also found that a single Lorentzian fitted the experimental data very well (Figure 3). Thus we did not see discrete lines due to the theoretical nine-line coupling pattern (from four I = 1 nuclei) but rather saw a single broad line. This could be due to a coupling constant whose magnitude is much less than the line width of an individual component of that pattern. However, the effects of exchange decoupling and rapid quadrupolar relaxation cannot be separated, and we will discuss only the observable result, i.e. the total line width.

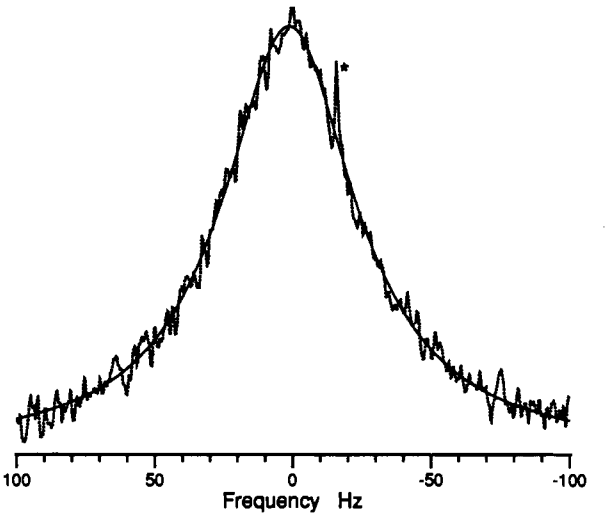

Figure 3. Experimental (dotted) and simulated (solid) line shapes, of the ^{119}Sn signal for (TPP)Sn(O_2CH)$_2$ under high-resolution conditions (see Experimental Section). The spike marked with an asterisk is an artifact.

As mentioned in the Introduction, Milgrom *et al.* postulated that large variations in line widths of ^{195}Pt resonances in their Pt(II) complexes are due to differences in ^{195}Pt–^{14}N coupling (presumably convoluted with relaxation effects, as they likewise did not see fine structure).[17] These variations were attributed to different degrees of π-back-bonding from the metal orbitals to the porphyrin e_g orbitals.[17] A plot of line width against pK_a of HX for the (TPP)SnX_2 complexes gives a good correlation (r = –0.949) and leads us to the conclusion that the line width reflects a quantity which might be termed an overall "extent of interaction" between the tin nucleus and the four nitrogens. This is a function of the coupling constant and the efficiency of quadrupolar relaxation, both of which increase as the σ-donation from the X ligand *decreases*, and it is expected therefore to be a function of the internuclear distance. The ^4J(Sn–H) values for these complexes were previously shown to correlate with pK_a,[7] and so it is not surprising that the line widths correlate very well with the former quantity (r = 0.968). This plot is shown in Figure 4 and indicates that increased σ-donation from the X ligand weakens the coordination in the porphyrin plane and that this *cis*-influence is reflected in the Sn–N bonds and throughout the σ-bond framework to the peripheral C–H bonds. It is perhaps surprising, in view of the δ_{Sn} results above, that the behavior of the carboxylates is "normal", with the point for X = formate being farthest from the regression line. Coupling constants involving heavy nuclei [e.g. J(Pt–P), J(Pt–C), and J(Pt–H)] have been shown to be useful indicators of bond lengths and *cis*- and *trans*-influences in square planar and octahedral complexes.[29] Indeed, the ^{119}Sn line widths are possibly more precise indicators of solution bond distances in this series of complexes than are those measured by X-ray crystallography or estimated by "core size" correlations using solid-state Raman spectroscopy.[9] Although we have only two ligands for comparison, changing the porphyrin to OEP results in an increase in line width, while the TTP complexes show a slight decrease for the three examples. The significance of these data is presently unknown, as the Sn–H couplings involving the *meso*-protons of (OEP)SnX_2 complexes are small ($\leq$*ca.* 4 Hz). The changes in $\nu_{1/2}$ are in the same

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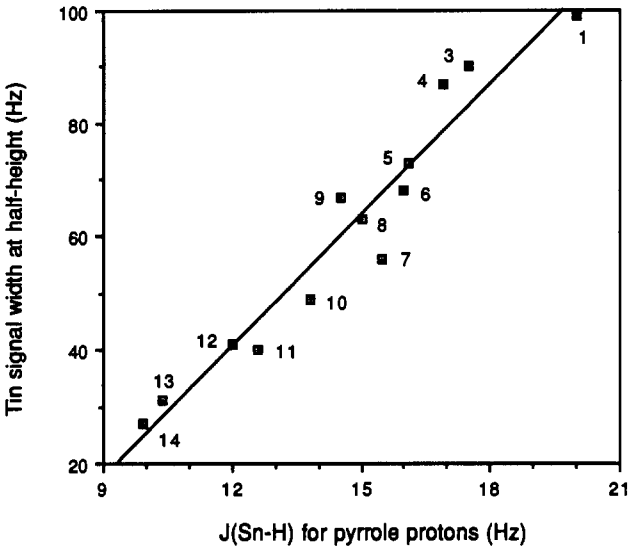

Figure 4. Plot of width at half-height for ^{119}Sn signals vs ^{4}J(Sn–H) (pyrrole β protons) for (TPP)SnX_2 complexes. Points are labeled according to Table 1.

direction (OEP > TPP) as those observed for ^{195}Pt in Pt(II) complexes.[17]

The halides again exhibit behavior totally different from that of the O-bound ligands, in that large variations are seen in $\nu_{1/2}$, with very small changes in ^{4}J(Sn–H) and indeed in Raman shifts of bands normally used for core size comparisons.[9] Here there may be other effects at work, such as quadrupolar broadening by ^{127}I (but apparently not from ^{35,37}Cl and ^{79,81}Br, all of which are quadrupolar). It is possible that the narrowing from X = F to X = Br represents a measure of stronger Sn–X bonding, as the valence orbital matching should be better, and hence this may be the first sensitive indicator of the *cis*-influences for the halides. We are presently awaiting crystallographic data on the series of halide complexes, to see if there are structural reasons for these trends.

Conclusions

The chemical shifts conform to the normal pattern for ^{119}Sn, namely that there are several interrelated factors governing the shielding constants. For axial ligands in which the point of variation is remote from the tin atom, increased shielding is associated with stronger donors. In the other cases, the reverse trend is observed, and there is evidence for the intrusion of more complications for the halides. For the TPP complexes, the line widths correlate well with ^{4}J(Sn–H) and so appear to be useful indicators of the tendency of the axial anions to weaken the bonding in the tin–porphyrin plane. In conjunction with ^{1}H NMR studies, measurements of ^{119}Sn chemical shifts and line widths should make possible the estimation of equilibrium constants for axial ligand exchange reactions. This is important for the potential biological and bioanalytical applications of complexes of tin(IV) with porphyrins and related macrocycles. It will be necessary now to examine systems in aqueous environments to approach more realistically the inter- and intracellular situations. It was recently reported that complexation with a tin(IV) ion changes significantly the degree of uptake and sites of cellular localization of various benzochlorins.[30] The data we present here, and the observations on the triflate and perchlorate complexes, suggest that ^{119}Sn NMR spectroscopy should be useful in understanding the biological properties of such species.

Acknowledgment. We thank Dr. P. A. Duckworth for assistance with the spectral simulations. The NMR spectrometer was purchased with the assistance of the Australian Research Council.

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