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TIN(IV) PORPHYRIN COMPLEXES—III.* NMR *TRANS*-INFLUENCES IN TIN(IV) TETRAPHENYLPORPHYRIN COMPLEXES

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Abstract—^{1}H NMR data are reported for the series of octahedral tin(IV) complexes Sn(TPP)(OCOH)X, where TPP is 5,10,15,20-tetraphenylporphyrin and X = OSO_2CF_3, ONO_2, NCS, $OCOCF_3$, OCOH, $OCOC_6H_4$-*o*-OH, $OCOC_6H_5$, $OCOCH_3$, OC_6H_4-*p*-CH_3, OH, OCH_3, F, Cl, Br and I. The mixed-ligand complexes were generated as mixtures also containing the symmetrical complexes $Sn(TPP)(OCOH)_2$ and $Sn(TPP)X_2$. The chemical shifts of the formate protons and the tin–proton coupling constants, ^3J(Sn—O—C(O)—H), show a fair correlation with the basicity of the ligand X for the O-bound ligands, but the halide complexes demonstrate the importance of π-bonding. The *trans*-influence and *cis*-influence are in the same direction, ie. a ligand which weakens the bond to the *trans*-formate ligand, also weakens the tin–porphyrin coordination.

The tin(IV) complexes of porphyrins and related ligands are proving useful in a range of chemical and biological fields. For example, tin(IV) protoporphyrin is an inhibitor of haem oxygenase, making it a possible agent for treatment of neonatal jaundice.[1,2] Tin complexes of modified porphyrins such as purpurins are being studied as photodynamic therapy drugs, and show good efficacy *in vitro*.[3] Meyerhoff and co-workers reported that poly(vinyl chloride) membrane electrodes impregnated with tin porphyrins display excellent but unexplained selectivity for salicylate over various other anions.[4,5] The determination of salicylate in blood and urine is an important measurement for patients undergoing aspirin therapy. The complexes of water-soluble synthetic porphyrins such as tetrakis(N-methyl-4-pyridyl)porphyrin were studied as possible solar energy capture agents.[6] Lastly, the favourable chemical and spectroscopic properties of tin(IV) porphyrins enable the study of metal–ligand interactions and electronic effects of porphyrin substituents. An understanding of these properties should be useful in extending the uses of these complexes.

Previous investigations have generated an NMR and electronic absorption spectroscopic *cis*-influence series for a number of anionic axial ligands, especially O-donors.[7] A preliminary report suggested the use of the formato ligand as an NMR probe of *trans*-influences,[8] while the instructional value of these complexes has also been pointed out.[9] We now report the results of studies of a series of formato complexes, Sn(TPP)(OCOH)X (Table 1), which yield the *trans*-influence data and allow the comparison of *cis*- and *trans*-influences in the same series.

RESULTS AND DISCUSSION

Preparations of complexes

The most general method for the preparation of tin(IV) porphyrins with identical axial ligands, $Sn(TPP)X_2$, is the acidolysis of $Sn(TPP)(OH)_2$

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* For Part II, see ref. 7.

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Table 1. Selected NMR data for Sn(TPP)(OCOH)X complexes[a]

Number in text	X	Pyrrole β-H		Formate H		X Ligand
		δ	^4J(Sn—H)	δ	^3J(Sn—H)	
1	OSO_2CF_3	9.35	17.6	3.67	70.8	
2	ONO_2	9.29	16.6	3.08	53.1	
3	NCS	9.30	15.9	2.82	46.1	
4	$OCOCF_3$	9.27	16.1	2.88	45.7	
5	OCOH	9.29[b]	15.5[b]	2.70[b]	42.9[b]	
6	$OCOC_6H_4$-*o*-OH	9.30	15.9	2.70	37.8	4.04 (br d, 6″), 5.74 (t, 5″), 6.04 (d, 3″), 6.63 (dt, 4″), 9.38 (br, OH)
7	F	9.32	—[c]	2.48	34.5	
8	$OCOC_6H_5$	9.28	15.9	2.45	31.1	4.97 (br d, 2″, 6″), 6.37 (t, 3″, 5″), 6.67 (dt, 4″)
9	Cl	9.30	—[c]	2.33	30.5	
10	I	9.24	14.4	2.30	29.9	
11	Br	9.23	15.4	2.28	29.7	
12	$OCOCH_3$	9.26	14.7	2.19	28.6	−0.88, ^4J(Sn—H) 4 Hz
13	OC_6H_4-*p*-CH_3	9.17	13.7	2.10	25.4	1.72 (s, CH_3), 1.79 (d, 2″, 6″), 5.49 (d, 3″, 5″)
14	OH	9.26	13.2	1.90	23.5	−6.9 (v br)[d]
15	OCH_3	9.28	12.8	1.89	22.4	−1.79, ^3J(Sn—H) 70.8 Hz

[a] Chemical shifts in ppm relative to $CHCl_3$ at 7.24. Protons of the *meso*-phenyl groups appeared at *ca* 7.8 (3′, 4′, 5′) and *ca* 8.2–8.4 (2′, 6′) ppm. Tin–proton coupling constants (Hz) are the average of the $J(^{119}Sn—H)$ and $J(^{117}Sn—H)$ values, where these were resolved.

[b] Averages of all determinations (see text).

[c] Obscured by other peaks.

[d] Literature value.[8]

with excess HX.[8,9] Reactions are rapid and quantitative even with carboxylic acids and phenols. The corresponding reaction of the mixed complex Sn(TPP)(OCOH)(OH) with one equivalent of HX, was investigated as a route to the required complexes Sn(TPP)(OCOH)X. Since the complex Sn(TPP)(OCOH)(OH) is always contaminated with the symmetrization products $Sn(TPP)(OCOH)_2$ and $Sn(TPP)(OH)_2$, the resulting product will likewise be contaminated with the diformato species and $Sn(TPP)X_2$. In any case, redistribution will occur to give more or less of these complexes. These will be the only three complexes present as long as (i) acidolysis is fast and (ii) only OH groups are protonated and displaced by X^-. This method was found to be satisfactory for the carboxylic acids, which could be added as solutions in CH_2Cl_2 or $CHCl_3$, and complexes **6**, **8** and **12** were prepared by this route.

When stronger acids (eg. HNO_3, HCl, HBr) were used as aqueous solutions in a two-phase reaction, the other two possible products, $Sn(TPP)(OH)_2$ and Sn(TPP)(OH)X, were also found as products. This could be due to either incomplete reaction with the dihydroxo complex or displacement of formic acid rather than water because of locally distorted stoichiometric ratios at the water–CH_2Cl_2 interface. The presence of five complexes in such cases was considered undesirable, so this method was subsequently abandoned. A cleaner method applicable to all species is the redistribution reaction between the two bis(acido) complexes

$$Sn(TPP)(OCOH)_2 + Sn(TPP)X_2 \rightleftharpoons 2Sn(TPP)(OCOH)X.$$

The extents and rates of these reactions varied considerably with the ligand X. More rigorous studies will be required before the significance of such variation can be determined. The redistribution reaction makes it virtually impossible to purify the mixed complexes, as the latter are usually the most soluble components in the mixtures. Since the complexes of interest in this study give unmistakable NMR spectra, the mixtures are just as suitable as the pure complexes for our purposes, provided there is no exchange broadening nor any extreme concentration dependence (see below).

NMR spectra (*Table* 1)

General

The formate resonances of the mixed complexes were easily assigned in all cases, since the diformato complex (**5**) was present in all samples. Comparison of peak heights and knowledge of chemical shift trends enabled assignment of the β-pyrrole resonances. In some cases, there was severe overlap of β-pyrrole peaks and/or satellites, making measurements of ^4J(Sn—H) difficult or impossible (eg. in **7** and **9**). Other axial ligand resonances were assigned by expected coupling patterns, peak heights, and comparison with pure samples of Sn(TPP)X_2 complexes.[7-10]

Concentration effects on chemical shifts and coupling constants were assessed by observing the signals due to the diformato complex. Over all the mixed samples, the range was 2.65–2.75 ppm, while pure samples of **5** gave a chemical shift of 2.75 ppm at 0.1 M and 2.63 ppm at 0.01 M. Comparisons of peak heights and known starting concentrations gave approximate values for the concentration of **5** in the mixed samples, but these showed extreme scatter when plotted against the chemical shift. The conclusion must therefore be that specific intermolecular effects are blurring the concentration dependence of this shift. As there are no apparent line broadening effects, this is presumably not a shift due to chemical exchange. Since the individual concentrations of the various species in each mixture are uncontrollable because of variations in equilibrium constants, the quoted shifts must be regarded as precise to only *ca* ±0.05 ppm. The extreme values of the ^3J(Sn—H) values for **5** were 42.6 and 43.2 Hz (average of ^{119}Sn and ^{117}Sn coupling constants), so concentration and ligand specific effects on the coupling constants appear to be of less significance, and the precision is *ca* ±0.2 Hz. The chemical shifts of the β-pyrrole protons also show a concentration dependence, for example, for **5**, $\delta = 9.33$ at 0.1 M and 9.24 at 0.01 M. This explains the small discrepancies between the present data and those reported previously,[7,8] the latter having been recorded at concentrations less than 0.02 M. Concentration effects on porphyrin chemical shifts are well known.[11]

The trans-*influence*

The *trans*-influence gives a relative estimate of the ability of a ligand to weaken the bond *trans* to itself in the ground-state of a complex.[12] In this series, the relative strengths of the tin–formate bonds are being studied. The *trans*-influence of a ligand can be examined by considering the chemical shift of the formate proton and the coupling constant ^3J(Sn—H). There is a strong correlation between these two parameters (Fig. 1, $r = 0.986$). It should be noted that the coordination of carboxylate anions to tin(IV) porphyrins is unidentate. This has been shown by IR spectra[13] and crystal structures.[10] The chemical shift presumably reflects the electron density at the nucleus of the formate proton, effects of *trans* ligands being transmitted by contact interactions through the σ-bonds of the Sn—O—C(O)—H fragment. Lengthening of the Sn—O bond (reflecting a strong *trans*-influence of X) might be expected to shift the formate signal downfield, as it would reside on average farther out in the shielding zone of the macrocycle. Clearly this is outweighed by the electronic effects. There is a limit to such lengthening, but bases stronger than methoxide would be required to probe any curvature in Fig. 1. The determination of bond distances in mixed complexes may prove impossible as they cannot be crystallized pure, so the relative magnitudes of these effects may not be assessable. Because of the relationship between δ_H and ^3J(Sn—H), discussion of the reasons for the *trans*-influence order will be confined from now on to the coupling constants, as these enable more precise comparison with *cis*-influences.

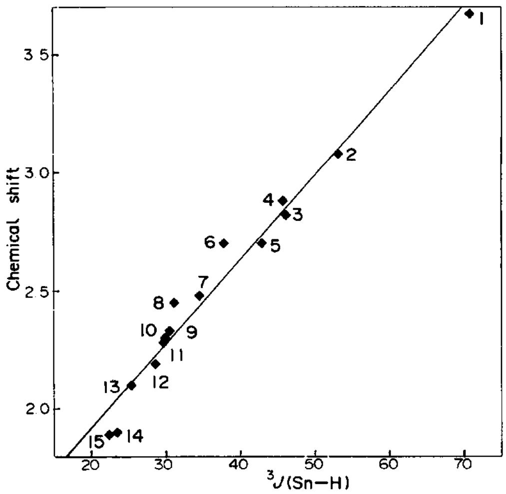

Fig. 1. Plot of chemical shift (δ, ppm) of the formate protons vs ^3J(Sn—H) (Hz) for Sn(TPP)(OCOH)X complexes. Numbering as in Table 1.

The coupling constant ^3J(Sn—H) is quite sensitive to changes in the *trans* ligand, varying from 22.4 to 70.8 Hz. Figure 2 shows the relationship between ^3J(Sn—H) and the pK_a of the conjugate acid of the ligand X.[14-16] The O-bound ligands and thiocyanate yield a fair correlation ($r = -0.940$), while the halides are quite different and appear to fit on another line of near-zero slope. The behaviour of the O-bound ligands appears to be broadly explicable in terms of the proton basicity of X^-. It has been assumed that the triflate ion is coordinated to the tin atom in complex **1**. The Sn(TPP) complexes containing triflate or perchlorate have very

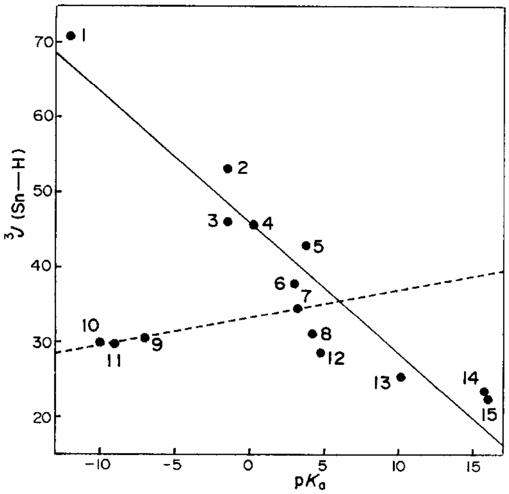

Fig. 2. Dependence of ^3J(Sn—H) (Hz) for formate protons in Sn(TPP)(OCOH)X complexes on the pK_a of the conjugate acids HX. Numbering as in Table 1. Solid line: linear regression for O-ligands; dashed line: linear regression for halides.

low solubility in chloroform, while they are readily soluble in acetone and THF. This is presumably due to coordination of solvent molecules (or adventitious water), with dissociation of the weakly basic anions. No other complexes in these series exhibit such behaviour. Kadish *et al.* have reported perchlorate dissociation in electrochemical studies of similar complexes.[17] The major species giving rise to sharp NMR lines in $CDCl_3$ solutions of **1** does seem to be the "covalent" form, since the chemical shifts and coupling constants fit in with other O-bound ligands for a pK_a of -12 rather than -1.74 as would be expected for X = H_2O. Slow crystallization of the bis(triflate) complex led, on the other hand, to the bis(aqua) salt.[10] In the present study, we could not obtain the data for the mixed formato/perchlorato complex because of dissociation and consequent precipitation.

The σ-bonding capacity of the ligands (as reflected by their donor strength to the proton) is probably the dominant factor for the first row donors. In fact, fluoride and N-bound thiocyanate also fit well with the trend shown by the O-donors. There are some notable deviations. The most surprising is the large difference between formate (**5**) and acetate (**12**). Complex **12** was prepared by both methods described above, with identical results. The scatter exhibited by the O-bound ligands is such that there are some less obvious effects at work, but the reasons for the formate/acetate discrepancy are particularly elusive. The difference between these ligands is apparent not only in the formate and β-pyrrole signals, but also in the acetate signals. The methyl group appears at -0.88 ppm in **12** and at -0.99 ppm in Sn(TPP)$(OCOCH_3)_2$, a shift consistent with that shown by the other protons.

The halides clearly exhibit very different effects from the O-donors. This is the first series of tin(IV) porphyrins examined by NMR which includes (i) all the halides and (ii) a range of O-ligands which spans such a spectrum of donor strengths. Gouterman *et al.* studied excited-state properties of the dihalo complexes of electron-rich porphyrins,[18] while other reports have examined more restricted sets of ligands.[7,17,19] The *trans* bond weakening abilities of Cl^-, Br^- and I^- are much greater than their proton basicity would suggest. This is not surprising since they possess unfilled *d*-orbitals available for π-backbonding from the filled tin d_{z^2} orbital, or molecular orbitals derived from it. However, the similarity of the coupling constants (and chemical shifts) for **9**, **10** and **11** argues that π-donation from filled p_π ligand orbitals to empty p_π and d_π orbitals on Sn is also important. The exact energies of the various orbitals will control the interplay of these effects. The ability of the TPP ligand to act as a π-acceptor presumably "softens" the tin centre (ie. it is very unlike a hard Sn^{4+} ion), and hence relatively strong interactions would be expected for the softer halides Br and I.

The cis-*influence vs the* trans-*influence*

These two effects can now be assessed *in the one series* of complexes Sn(TPP)(OCOH)X, by comparing ^4J(Sn—H) (β-pyrroles) with ^3J(Sn—H) (formates). The chemical shifts could also be used, but suffer from the concentration effects noted above. Unfortunately, the changes in the former coupling constants are rather small compared with their precision. Figure 3 shows this comparison, and the clustering of values around *ca* 15.5 Hz is apparent. There is a broad trend, although the correlation is not well defined. Greater sensitivity would be possible by using ^4J(Sn—H) in the series Sn(TPP)X_2, as the range of values is wider, but this is not a valid comparison, since the *trans*-interactions of the X ligands may be convoluted with the *cis*-influences. Figure 3 does show that the two influences are generally in the *same direction*, which is not necessarily the case for other complexes, for example, in various platinum(II) alkylbis(tertiary phosphine) and similar complexes, the two influences are often in opposite directions.[20] This implies that a ligand which weakens the *trans* Sn—O bond also weakens the bonding in the porphyrin plane, presumably by placing a higher demand on the electrons of the tin atom. The quantities being mea-

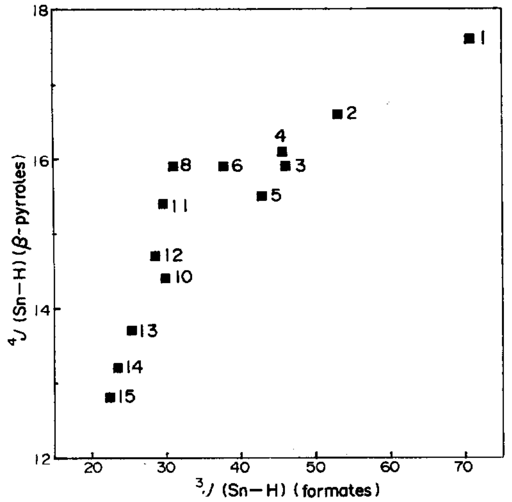

Fig. 3. Relationship between ^4J(Sn—H) (Hz) for the β-pyrrole protons and ^4J(Sn—H) (Hz) for the formate protons in Sn(TPP)(OCOH)X complexes. Numbering as in Table 1. The data for complexes **7** and **9** are missing because of peak overlap.

sured, ie. tin–proton coupling constants, are intrinsically dependent only on *s* orbital electron density or the *s* character of relevant molecular orbitals, since these are the only orbitals with non-zero coefficients at the nuclei.[12] However, it is clear from these data that π-effects are transmissible through the tin–porphyrin and tin–formate bonding orbitals, and can be felt at the β-pyrrole and formate proton nuclei.

In summary, the two series Sn(TPP)X_2[7] and Sn(TPP)(OCOH)X have demonstrated the utility of NMR chemical shifts and metal–proton coupling constants in probing metal–ligand binding. Further studies are now required to relate these ground state effects to data such as redistribution and ligand substitution equilibrium constants.

EXPERIMENTAL

General

Instruments were as described previously.[7] Chloroform was distilled from anhydrous Na_2CO_3. Other solvents, acids, etc., were A.R. or "zur Synthese" grade. Starting materials (Sn(TPP)$(OH)_2$, Sn(TPP)(OCOH)(OH), and various Sn(TPP)X_2 complexes) were available from previous studies.[7,8] The preparations and crystal structures of Sn(TPP)$(OSO_2CF_3)_2$, Sn(TPP)$(OCOC_6H_5)_2$ and Sn(TPP)$(OCOC_6H_4$-*o*-$OH)_2$ will be described elsewhere.[10]

Preparation of new Sn(TPP)X_2 *complexes*

X = F. A solution of Sn(TPP)$(OH)_2$ (38 mg, 0.05 mmol) in CH_2Cl_2 (20 cm^3) was shaken in a separating funnel with aqueous HF (1 M, 5 cm^3) for 30 min. The organic layer was separated, dried over anhydrous Na_2SO_4 and the solvent was evaporated. The residue was recrystallized from CH_2Cl_2–hexane to yield shiny purple prisms (31 mg, 80%). (Found: C, 68.8; H, 3.6; N, 7.3. $C_{44}H_{28}F_2N_4Sn$ requires: C, 68.7; H, 3.7; N, 7.3%); δ_H *ca* 7.8 (m, *meta*-, *para*-H), *ca* 8.4 (m, *ortho*-H) and 9.24 (s, β-pyrrole, ^4J(Sn—H) 14.9 Hz); λ_{max} ($\varepsilon \times 10^{-3}$) ($CHCl_3$) 419 (695), 514 (3.5), 553 (24.4) and 591 (9.8) nm.

X = $OCOCF_3$. Trifluoroacetic acid (3.1×10^{-2} cm^3, 0.4 mmol) was added dropwise with stirring to a solution of Sn(TPP)$(OH)_2$ (77 mg, 0.1 mmol) in CH_2Cl_2 (10 cm^3). After 15 min, the solution was dried over anhydrous Na_2SO_4 and the solvent was evaporated. The residue was recrystallized from CH_2Cl_2–hexane to yield sparkling purple prisms (52 mg, 54%). (Found: C, 61.1; H, 2.9; N, 5.7. $C_{48}H_{28}F_6N_4O_4Sn$ requires: C, 60.2; H, 3.0; N, 5.9%); δ_H *ca* 7.8 (m, *meta*-, *para*-H), *ca* 8.3 (m, *ortho*-H) and 9.25 (s, β-pyrrole, ^4J(Sn—H) 16.9 Hz); λ_{max} ($\varepsilon \times 10^{-3}$) ($CHCl_3$) 420 (622), 514 (3.4), 553 (23.1) and 592 (8.3) nm; ν_{max} (KBr) 1718, 1202, 1174 and 1148 (all vs) cm^{-1} ($OCOCF_3$).

Preparations of Sn(TPP)(OCOH)X *complexes*

(a) *By acidolysis of* Sn(TPP)(OCOH)(OH). A solution of the acid HX (one equivalent) in CH_2Cl_2 was added dropwise to a solution of Sn(TPP)(OCOH)(OH) (38 mg, 0.05 mmol) in CH_2Cl_2 (5 cm^3). After stirring for 30 min, the solution was filtered through anhydrous Na_2SO_4, and the solvent was evaporated. The vacuum-dried residue was dissolved in $CDCl_3$ (0.5 cm^3) and filtered into an NMR tube.

(b) *By redistribution of* Sn(TPP)$(OCOH)_2$ *and* Sn(TPP)X_2. Equimolar amounts of the two complexes (0.01–0.025 mmol) were separately dissolved in $CDCl_3$, mixed, filtered into an NMR tube, and the volume was made up to *ca* 0.5 cm^3. In this way, the *total* Sn(TPP) concentration was in the range 0.02–0.1 M. The reactions were monitored by NMR until no further change was apparent.

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