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SPECTROSCOPIC *CIS*-INFLUENCES IN OCTAHEDRAL TIN(IV) *MESO*-TETRAPHENYLPORPHYRIN COMPLEXES

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Abstract—Visible absorption and ^1H NMR spectra have been measured for a series of octahedral tin(IV) porphyrin complexes $Sn(TPP)X_2$, where TPP is *meso*-tetraphenylporphyrin and X is Cl, OH, OMe, OAc, NO_3, ClO_4, Br, I, NCS and OC_6H_4-*p*-Me. The tin–proton coupling constants to the β-pyrrole protons decrease from 19.2 Hz ($X = ClO_4$) to 9.9 Hz (X = OMe), and for the oxygen-bound ligands, correlate well with the basicity of the ligands. The halides do not fit this relationship, perhaps because of π-bonding effects. The chemical shifts of the β-protons also depend on the nature of X, and vary from 9.35 ($X = ClO_4$) to 9.04 ($X = OC_6H_4$-*p*-Me) ppm. Increasing basicity of X causes red shifts in the visible spectra, as well as a decrease in the molar absorption coefficient ratio ($\varepsilon_\beta/\varepsilon_\alpha$) for the visible absorption bands. Tin–proton coupling constants for the axial ligands OH, OMe and OAc are reported. The complex $Sn(TPP)(ClO_4)_2$ exhibits unusual NMR behaviour in $CDCl_3$ solutions, possibly due to self-aggregation.

NMR spectra of diamagnetic metalloporphyrins containing spin-$\frac{1}{2}$ magnetically active metal ions have been exploited to a limited extent in structural and reactivity studies. Various data for thallium(III),[1–3] mercury(II),[3] phosphorus(V),[4] platinum(II)[5–7] and tin(IV)[8–11] complexes of octaethylporphyrin (OEP) and tetraphenylporphyrin (TPP) have been published, including some metal–^1H and metal–^{13}C coupling constants. Some data have also been forthcoming on the NMR properties of proton-bearing axial ligands in tin(IV) complexes,[8–11] including interesting long-range couplings between axial OH protons and ^{13}C nuclei on the porphyrin periphery.[8] Studies of five-coordinate indium(III) porphyrins have revealed correlations between the donor strengths of axial ligands and electro- and spectrochemical properties,[12] although the absence of a spin-$\frac{1}{2}$ isotope necessarily restricted the NMR data to chemical shifts.

The present study was undertaken to evaluate the utility of coupling constants involving ^{117}Sn and ^{119}Sn in studies of the chemistry of these metalloporphyrins, in particular with respect to the reactions of axial ligands. In this paper, the syntheses, visible absorption and ^1H NMR spectra of a series of octahedral Sn(IV) TPP complexes (Fig. 1) are reported, and correlations between spectroscopic properties and the nature of the axial ligands are discussed.

RESULTS AND DISCUSSION

IR spectra

Complexes containing IR-active axial ligands exhibited the expected bands in solid-state spectra (Table 1). The hydroxo ligands in **2** were identified by a weak, sharp doublet at 3590 and 3610 cm^{-1}.[8] The low frequency of the ν(CN) band in the spectrum of **9** suggests that the thiocyanate ligands are N-bound.[13] NMR data support this conclusion (see below).

The situation with the O-bound ligands in complexes **3**, **5** and **6** is less clear. It appears that, especially for **3**, both unidentate and bidentate ligands are present in the solid state. In $Zr(OEP)(OAc)_2$, bands at 1560, 1460 and 690 cm^{-1} were assigned to chelating acetates, while in $Sn(OEP)(OAc)_2$, bands at 1640 and 1380 cm^{-1} indicated unidentate ligands.[14] Intermediate coordination has been found crystallographically for In(OEP)(OAc) which absorbs at 1570 and 1405 cm^{-1}.[15]

Table 1. Visible absorption and selected IR data for $Sn(TPP)X_2$ complexes

Axial ligand	IR data for axial ligands	Visible absorption data: λ_{max} nm ($\varepsilon \times 10^{-3}$) $B(0,0)$ (Soret)	$Q(2,0)$	$Q(1,0)(\beta)$	$Q(0,0)(\alpha)$	$\varepsilon_\beta/\varepsilon_\alpha$
ClO_4[a]	1135, 1095, 1030 s, br, 920 m, 618 m	424 (520)	513 (3.1)	552 (20.3)	591 (8.5)	2.39
NO_3[b]	1515 s, 1380 s, br, 1275 s, br, 958 s, br	423 (606)	514 (3.3)	553 (22.7)	593 (8.4)	2.70
OAc[b]	1660 s, 1560 m, br, 1465 m, 1275 s, br	425 (555)	518 (3.1)	557 (19.9)	596 (8.5)	2.34
NCS[a]	1998 vs, 845 w	425 (598)	519 (3.6)	559 (19.4)	598 (11.2)	1.73
OMe		427 (30.1)[c]	520 (0.17)[c]	559 (1.00)[c]	598 (0.60)[c]	1.67
OH[a]	3610 vw, 3590 vw	426 (636)	521 (3.6)	560 (21.7)	600 (13.2)	1.64
Cl		427 (691)	520 (3.9)	561 (21.0)	600 (13.1)	1.60
OC_6H_4Me[a]	1252 s, br	425 (575)	522 (3.7)	561 (19.0)	601 (10.4)	1.82
Br		429 (617)	525 (3.5)	565 (19.8)	605 (14.6)	1.36
I[d]		428 (13.5)[c]	530 (0.24)[c]	568 (1.00)[c]	614 (0.8)[c]	1.25

[a] IR in Nujol mull.

[b] IR in KBr disc.

[c] ε given relative to $Q(1,0)$ band.

[d] All bands broad, shoulders at *ca* 434 and 604 nm.

Complex **3** shows bands for both types (Table 2), while the NMR spectrum of a solution of the same material showed only single Sn-porphyrin and acetate methyl signals. The situation for the dinitrato analogue (**5**) is similarly ambiguous from the IR spectrum.[13] A poorly resolved envelope of bands from 1135 to 960 cm^{-1} for **6** is consistent with O-bound perchlorate ligands.[13–16]

Visible absorption spectra

The spectra (Table 1) of all the complexes except (**8**) are typical of Sn(IV) porphyrins, and exhibit the "normal" type of metalloporphyrin spectrum.[17] The compounds are displayed in Table 1 in order of increasing red shift of the α band. The other bands show a similar trend, although shifts for the

Table 2. Selected ^1H chemical shifts[a] and Sn–H coupling constants (Hz) for $Sn(TPP)X_2$ complexes

Axial ligand	Pyrrole β-H resonance δ	$^4J(Sn–H)$[b]	Axial ligand resonances δ	$J(Sn–H)$
ClO_4	9.35	19.2		
NO_3	9.28	17.5		
NCS	9.24	16.0		
Cl	9.18 (9.20)[c]	15.2 (15.5)[c]		
Br	9.18	15.2		
OAc	9.14	14.5	−0.96	3.6 (^4J)[b]
I	9.13	13.7		
OC_6H_4Me	9.04	12.0	1.68 (*p*-Me) 1.72 (2′, 6′), 5.42 (3′, 5′)[d]	Not observed
OH	9.14 (9.12)[c]	10.4 (9.5)[c]	−7.55 br (−7.46)[c]	*ca* 36 (^2J)[b] (37)[c]
OMe	9.08	9.9	−2.04	70.3 [$^3J(^{119}Sn–H)$] 67.1 [$^3J(^{117}Sn–H)$]

[a] In ppm relative to $CHCl_3$ at 7.24. Protons of the *meso*-phenyl groups appeared in all complexes as two multiplets centred at *ca* 8.3 (ortho) and 7.8 (meta, para).

[b] Separate couplings to ^{119}Sn and ^{117}Sn not resolved, average value given.

[c] Literature values.[8]

[d] AA′XX′; doublet separation 8.1 Hz.

Soret band are very small. Gouterman *et al.*[18] studied a smaller series of Sn(etioporphyrin-I)X_2 complexes (X = F, OCOPh, OH, Cl, Br, I) and found a similar red shift of the α band. The complex (**8**) is somewhat unstable in $CHCl_3$ solution, but it is clear that it exhibits an unusual spectrum, in that the bands are all broadened and have reduced ε_{max} compared with the other compounds. Both the instability and the spectral differences were noted for Sn(Etio-I)I_2, and to a lesser extent for Sn(Etio-I)Br_2.[18] The red shift for **8** is such that the solid appears almost black and thin films of the solution are greenish, while all the others appear red, purple or violet.

The second parameter which changes significantly over the series is the ratio of the molar absorption coefficients for the β and α bands ($\varepsilon_\beta/\varepsilon_\alpha$). A general relationship between red shift and decreasing ratio is clear, but the trend is not smooth. With the exception of X = ClO_4, the O-donors show a rough dependence of $\varepsilon_\beta/\varepsilon_\alpha$ on the strength of their conjugate acids. As discussed under NMR spectra below, the positions of the halides are exceptional. The behaviour of complex **6** may reflect aggregation (see below). The limit of these trends is probably Sn(TPP)$(CH_2SiMe_3)_2$ reported by Pommier *et al.*[10] The powerful σ-donor ligands cause a red shift of the α band to 660 nm, and a reduction of $\varepsilon_\beta/\varepsilon_\alpha$ to *ca* 0.5. A parallel series of TPP complexes is In(TPP)R, where R was varied from ClO_4 through Cl and increasingly basic alkyl groups to *t*-butyl.[12] The α-band shifted from 595 to 639 nm, and $\varepsilon_\beta/\varepsilon_\alpha$ decreased from 1.94 to 0.72. A striking difference appears, however, on perusal of the data for the electron-rich macrocycles OEP and Etio-I. The same red shift trend is evident in In(OEP)R, but the effect on $\varepsilon_\beta/\varepsilon_\alpha$ is large, and in the opposite sense to that the TPP series, viz. 0.96 (ClO_4) to 3.78 (t-Bu).[12] This reversal is also present in Sn(Etio-I)X_2, for which the ratio changes from 0.87(X = F) to 1.77(X = I),[18] and in Tl(OEP)X_2, where $\varepsilon_\beta/\varepsilon_\alpha$ varies from 1.18 (X = $OCOCF_3$) to 1.54 (X = CN).[1] Such an inversion has been noted before in comparisons of OEP and TPP complexes for different metal ions. A high value of $\varepsilon_\beta/\varepsilon_\alpha$ for TPP complexes generally indicates more stable metal ion coordination, as expected in this series for weaker donors such as NO_3, whereas the opposite is found for OEP complexes.[19] A theoretical explanation has apparently not yet been advanced.

^1H NMR spectra

The relevant ^1H data for complexes **1–10** are displayed in Table 2, together with comparable literature data. The spectra are typical of TPP metal complexes, consisting of singlet β-pyrrole resonances at lowest field, the *meso*-phenyl groups in the normal regions of 8.3 and 7.8 ppm, and signals for proton-containing axial ligands at high field. The β-pyrrole and axial ligand (X = OH, OMe, OAc) signals are flanked by Sn satellites due to coupling with ^{119}Sn and ^{117}Sn (spin-$\frac{1}{2}$, abundances 8.6 and 7.6%, respectively). Although the ^1H spectra of various Sn(IV) porphyrin complexes, e.g. Sn(OEP)X_2 (X = Cl, OMe, OPh, OAc)[9,20,21] and Sn(TPP)X_2 (X = Cl, OH)[8] have been reported, Sn—H coupling information has been unavailable until recently,[8] presumably because of signal-to-noise problems. With the advent of high-field FT instruments, such information is now accessible even for very insoluble complexes.

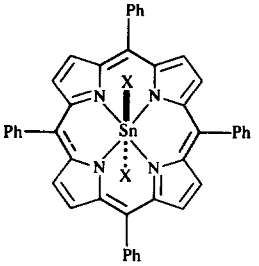
Formula	Number in text	X
	**1**	Cl
	2	OH
	3	OAc
	4	OMe
	5	NO_3
	6	ClO_4
	7	Br
	8	I
	9	NCS
	10	OC_6H_4-*p*-Me

Fig. 1. Structures of Sn(TPP)X_2 complexes.

Sn–H coupling constants

The compounds are listed in Table 2 in order of decreasing magnitude of ^4J(Sn–H) for the β-pyrrole signals. Individual couplings to ^{119}Sn and ^{117}Sn were not resolved so average values are given. If only O-bound ligands are considered, it is apparent that a representative selection of such ligands is present, spanning a wide range of donor abilities. Moreover, the coupling constants for this smaller set show a good correlation ($r = 0.991$, $n = 6$) with the pK_as of the conjugate acids[22] of the ligands (Fig. 2). This dependence may be useful in structural assignment and reactivity studies. The halides, however, do not fit this correlation, although they span a very small pK_a range, and changes in J are small. The difference in ^4J(Sn–H) for two of the complexes, i.e. **1** and **2**, has been recorded by Milgrom and Sheppard.[8] The larger value of J for X = Cl was attributed to the tendency of that ligand to engage in p_π–d_π bonding, which causes an increase in σ-overlap in the Sn–N bonds.[8] However, ^4J(Sn–H) for **8** (X = I) is slightly less than that for **1**, while the effects of π-bonding would be expected to be greater, since the 5*p* orbitals of I should be more compatible with the empty Sn 5*d*

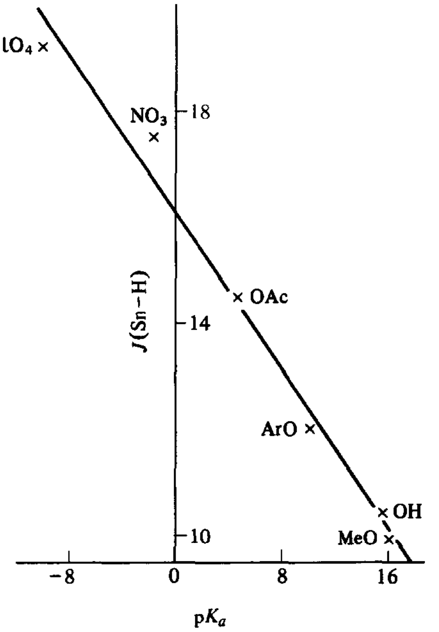


Fig. 2. Dependence of ^4J(Sn–H) (Hz) for β-pyrrole protons in Sn(TPP)X_2 complexes on the pK_a of the conjugate acids HX.

orbitals than are the 3*p* orbitals of Cl. It appears, therefore, that both increased π-donation (e.g. for the halides) and increased σ-donation (for the oxygen ligands) cause a weakening of the Sn–N bonds, which is transmitted to the peripheral protons, thus decreasing ^4J(Sn–H). Transmission of electronic effects to the β-pyrrole protons in TPP complexes has been attributed mainly to contact interactions between the electrons of the σ-bonds in the macrocycle.[1-7]

Where the two series have ligands X in common, a surprising correlation ($r = 0.996$, $n = 7$) (Fig. 3) exists between ^4J(Sn–H) in Sn(TPP)X_2 and ^1J(Pt–P)(*trans* to X) in PtX(Me)(dppe) [dppe = 1,2-bis(diphenylphosphino)ethane].[23] A naive inference is that these ligands in two completely different families of compounds are exerting similar influences on very different coupling constant types. Here the *cis*-influence in the Sn(IV) series operates in the same sense as the *trans*-influence in the Pt(II) series, which is often not the case when comparisons are made within a single type of complex, e.g. [Pt(Ar)(PEt$_3$)$_3$]BF$_4$.[24] While very little can be concluded from such an obscure comparison, perhaps the σ-transmission arguments above are reinforced by it. Interestingly, the thiocyanate point lies well off the line, suggesting again that it is N-bonded in **9**, since it has been convincingly argued that it is S-bonded in the Pt series.[23]

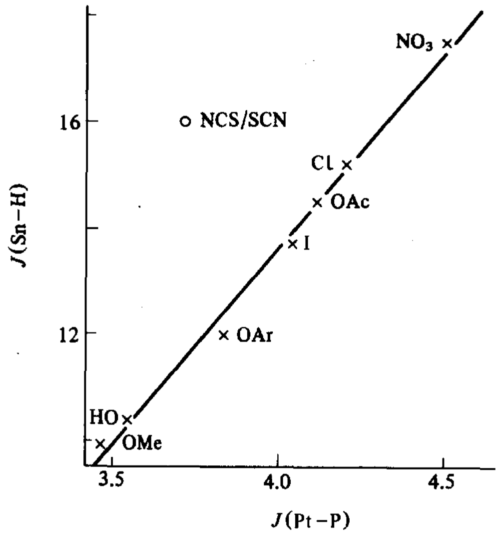


Fig. 3. Plot of ^4J(Sn–H) (Hz) for β-pyrrole protons in Sn(TPP)X_2 complexes vs ^1J(Pt–P) (kHz) in PtX(Me)(dppe) complexes [from Ref. 23, in which ArO = *p*-(MeO)C_6H_4O]. (NCS/SCN point not included in linear-regression analysis.)

β-Pyrrole chemical shifts

These chemical shifts show a similar dependence on ligand basicity, with weaker bases causing downfield shifts. A plot of ^4J(Sn–H) against δ (Fig. 4) indicates a good correlation ($r = 0.993$, $n = 8$), if the points for X = OH and OMe are excluded. Since the *J* values for these complexes fit well with the pK_a dependence, these chemical shifts seem anomalous. Literature data for X = OH are closely comparable with the present ones.[8] Inclusion of the β-pyrrole chemical shift for Sn(TPP)(CH$_2$CH$_3$)$_2$, *ca* 8.8 ppm,[11] indicates a continuation of the upfield shift for even more basic ligands. A similar dependence on the base strength of X has been reported for the chemical shifts of the β-pyrrole protons in In(TPP)X and the *meso*-protons in In(OEP)X complexes.[12]

Other NMR data

The protons in axial ligands appear at high field because of their location within the shielding zone of the macrocycle. Such chemical shifts for phenoxy, acetoxy and methoxy protons have been observed for Sn(OEP)X_2 complexes,[9] but Sn–H coupling constants were not reported. Recently, both δ and *J*(Sn–H) data were given for (**2**).[8] The trend of ^3J(Sn–H) > ^2J(Sn–H) > ^4J(Sn–H) evident in the series is similar to that observed for organotin(IV) compounds.[25] The OH ligand is subject to proton exchange with water, since marked broad-

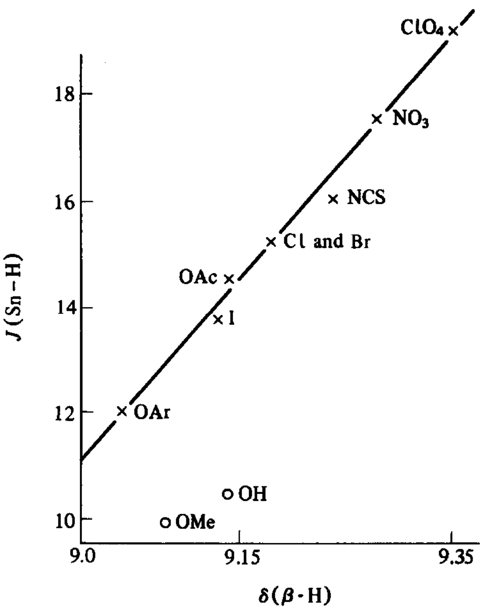


Fig. 4. Plot of ${}^4J$(Sn–H) (Hz) vs chemical shift [δ (ppm)] for β-pyrrole protons in Sn(TPP)X_2 complexes. (OH and OMe points not included in linear-regression analysis.)

ening and a downfield shift occur when the $CDCl_3$ is not specially dried.

Complex **6** exhibits unusual behaviour in $CDCl_3$ solutions which is not apparent for any of the other compounds. A fresh solution of **6** in $CDCl_3$ shows two sets of peaks. The data in Table 2 refer to one set, which remains sharp. The other signals ($\delta_{pyrrole}$ 9.13, ${}^4J$(Sn–H) = 13.5 Hz, δ_{ortho} 8.1, $\delta_{meta,para}$ 7.75) are broader. On standing for less than 24 h, a purple precipitate appears, accompanied by the loss of these broad peaks. The peaks assigned to the monomeric complex (**6**), whose δ and *J* values are internally consistent with those of the rest of the series, gradually disappear as precipitation continues. In acetone-d_6 and pyridine-d_5 solutions, single species exhibiting sharp peaks are present (δ 9.56, *J* = 18.0 Hz and δ 9.35, *J* = 13.2 Hz, respectively), and no precipitation occurs over many days. The precipitate can be dissolved in acetone to give a solution whose visible spectrum is virtually identical with that of the original solid **6** in acetone. Washing the precipitate with $CHCl_3$ slowly dissolves some of it, producing a spectrum very similar to that of the supernatant in $CDCl_3$. This behaviour seems consistent with aggregation in the weakly polar solvent, which does not occur in acetone or pyridine. Perhaps intermolecular perchlorate bridges are formed, leading to oligomerization. These phenomena are under investigation.

EXPERIMENTAL

General

${}^1H$ NMR spectra were recorded on the Bruker CXP-300 F.T. instrument at the Brisbane NMR Centre, Griffith University, using $CDCl_3$ as solvent. Preliminary spectra were obtained on a Varian EM-360 spectrometer. UV–visible spectra were recorded on a Varian DMS-100 spectrometer in $CHCl_3$ solutions. IR spectra were obtained on a Jasco IR-810 instrument in either Nujol mulls or KBr pellets. Microanalyses were carried out by the Microanalytical Service, University of Queensland. The ligand *meso*-tetraphenylporphyrin (TPP) was prepared and purified ("chlorin-free") by the literature method.[26] Inorganic salts were A.R. grade.

Preparations of Sn(TPP)X_2

X = Cl. This complex was prepared according to the literature[27] and recrystallized from $CHCl_3$–hexane to yield violet crystals.

X = OH. A solution of Sn(TPP)Cl_2 (100 mg) in CH_2Cl_2 (10 cm^3) was stirred with basic alumina (Woelm, activity IV, 2 g) for 15 min. The suspension was filtered through a short column of the same alumina, eluting with CH_2Cl_2. The major red–purple band was collected and concentrated, and then hexane was added to yield maroon microcrystals (70 mg, 73%), which were dried at 70°C under vacuum (< 1 mmHg).

X = OMe. A suspension of Sn(TTP)Cl_2 (50 mg) in dry $CHCl_3$–MeOH [1 : 1 (v/v), 10 cm^3) was stirred under dry N_2 with basic alumina (Woelm, activity IV, 1 g). After 10 min, the suspension was percolated through a short column of the same alumina, eluting with dry MeOH. The major band was collected, concentrated and cooled to yield the product as maroon microcrystals (25 mg, 50%), which were dried under vacuum at room temperature and stored in a desiccator. This material was shown to be >95% pure by ${}^1H$ NMR.

X = OAc. A mixture of Sn(TPP)Cl_2 (110 mg), AgOAc (130 mg) and glacial acetic acid (25 cm^3) was heated under reflux for 3 h, filtered while hot, then left at room temperature for 3 days. White crystals of excess AgOAc were removed by filtration, then the volume was reduced and hexane was added to yield shiny purple crystals, shown by NMR to be contaminated with acetic acid. Grinding and vacuum drying (70°C, < 1 mmHg) gave a maroon powder, which was recrystallized from CH_2Cl_2–hexane to yield shiny violet prisms. (Found: C = 67.7, H = 4.1, N = 6.5.

$C_{48}H_{34}N_4O_4Sn$ requires C = 67.9, H = 4.0, N = 6.6%.)

X = NO_3. A mixture of Sn(TPP)Cl_2 (70 mg) and $AgNO_3$ (70 mg) was refluxed in dry benzene (25 cm^3) for 3 h. Precipitated AgCl was removed by filtration, the solution was evaporated to dryness, and the residue was recrystallized from $CHCl_3$–hexane to give purple microcrystals in nearly quantitative yield. Recrystallization from CH_2Cl_2–hexane gave shiny purple prisms. (Found: C = 62.2, H = 3.4, N = 9.7. $C_{44}H_{28}N_6O_6Sn$ requires C = 61.8, H = 3.3, N = 9.8%.)

X = ClO_4. A solution of Sn(TPP)Cl_2 (80 mg) in dry benzene (10 cm^3) was stirred at 55°C. A solution of $AgClO_4$ (82 mg) in dry benzene (3 cm^3) was added, and stirring was continued at 55°C for 30 min. The purple complex and AgCl precipitated, leaving a bluish-purple supernatant. All solids were collected by filtration, then the porphyrinic materials were extracted by washing the residue with successive small portions of boiling $CHCl_3$, and filtering the resulting solution through Celite. Hexane was added and the solution concentrated to yield violet prisms (64 mg, 69%). Recrystallization from CH_2Cl_2–hexane gave maroon microcrystals. (Found: C = 56.7, H = 3.2, N = 5.8. $C_{44}H_{28}Cl_2N_4O_8Sn$ requires C = 56.8, H = 3.0, N = 6.0%.)

X = Br. A solution of Sn(TPP)$(ClO_4)_2$ (33 mg) in acetone (10 cm^3) was treated with LiBr (30 mg). The purple precipitate was collected after 30 min stirring, washed with acetone and dried. Recrystallization from CH_2Cl_2–hexane gave violet prisms (20 mg, 63%). (Found: C = 59.3, H = 3.2, N = 6.2. $C_{44}H_{28}Br_2N_4Sn$ requires C = 59.3, H = 3.2, N = 6.3%.)

X = I. A solution of Sn(TPP)$(ClO_4)_2$ (30 mg) in acetone (5 cm^3) was treated with KI (20 mg). Sparkling black prisms (21 mg, 66%) were formed directly from the reaction mixture, and were collected, washed with acetone and dried. Recrystallization from CH_2Cl_2–hexane gave very dark green crystals with a purple reflectance. (Found: C = 54.7, H = 2.9, N = 5.9. $C_{44}H_{28}I_2N_4Sn$ requires C = 53.6, H = 2.9, N = 5.7%.)

X = NCS. A solution of Sn(TPP)$(ClO_4)_2$ (30 mg) in acetone (5 cm^3) was treated with KSCN (20 mg). The mixture was stirred for 30 min, then filtered to yield purple crystals which were washed with acetone and dried (15 mg, 55%). Recrystallization from CH_2Cl_2–hexane gave glistening purple prisms. (Found: C = 63.7, 65.9; H = 3.2, 3.5; N = 9.6, 9.3. $C_{46}H_{28}N_6O_2Sn$ requires C = 65.7, H = 3.3, N = 9.9%.)

X = OC_6H_4-*p*-Me. A mixture of Sn(TPP)$(OH)_2$ (26 mg), *p*-cresol (20 mg) and benzene (5 cm^3) was stirred and refluxed for 1 h. The solvent was removed by distillation then the product was dissolved in CH_2Cl_2 and precipitated with hexane (19 mg, 59%). Recrystallization from CH_2Cl_2–hexane gave dark maroon microcrystals. [Found: C = 72.8, H = 4.4, N = 5.9. $C_{58}H_{42}O_2N_4Sn$ requires C = 73.7, H = 4.5, N = 5.9%.)

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