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Review

# The coordination chemistry of tin porphyrin complexes

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## Contents

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## Abstract

The complexes of porphyrins with tin(IV) are readily prepared and are stable even in the presence of strong acids. The Sn(IV) centre is usually six-coordinate with two *trans* axial ligands, and many derivatives have been prepared with a variety of anions, ranging from very weakly coordinated oxyanions through to carbanions. Due to the oxophilic nature of the Sn(IV) centre, the complexes with carboxylate and aryloxide axial anions are readily prepared and tractable, making them ideal building blocks for the construction of elaborate arrays containing more than one porphyrin. The spectroscopic properties of the Sn(IV) porphyrins, particularly their diamagnetism and luminescence, make them convenient for chemical study. This review concentrates on the coordination chemistry and structures of mainly Sn(IV) porphyrins, although the rarer Sn(II) complexes are also described. Studies of mechanisms of axial substitution reactions are included, as are descriptions of multiporphyrin arrays based on Sn(IV) porphyrin cores. References to various uses of Sn(IV) porphyrin complexes are also included.

*Keywords:* Porphyrins; Tin; Metalloporphyrins; Axial substitutions; Spectroscopy

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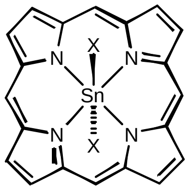
## 1. Introduction

Tin(IV) porphyrins (**1**, M: Sn, X: monoanionic ligand; see Table 1) offer the chemist many advantages due to the particular properties conferred by the highly charged main group metal centre. The large Sn(IV) ion can be accommodated in the porphyrin core without distorting the planarity of the macrocyclic ligand. The complexes are diamagnetic and usually six-coordinate with *trans*-diaxial anionic (or occasionally neutral) ligands. These ligands can be manipulated readily in most cases. The presence of $^{117}$Sn and $^{119}$Sn ($I = 1/2$, 7.6 and 8.6% abundance, respectively) affords extra NMR information in many cases. These data have not been fully exploited in the past, and we hope that this review will draw more attention to these aspects. It is essential that NMR spectra be used for characterisation, as several workers have found that some methods of preparation can result in mixtures of various axially-ligated complexes, and some porphyrins seem to be rather recalcitrant in yielding pure complexes. UV-Vis spectra can mask impurities that should be readily detectable in NMR spectra. The optical properties are attractive, in that the complexes give “normal”’ visible absorption spectra according to the Gouterman classification, and the complexes are luminescent. The high charge on Sn(IV) causes the complexes to be amongst the most readily ring-reduced of all metalloporphyrins. The ease of reduction and difficulty of oxidation contrast with the exactly opposite behaviour of the popular Zn(II) porphyrins. The complexes are also the most stable to acid-induced demetallation, being unchanged even in concentrated $H_2SO_4$, yet Sn(IV) is very easily inserted into free-base porphyrins. The particular oxophilicity of the Sn(IV) centre confers a notable preference for coordination of carboxylates and aryloxides, and these properties have been exploited recently by several workers for the preparation of elegant and elaborate multiporphyrin arrays. Although various other M(IV) porphyrins are known, for example those of other Group 14 metals and transition metals such as Ti, Zr, Hf, Th, Mo, Ru, Os and Pt, we intend to showcase the tin species as having a particular combination of chemical and spectroscopic properties that make them attractive for further study, especially with respect to new applications in the construction of multiporphyrin molecules. Tin(II) porphyrins are more of a rarity because of their air-sensitivity, but have been used as synthetic precursors to Sn(IV) derivatives.

Table 1
Abbreviations

| Abbreviation | Interpretation |
|---|---|
| Porphyrins | |
| $H_2$(P) | General porphyrin |
| $H_2$(Etio I) | Etioporphyrin I (2,7,12,17-tetraethyl-3,8,13, 18-tetramethylporphyrin) |
| $H_2$(OEP) | 2,3,7,8,12,13,17,18-Octaethylporphyrin |
| $H_2$(TAP) | General 5,10,15,20-tetraarylporphyrin |
| $H_2$(TBPP) | 5,10,15,20-Tetrakis(4-*tert*-butylphenyl)porphyrin |
| $H_2$(TCPP) | 5,10,15,20-Tetrakis(4-carboxyphenyl)porphyrin |
| $H_2$(THxTMeDPP) | 2,8,12,18-Tetrahexyl-3,7,13,17-tetramethyl-5,15-diphenylporphyrin |
| $H_2$(THxTMeP) | 2,8,12,18-Tetrahexyl-3,7,13,17-tetramethylporphyrin |
| $H_2$(TMP) | 5,10,15,20-Tetrakis(2,4,6-trimethylphenyl) porphyrin |
| $H_2$(TmTP) | 5,10,15,20-Tetrakis(*m*-tolyl)porphyrin |
| $H_2$(TpBrPP) | 5,10,15,20-Tetrakis(4-bromophenyl)porphyrin |
| $H_2$(TpClPP) | 5,10,15,20-Tetrakis(4-chlorophenyl)porphyrin |
| $H_2$(TpOMePP) | 5,10,15,20-Tetrakis(4-methoxyphenyl)porphyrin |
| $H_2$(TPP) | 5,10,15,20-Tetraphenylporphyrin |
| $H_2$(TpTP) | 5,10,15,20-Tetrakis(*p*-tolyl)porphyrin |
| $H_2$(TPyP) | 5,10,15,20-Tetrakis(4-pyridyl)porphyrin |
| $H_2$(TPC) | 5,10,15,20-Tetraphenylchlorin |
| $H_2$(TPiBC) | 5,10,15,20-Tetraphenylisobacteriochlorin |
| Others | |
| $M^{n+}$ | General metal cation |
| $X^-$ | General monoanionic ligand |
| R | General alkyl |
| Ar | General aryl |
| Bu | *n*-Butyl |
| Et | Ethyl |
| Me | Methyl |
| Ph | Phenyl |
| $OAc^-$ | Acetate |
| $OAr^-$ | General aryloxide |
| $OBz^-$ | Benzoate |
| $OMe^-$ | Methoxide |
| $ONap^-$ | Naphthyloxide |
| $OPh^-$ | Phenoxide |
| $OTf^-$ | Triflate (trifluoromethanesulfonate) |
| $sal^-$ | Salicylate |
| $Acsal^-$ | Acetylsalicylate |
| $Cp^-$ | $\eta^5$-Cyclopentadienide anion |
| DME | 1,2-Dimethoxyethane |
| DMF | *N*,*N*-Dimethylformamide |
| py | Pyridine |
| THF | Tetrahydrofuran |
| TMEDA | *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine |



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There have been several reviews containing material on tin porphyrins, mostly in collections such as “The Porphyrins” and “Porphyrins and Metalloporphyrins” (Buchler) [1] and “The Porphyrin Handbook” (Sanders et al.) [2]. In 1979, Pommier published a review “Chemistry of Group IV Porphyrins and Phthalocyanines” [3] that is a good source of information on the early work in this broader field, and Gouterman and co-workers contributed an Account in 1982 entitled “Metalloid Porphyrins and Phthalocyanines” [4]. Brothers briefly mentioned some recent work on tin porphyrins in a mini-review on main group complexes in 2002

[5]. Given their broader scope, these compilations generally do not discuss details, and it is our aim in the present work to concentrate on the practical coordination chemistry of tin porphyrins, especially emphasising comparisons of synthetic methods, spectroscopic and other characterisation data and the dependence of structures and properties on the nature of the porphyrins and especially the properties of the axial ligands. We also do not set out to compare in detail the properties of the tin(IV) porphyrins with those of other M(IV) derivatives, and the reader is directed to the compilations mentioned above for such material. Our aim is to concentrate on comparisons of the various ligand types when coordinated to the Sn(IV) porphyrin fragment and indicate how this knowledge can be used to manipulate ligands and hence create novel and useful structures.

Tin porphyrinoids have been investigated for several biomedical applications. It is not our intention to cover the extensive literature on the medical applications of tin porphyrins, phthalocyanines, chlorins, benzochlorins and purpurins, but some recent applications will be mentioned briefly. The major use has been for photodynamic therapy against cancer and non-cancerous proliferative skin conditions [6a-d]. Photodynamic treatment has also been applied to inactivation of bacteria [6e]. Non-cytotoxic antiproliferative action has been applied to the problem of restenosis following angioplasty [7]. A particularly useful property of tin(IV) complexes of natural porphyrins and their allies is their inhibition of heme oxygenase, making them candidates for the treatment of hyperbilirubinemia [8a,b]. In addition, they offer protection against acute oxidative injury [8c]. Tin porphyrins have also been included, with other metalloporphyrins, in studies of antiviral action, particularly for preventing HIV infection [9]. Given the fact that the axial ligation of these Sn(IV) macrocyclic complexes is often totally ignored in many medically- or biologically-oriented studies in this field, it is hoped that our emphasis on these angles may stimulate more detailed appreciation of this fact. The assumption that the ligands on tin porphyrins (or chlorins, etc.) are chlorides (or even hydroxides or water in aqueous media) when they are used in biological studies may not always be valid, and this question may be relevant to their efficacy.

Tin porphyrins have also been studied extensively in catalytic or photocatalytic applications, including splitting of water for the production of hydrogen. In many ways Sn(IV) porphyrins are the ideal candidates in this regard, because of their ease of reduction, single metal oxidation state, stable coordination (to the porphyrin), and favourable photophysics. Some recent articles give a flavour of these applications [10]. In most cases, we have concentrated on non-aqueous chemistry and hence lipophilic porphyrins, and there is one obvious reason for this—the chemistry is more clear-cut, and side equilibria involving water as a ligand are (largely) eliminated. Tin(IV) complexes of the synthetic water-soluble porphyrins are known, and their chemistry is mentioned in the review chapter by Hambright [11]. The (mainly non-aqueous) electrochemistry of tin porphyrins [both Sn(II) and Sn(IV)] was covered thoroughly by Kadish in "The Porphyrin Handbook" [12] and also by Lemke and Lorenz in 1999 [13], so redox potentials will not be revisited here. The spectroscopic properties will be mentioned frequently as an adjunct to characterisation, but will not be reviewed in detail. The abbreviations used for porphyrins, other ligands, solvents, etc. are collected in Table 1.

## 2. Complexation of tin by porphyrins

### 2.1. Insertion of tin into porphyrins

#### 2.1.1. Sn(II) porphyrins

Tin(II) is an uncommon oxidation state in porphyrin complexes as there is a strong tendency to oxidise to Sn(IV). During the preparation of Sn(IV) porphyrins by treating $SnCl_2$ with free base porphyrins in aerobic conditions, transient green colours appear immediately, to be replaced by the familiar maroon to purple colours of the Sn(IV) complexes. The first well-defined Sn(II) porphyrin was reported by Whitten et al. [14] who prepared Sn(OEP) on a very small scale by treatment of rigorously dried and degassed pyridine solutions of $H_2$(OEP) with freshly prepared anhydrous $SnCl_2$. The characteristic absorption bands at 495 and 600 nm were recorded and the proton NMR data supported the out-of-plane Sn(II) formulation. Landrum et al. [15] reported the synthesis of Sn(TPP) in 1984 from $H_2$(TPP) and $SnCl_2$ in THF and pyridine. The visible spectrum shown in this paper indicates that the product was a mixture of Sn(TPP) and $H_2$(TPP), but the signature bands of the former at 397, 488 and 692 nm were evident. The Guilard group [16] then produced the complete and unambiguous characterisation of Sn(P), (P = OEP, TPP, TpTP, TmTP, TMP), including X-ray structural analysis of Sn(OEP) and electrochemical studies of several derivatives. Their method of preparation was the same as that of Landrum but a longer reaction time ensured complete metallation. The very air-sensitive complexes could be chromatographed under rigorous conditions and yields of 27–76% were achieved. Recently, Wang et al. [17] introduced a new method for preparing Sn(II) porphyrins by the reduction of Sn(TpTP)$Cl_2$ with $NaBEt_3H$ in toluene. This method avoids chromatography and gave 76% yield of the Sn(II) complex. This appears to be the most convenient method so far published and is the only reductive method that has succeeded in producing the divalent complexes rather than inducing the common reaction of ring-reduction to give Sn(IV) chlorins and bacteriochlorins [18].

#### 2.1.2. Sn(IV) porphyrins

The most common and convenient method for the insertion of Sn(IV) is to heat the free base porphyrin with excess hydrated $SnCl_2$ in pyridine [19]. This produces the complex Sn(P)$Cl_2$ that can be isolated as such by simply pouring into water. However, the solid is contaminated with uncharacterised grey material. The crude product can then be digested with chloroform or dichloromethane, the solution filtered, concentrated, and layered with hexane to produce crystals. It should be noted that chromatography at this stage is inadvisable if the chloro complex is the desired product, as alumina will cause hydrolysis to the hydroxo complex. It is unclear whether silica gel causes the same reaction as this does not seem to have been reported. If ethanol is present in the chloroform, it may be entrained in the resulting crystals or cause the formation of some ethoxo complexes, and if so, this is clearly evident from NMR spectra [20]. This method is usually successful for all lipophilic porphyrins, including dinuclear ligands [21,22]. The use of acetate-containing media, e.g. acetic acid with sodium acetate, has been claimed to produce diacetato complexes, reported in ref. [23], but in our hands mixtures of dichloro, acetatochloro and diacetato complexes are formed. For example, our use of this method with $H_2$(OEP) gave a mixture of Sn(OEP)$(OAc)_2$, Sn(OEP)(OAc)Cl and Sn(OEP)$Cl_2$ in the proportions 50:40:10 (by NMR) [24]. Remarkably, with TPP, the result was the formation, almost exclusively, of the dichloro complex. Grigg and Norbert [25] noted the formation of mixed OAc/Cl complexes for a series of aminomethyl-substituted TPPs. In their studies of the luminescence of Group 14 metalloporphyrins, Gouterman et al. [26] washed the crude product of the acetate insertion method with 10 M HCl, resulting in the formation of pure dichloro complex. This simple procedure is an alternative to the pyridine method as long as there are no acid-sensitive groups on the porphyrin. The pure diacetato complexes are readily accessible by other means (see below). Tin has also been inserted by the “Adler method”, namely $SnCl_2$ in refluxing DMF [27], but this method has not become at all popular and its use has not been reported recently.

One trap for inexperienced workers in this field is the fact that Sn(IV) porphyrins are readily reduced, and the metallation medium containing $SnCl_2$, especially in the presence of light and water, is an ideal one for the reduction of Sn(IV) porphyrins to the corresponding chlorin and bacteriochlorin (i.e. di- and tetrahydroporphyrins, respectively) [28]. Indeed, Sn(IV) chlorin complexes can be prepared quantitatively by photolysis in the presence of TMEDA/acetic acid or other reagents [28]. This means the crude Sn(P)$Cl_2$ products are often contaminated with the chlorin complex. There are also other methods for readily reducing Sn(IV) porphyrins to chlorins [28]. Reductions to the chlorin via 5,15-dihydroporphyrins have also been investigated [29]. Various workers over the years have drawn attention to the presence of chlorin contamination [14,30], while others have apparently not been aware of it. It is easy to detect the presence of chlorin complex by its absorption band near 625 nm, whereas the longest wavelength band of the porphyrin dichloro complex appears at ca. 600–605 nm [31]. Note that in some early work on tin porphyrins, they were incorrectly assigned as Sn(II) complexes [19b,31]. Serious contamination by chlorin is also obvious in NMR spectra. Careful recrystallization (or chromatography if the axial ligands are hydroxides) will remove the impurity, and the bluish mother liquor is a good sign that one is succeeding. It has been noted by Jiang et al. [32] that extended heating of the metallation mixture in the presence of light exacerbated the problem in the metallation of TPyP. So the general advice is to (i) use chlorin-free porphyrins; (ii) heat with $SnCl_2$ for the shortest time possible (check with TLC and visible spectroscopy); and (iii) avoid direct light.

### *2.2. Demetallation of tin porphyrins*

This is so difficult by conventional acid treatments applicable to other metalloporphyrins that it would not normally be attempted. Russian workers have studied so-called “super-stable” metalloporphyrins, namely Ge and Sn(IV) complexes [33]. They found that appreciable demetallation occurred only at $H_2SO_4$ concentrations near 100% at temperatures above 340 K. However, it is possible to remove tin using basic or reductive conditions, for example lithium in the presence of amines [34]. Fuhrhop [35] reported that Sn(OEP)$(OH)_2$ could be demetallated in 70% yield using sodium borohydride in chloroform/ethanol with strict exclusion of air. In the only known example of transmetallation of an Sn(IV) porphyrin, treatment of Sn(OEP)$(OAc)_2$ with $Bu_2AlH$ led to formation of the Al(III) porphyrin, although the yield after 2 h was less than 20% [36]. There is also an isolated report of the reversible demetallation of Sn(TPyP)$Cl_2$ adsorbed in hectorite clay when the system is dehydrated/rehydrated, but the reasons for the radical difference between this medium and normal solutions are not obvious [37].

## 3. Structures, properties and coordination chemistry of tin porphyrins

### *3.1. Comments on the spectroscopy of tin porphyrins*

Throughout this review, we will draw attention to the favourable spectroscopic properties of tin porphyrins. Some typical NMR and UV-Vis data for a range of porphyrins and axial ligands are collected in Table 2. In our descriptive studies of Sn(TAP)$X_2$, we found that the bonding properties of the axial ligands can often be compared readily using several NMR parameters [38–43]. The β-unsubstituted porphyrins are especially useful as the coupling constants to the β-pyrrole protons, $^4J$(SnH), are moderately sensitive to the nature of the axial ligands and vary over a range of ca. 8–22 Hz, becoming larger as the basicity of the ligand decreases. However, rather few authors have ever reported these values as characterisation data and we encourage such recording in future for the assistance of other workers. For β-octasubstituted porphyrins, the coupling constants to the *meso* protons are much smaller, e.g. less than 4.5 Hz for common anionic ligands. The couplings of $^{119}$Sn and $^{117}$Sn to

Table 2
Representative NMR and electronic absorption data for some complexes $Sn(P)X_2$ (chemical shifts in ppm; coupling constants and linewidths in Hz; NMR solvent $CDCl_3$ unless specified; UV/vis solvent $CHCl_3$ unless specified).

| P | X | $\delta_P$ [a] | $^4J(SnH)$ [b] | $\delta_X$ [c] | $^nJ(SnH_X)$ [d] | $\lambda_{max}$ (nm) | | | $\varepsilon(1,0)/\varepsilon(0,0)$ | $\delta_{Sn}$ [e] | $\nu_{1/2}$ [f] | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Soret | Q(1,0) | Q(0,0) | | | | |
| TPP | F | 9.24 | 14.9 | | | 419 | 553 | 591 | 2.49 | −621.1 | 78 | [40] |
| | Cl | 9.18 | 15.2 | | | 427 | 561 | 600 | 1.60 | −589.7 | 50 | [43] |
| | Br | 9.18 | 15 | | | 429 | 565 | 605 | 1.36 | −711.7 | 37 | [43] |
| | I | 9.13 | 13.7 | | | 428 | 568 | 614 | 1.25 | −977.6 | 192 | [43] |
| | OTf | 9.36 | 20.0 | | | 420 | 549 | 588 | 3.30 | −630.9 | 99 | [57] |
| | $NO_3$ | 9.28 | 17.5 | | | 423 | 553 | 593 | 2.70 | −623.3 | 90 | [43] |
| | OCOH | 9.24 | 15.3 | 2.70 | 43.8, 42.0 | 422 | 556 | 595 | 2.12 | −618.1 | 56 | [41] |
| | OAc | 9.14 | 14.5 | −0.96 | 3.6 | 425 | 557 | 596 | 2.34 | −635.7 | 67 | [43] |
| | OBz | 9.18 | 15.0 | | | 423 | 556 | 596 | 2.25 | −631.1 | 63 | [57] |
| | $OC_6H_4$-4-Me | 9.04 | 12.0 | 1.72 | | 425 | 561 | 601 | 1.83 | −602.0 | 41 | [43] |
| | OH | 9.14 | 10.4 | −7.55 | ca. 36 | 426 | 560 | 600 | 1.64 | −569.6 | 31 | [43] |
| | OMe | 9.08 | 9.9 | −2.04 | 70.3, 67.1 | 427 | 559 | 598 | 1.67 | −561.7 | 27 | [43] |
| TpTP | Cl | 9.21 | 15.25 | | | 428 | 562 | 603 | 1.29 | | | [76] |
| | $ClO_4$ | 9.30 | 17.4 | | | 425 | 557 | 598 | 1.47 | | | [76] |
| | OCOH | 9.26 | 15.5 | 2.51 | 39.2, 37.3 | 425 | 558 | 597 | 1.52 | −617.1 | 47 | [41] |
| | OH | 9.14 | 10.3 | −7.46 | | 427 | 563 | 603 | 1.25 | −569.9 | 28 | [41] |
| | $C_2Ph$ | 9.21 | | | | 441 | 585 | 629 | | | | [71] |
| | NHPh | 9.08 | | −4.37 | | 429 | 565 | 609 | | | | [71] |
| | *trans*-Ph | 9.06 | | 0.84 | | 450[g] | 600[g] | 646[g] | | | | [50] |
| | *cis*-Ph | 8.89 | | 3.36 | 95 | 442[g] | 582[g] | 632[g] | | −520[h] | | [50] |
| OEP | Cl | 10.62 | 4.4 | | | 403[i] | 538[i] | 575[i] | 1.07[i] | −591.2 | 78 | [24] |
| | OH | 10.47 | ca. 3 | −8.07 | | 407 | 538 | 575 | 1.04 | −570.9 | 48 | [24] |
| | Me/I | 10.73 | | −5.00 | 88 | 409 | 541 | 578 | | | | [45] |
| OEP | –[j] | 10.39 | | | | 386, 495 | | 595 | | | | [16] |

[a] β-Pyrrole or *meso* proton signal, as appropriate.
[b] $^{119}Sn$-$^1H$ or average of $^{119}Sn$- and $^{117}Sn$-$^1H$ coupling constants to β-pyrrole or *meso* proton, as appropriate.
[c] Chemical shift for signal of axial ligand proton(s) nearest to Sn.
[d] $^{119}Sn$-$^1H$, $^{117}Sn$-$^1H$ or average of $^{119}Sn$- and $^{117}Sn$-$^1H$ coupling constants for signal of axial ligand proton(s) nearest to Sn.
[e] $^{119}Sn$ chemical shift ($Me_4Sn = 0$ ppm) (from ref. [39], except where noted).
[f] Width at half-height of proton-decoupled $^{119}Sn$ signal (from ref. [39]).
[g] In benzene.
[h] For the TBPP complex, from ref. [50].
[i] In $CH_2Cl_2$, from ref. [26].
[j] Sn(II) complex.

protons on axial ligands can also be observed for hydroxide (when water is absent), alkoxides, carboxylates and alkyls, although for the last of these they have been reported infrequently [44,45]. The most noteworthy NMR property of axial ligands is the strong shielding they experience due to the proximity of the aromatic porphyrin ligand. The signal at highest field is that for OH bound to Sn(IV), which appears at ca. −7.5 ppm for TAP complexes. Sn-bound methyl groups resonate near −5.5 ppm, methoxide at ca. −2 ppm, and other acido ligands successively further downfield [42]. The magnetic anisotropy of the porphyrin macrocycle and its effect on the chemical shifts of axially-bound ligands are described in the chapter by Scheer and Katz in “Porphyrins and Metalloporphyrins” [46]. The coupling constant to $^{119}Sn$ is still observable for acetate protons (ca. 4 Hz), but not for aryloxo *ortho* protons. Tin–carbon couplings have been reported in a few cases, but are rather difficult to observe unless the spectra are noise-free [47].

The presence of $^{119}Sn$ in these complexes enables the observation of the central metal NMR signal. There are still very few such data in the literature, a situation hardly different from that when we reported the first systematic studies in 1994 [39]. Until then, there were only two reports of direct observation of the $^{119}Sn$ in Sn(IV) porphyrins [48,49]. J. Arnold and co-workers [50] reported the tin spectra of *cis*-$Sn(P)Ph_2$ (P = TBPP, OEP) and recently Crossley et al. [21] used $^{119}Sn$ NMR to assist in characterising a series of Sn(IV) porphyrins, including dinuclear examples. This group introduced two-dimensional HMQC indirect detection of $^{119}Sn$, a method far superior in sensitivity to the direct detection method we used. As many laboratories are now equipped to undertake proton-detected heteronuclear NMR, reports of $^{119}Sn$ spectra as characterisation data should be more frequent. We found that the width-at-half-height of the proton-decoupled $^{119}Sn$ resonance was sensitive to the electronic properties of the axial ligands, although as usual with all the correlations we studied, the halide ligands with their different π-bonding propensities, do not fit correlations established for O-bound anions [39]. The carboxylate ligands displayed some rather anomalous behaviour with respect to their $^{119}$Sn chemical shifts and linewidths, suggesting factors other than simply acidity and electron density are at work.

Apart from NMR properties, the most obvious data that should be measured for porphyrins are the UV-Vis spectra. Tin(IV) porphyrins display "normal" spectra, with an intense Soret band and three bands in the Q region, the Q(2,0) band being rather weak [4]. The ratio of the intensities of the Q(1,0) and Q(0,0) is another measure of the basicity of the axial ligands (for first row atoms), weaker bases resulting in a higher $\varepsilon(1,0)/\varepsilon(0,0)$ ratio for TAP ligands [43]. This relationship is of sufficient utility that a selection of values from the literature spanning the major ligand classes is included in Table 2, and we encourage the reporting of intensity ratios (or quantitative measurement of absorptivities) whenever the stabilities and purities allow it. Many fluorescence and other luminescence and optical measurements have been undertaken on Sn(IV) porphyrins (see, for example, [4,25,26,30a,51,52]). The nuclear properties of tin are such that Mössbauer spectroscopy is also available to study, for example, the oxidation state of the tin centre [16b,30b,53,54]. Our FT-Raman study of a series of complexes Sn(TPP)$X_2$ is one of the few detailed reports of Raman spectra of Sn(IV) porphyrins [55,56]. Raman shifts of several skeletal vibrations were shown to vary systematically in line with other measures of axial ligand bonding properties [55].

### 3.2. Crystal structures

Considering their accessibility and stability, it is surprising that relatively few Sn(IV) porphyrins have been characterised crystallographically. With the increasing use of Sn(IV) porphyrins in supramolecular chemistry, this number should increase. The bond length data for the coordination sphere (Sn–N and Sn–$X_{axial}$) are collected in Table 3. These have been edited to include only mean Sn–N, Sn–O and Sn–X data, and thus estimated standard deviations have been omitted. For crystallographic details, please see the original references. Where sufficient comparative data are available, the *trans* and *cis* influences of the ligands can be characterised and discussed in terms of the electronic properties of the porphyrins and the axial ligands [57]. There are representatives of four-, five- and six-coordination and for the last of these, examples containing halo [32,38,58,59], hydroxo [57,60], methoxo [61], aryloxo [62–66], carboxylato [57,67–69], nitrato [38], perchlorato [70], alkynyl [71] and aryl [50] ligands. Hoard summarized the pioneering work on the structure of Sn(TPP)$Cl_2$ as a prototypical planar metalloporphyrin and delineated the fact that Sn(IV) produces the most tension-free planar porphyrin ring [72].

Amongst the group of six-coordinate complexes whose crystal structures have been determined, only one example of *cis* coordination of the ancillary ligands is known, namely Sn(TBPP)$Ph_2$ (Fig. 1) [50]. The Sn(IV) centre lies 1.11 Å out-of-plane, and the porphyrin is both ruffled and domed to accommodate the *cis* arrangement. The Sn–C bond lengths are very similar to those in the *trans*-diphenyl derivative Sn(TPP)$Ph_2$ (ca. 2.20 Å). However, the different coordination geometry is reflected in the very long Sn–N distances in the *cis* complex ($Sn–N_{av} = 2.27$ versus 2.134 Å for the *trans*-diphenyl complex) [50].

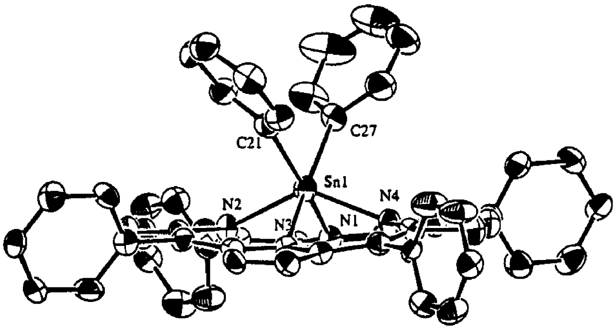


Fig. 1. ORTEP view of the molecular structure of *cis*-Sn(TBPP)$Ph_2$ as determined by X-ray crystallography. Ellipsoids drawn at 50% probability and *t*-butyl groups and hydrogen atoms omitted for clarity. Reprinted with permission from ref. [50]. Copyright 1996 American Chemical Society.

For several complexes Sn(TPP)$X_2$, we investigated correlations between $^{119}$Sn NMR linewidths and Sn–N distances, as well as Raman shifts of the $\nu(C_\alpha - C_\beta)$ vibration and Sn–N distances [38]. These quantities showed good correlations for X = $ClO_4$, $NO_3$, salicylate, benzoate, Cl and OH but not for X = F. Now that more data are available, including for aryloxides and the organometallics, these relationships can be explored over a broader range of ligands. Fig. 2 shows a plot of average Sn–N distances versus average Sn–O distances for all anionic O-bound ligands for the *meso*-tetraaryl porphyrins TPP, TpTP, TpClPP and TpOMePP.

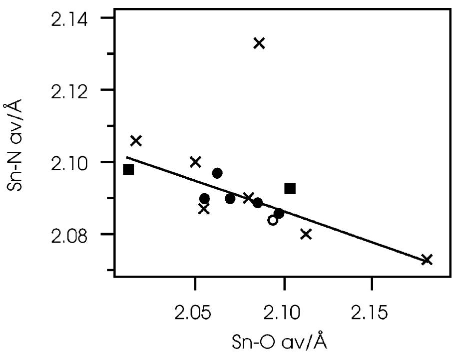


Fig. 2. Plot comparing mean Sn–N bond lengths and mean Sn–O bond lengths determined by X-ray crystallography for Sn(IV) tetraarylporphyrin complexes having O-bound anionic ligands [crosses: TPP complexes; filled circles: TpTP complexes; filled squares: TpOMePP complexes; open circle: TpClPP complex; the cross that lies well away from the others is that for Sn(TPP)$(OAc)_2$, whose values were not included in the linear regression calculation (see text)].

Table 3
Selected X-ray crystallographic data for complexes Sn(P)X$_2$

| P | X | Sn–N (Å)[a] | Sn–O (Å)[b] | Sn–X (Å)[c] | Ref. |
|---|---|---|---|---|---|
| Sn(IV) *trans* | | | | | |
| TPP | Cl | 2.098 | | 2.420 | [58] |
| | F | 2.064 | | 1.946 | [38] |
| | OH | 2.106 | 2.017 | | [57] |
| | OAc | 2.133 | 2.018 | | [68] |
| | OBz | 2.087 | 2.086 | | [57] |
| | sal | 2.09 | 2.055 | | [57] |
| | Acsal | 2.10 | 2.08 | | [57] |
| | NO$_3$ | 2.08 | 2.113 | | [38] |
| | ClO$_4$ | 2.073 | 2.181 | | [70] |
| | H$_2$O | 2.06 | 2.16 | | [57] |
| | Ph | 2.134 | | 2.204 | [50] |
| | [C–Re(CO)$_3$] | 2.07 | | 2.14 | [74] |
| TpTP | C≡C-Ph | 2.117 | | 2.167 | [71] |
| | 1-ONap | 2.09 | 2.085 | | [62] |
| | 2-ONap | 2.097 | 2.062 | | [63] |
| | OPh | 2.09 | 2.055 | | [66] |
| | OC$_6$H$_4$-4-NO$_2$ | 2.09 | 2.083 | | [66] |
| | OC$_6$H$_4$-2-NO$_2$ | 2.09 | 2.07 | | [64] |
| | OC$_6$H$_4$-2-OH | 2.086 | 2.097 | | [65] |
| TpOMePP | OMe | 2.10 | 2.01 | | [61] |
| | OAc | 2.093 | 2.103 | | [73] |
| TpClPP | OCOEt | 2.084 | 2.093 | | [67] |
| OEP | Cl | 2.082 | | 2.453 | [59] |
| TPyP | Cl | 2.081 | | 2.435 | [32] |
| THxTMeDPP | Rh(P)(pyCOO)[d] | 2.092 | 2.117 | | [69] |
| Sn(IV) *cis* | | | | | |
| TBPP | Ph | 2.27 | | 2.20 | [50] |
| Sn(II) | | | | | |
| OEP | – | 2.28 | | | [16b] |
| | Fe(CO)$_4$ | 2.19 | | 2.494 | [54] |
| | Mn(CO)$_4$HgMn(CO)$_5$ | 2.18 | | 2.554 | [75] |

[a] Mean Sn–N distance.
[b] Mean Sn–O distance for O-bound ligands.
[c] Mean distance tin to axial atom other than O.
[d] P: THxTMeDPP.

There are two structures extant for Sn(TPP)(OH)$_2$. The first of these was determined on a crystal of rather poor quality [actually a bis(chloroform), bis(carbon tetrachloride) solvate], and the final $R$ quoted was 15.14% [60]. One of the Sn–N lengths is particularly short at 2.04(5), and this biases the average so that it is well below the one we determined in a more precise structure of this complex ($R = 4\%$) [57]. Therefore, only the latter values have been included in the plots in this section. The Sn–N bond distances determined for Sn(TPP)(OAc)$_2$ were 2.197(5) and 2.068(4) Å [68]. Averaging these places the data point for X = OAc well away from the rest of the data, as is obvious from Fig. 2. So this point, although shown on the plot, has not been included in the linear regression. Instead, data for a very similar complex [Sn(TpOMePP)(OAc)$_2$] have been included [73]. It is unclear why the former complex has two Sn–N bonds that are longer than any others determined for Sn(IV) porphyrins (even longer than in complexes of strongly basic C-bound ligands), but it may be due to the presence of two molecules of acetic acid per Sn unit in the crystal. Clearly the correlation is fair ($r = -0.86$) and the exact nature of the aryl substituent on the porphyrin is of little consequence, as expected. The general inverse relationship between the equatorial and axial bond lengths reflects the tendency for higher electron demand by the axial ligand to be accommodated by a weakening of bonds in the porphyrin plane. Thus ligands of high basicity like methoxide have short Sn–O bonds and long Sn–N bonds. The *cis* and *trans* influences oppose each other.

The effects of ligand basicity are clearly evident in a plot of Sn–N (or Sn–O) bond distance versus $pK_a$ of the conjugate acid of the axial anion (Fig. 3). The correlation here is quite clear [$r = 0.942$, again omitting the point for Sn(TPP)(OAc)$_2$]. The acetylsalicylate seems to be a little aberrant, perhaps reflecting some steric effects. However, if the axial bond length extends due to crowding, one

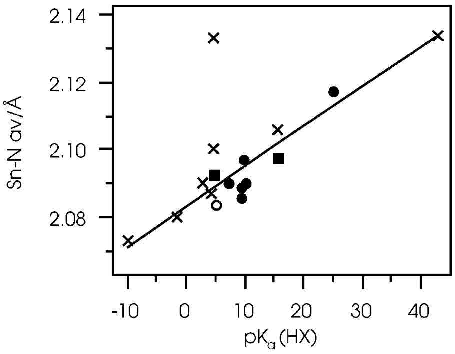


Fig. 3. Plot of mean Sn–N bond lengths determined by X-ray crystallography vs. p$K_a$ of the conjugate acids of the axial anionic ligands for Sn(IV) tetraarylporphyrin complexes [crosses: TPP complexes; filled circles: TpTP complexes; filled squares: TpOMePP complexes; open circle: TpClPP complex; the cross that lies well away from the others is that for Sn(TPP)(OAc)$_2$, whose values were not included in the linear regression calculation (see text)].

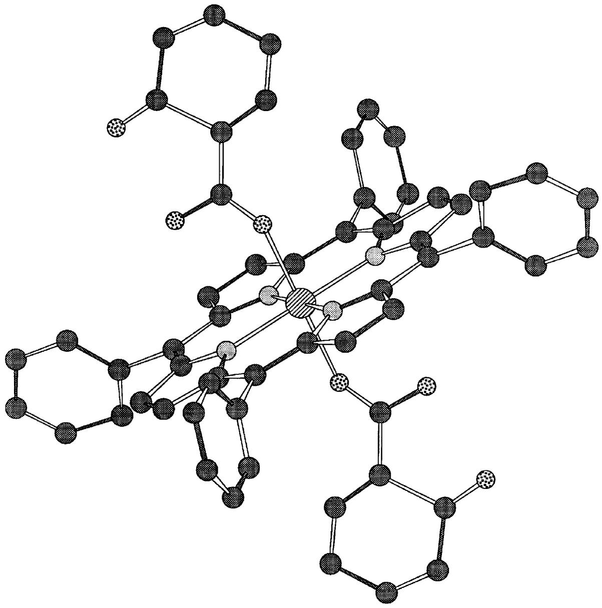


Fig. 4. Molecular structure of Sn(TPP)(salicylate)$_2$ determined by X-ray crystallography. Diagram produced using Chem 3D$^{TM}$ from the data of ref. [57].

would expect the Sn–N bond length to shorten, rather than lengthen. This p$K_a$ relationship is presumably a reflection of the properties of the highly charged Sn(IV) porphyrin centre, in which bonding is governed mainly by electrostatics, i.e. the Sn(IV) porphyrin moiety is a rather hard acid. On the other hand, the presence of the soft porphyrin ligand, which is both a π-donor and -acceptor, may soften the bonding properties of the tin centre to some extent. The fact that Sn(IV) porphyrins have such a high affinity for carboxylate anions (and also for phenolates) may indicate that the ideal geometry for Sn(TAP)X$_2$ is an M–N distance of 2.05–2.09 Å (and coincidentally an Sn–O distance that is very similar). Some more details of recent aryloxo structures with interesting intermolecular interactions are mentioned in Section 3.5 below [64]. It is also remarkable that the correlation of Sn–N distance with p$K_a$ extends from −10 to 43 with the inclusion of X = perchlorate, phenylacetylide and phenyl, even though the last two are C-bonded.

It might therefore be expected to apply to all first row elements, but the point for X = fluoride is far off the line in Fig. 3, with an average Sn–N distance of 2.06 Å, much shorter than that predicted by the correlation. Sn(TPP)F$_2$ is also unusual in other ways. For example, the linewidth of its $^{119}$Sn resonance and Raman shifts of skeletal vibrational modes do not correlate with the average Sn–N distances [38]. Its stability towards hydrolysis was noted many years ago [1a]. It would be informative to extend the range of ligands still further to investigate the full scope of these correlations. The sole example of a second-row element coordinated to Sn(P) is X = chloride, represented by Sn(TPP)Cl$_2$ [58], Sn(TPyP)Cl$_2$ [32] and Sn(OEP)Cl$_2$ [59]. These have average Sn–N lengths of 2.098, 2.081 and 2.083, and Sn–Cl lengths of 2.420(1), 2.435(5) and 2.453(2) Å, respectively. This is the only case where data are available for three different porphyrins and the same axial ligand, but the small sample does not allow any conclusions to be drawn about the relative electronic demands of the three porphyrin ligands.

It is clear, however, that the Sn–N coordination distance remains in the apparently ideal Sn(IV) porphyrin range, but that its correlation with p$K_a$ fails for the second row ligand chloride. Our structure of [Sn(TPP)(H$_2$O)$_2$](CF$_3$SO$_3$)$_2$ is the only crystallographically characterized Sn(IV) porphyrin with neutral axial ligands, and its bond lengths do not fit the pattern of the O-bound acido complexes of weakly basic ligands, notably in having both Sn–O and Sn–N shorter than for the perchlorato complex [57,70]. This may be a reflection of the high charge on the Sn centre.

In order to see if there were particular structural factors favouring coordination of salicylate to Sn(IV) porphyrins that would explain their remarkable selectivity when used as components of ion-selective electrodes, we compared the structures of Sn(TPP)X$_2$ (X = benzoate, salicylate, acetylsalicylate) [57]. The structure of the salicylate complex shown in Fig. 4 did not reveal any notable features other than the expected internal H-bond that maintained planarity of the whole axial ligand. This structure shows the typical monodentate carboxylate coordination found for all examples so far.

There is one other unusual C-bound complex known, namely Sn(TPP)[CRe(CO)$_3$]$_2$, in which two rhenium carbide ligands are sigma bonded to the Sn(IV) centre. It is very different from the other two C-bound *trans* derivatives in having Sn–N bond length of 2.07 Å and Sn–C of 2.14 Å [74], compared with the respective values of 2.134, 2.204 Å for Sn(TPP)(C$_6$H$_5$)$_2$ [50] and 2.117, 2.167 Å for Sn(TpTP)(C$_2$C$_6$H$_5$)$_2$ [71]. This Re complex therefore has a much tighter coordination sphere than the other two.

The only crystal structure determination of a ‘bare’ Sn(II) porphyrin, namely Sn(OEP), was reported by the Guilard group [16b]. As expected, the Sn(II) ion lies out-of-plane, by the large distance of 1.018 Å. This is similar to, but greater than, the value for the Sn(II) metal–metal bonded derivatives Sn(OEP)[Fe(CO)$_4$] (0.818 Å) [54] and Sn(TPP)[Mn(CO)$_4$HgMn(CO)$_5$] (0.85 Å) [75].

### *3.3. Axial coordination chemistry*

In this section, the methods for the preparation of Sn(IV) porphyrin complexes possessing a wide variety of axial ligands will be reviewed and their chemistry will be described. We think it is useful to collect all the relevant literature here, including some that is rather old, because this may save time for new workers in the field. The mechanisms of axial ligand substitutions are not well known, but to draw attention to possible areas for future investigations, mechanistic studies will be highlighted in Section 3.4. The use of axial ligation to generate multiporphyrin arrays will be covered in Section 3.5. There are two preferred starting materials for the wide variety of complexes Sn(P)X$_2$, namely the dichloro and dihydroxo species. Most of the work on axial ligand exchange reactions has been carried out on tetraarylporphyrin systems, notably TPP and TpTP, although lately more complex porphyrins have been involved, and OEP complexes were also studied in some detail, especially prior to 1980.

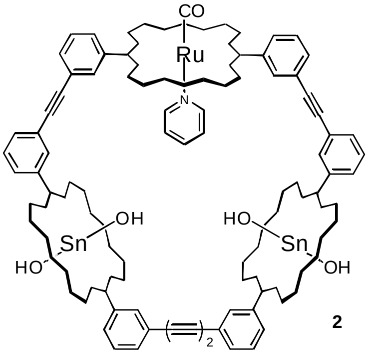
#### *3.3.1. Halo complexes*

As noted above, the dichloro complexes Sn(P)Cl$_2$ are the usual entry into the chemistry of Sn(IV) porphyrins. They serve as the precursors to the very useful dihydroxides (see Section 3.3.2), and thence to a wide range of bis(acido) complexes. They are the natural starting materials for metathesis using strongly basic reagents such as LiNR$_2$, ZnEt$_2$ [71] and MgPh$_2$ [50]. Reactions with silver salts can also be used to replace the chlorides, e.g. to form acetato, nitrato, perchlorato and triflato complexes [43,57]. The halo complexes can be prepared from the hydroxides or acetates by treatment with hydrogen halides, e.g. Sn(Etio I)X$_2$ (X = F, Cl, Br, I) [26]. We prepared Sn(TPP)F$_2$ from Sn(TPP)(OH)$_2$ by shaking a CH$_2$Cl$_2$ solution of the porphyrin with 1 M aqueous HF [40]. Kadish et al. made Sn(P)X$_2$ (P = TpTP, TmTP; X = Br, F) by treating Sn(P)Cl$_2$ with the appropriate HX, but details were not given [76]. In a quite different method, we prepared the heavier halo complexes Sn(TPP)Br$_2$ and Sn(TPP)I$_2$ by reacting the labile Sn(TPP)(ClO$_4$)$_2$ with LiBr or KI in acetone. This conveniently takes advantage of the solubility of the perchlorate and the metal salts in this solvent, coupled with the subsequent insolubility of the product dihalo complexes [43]. The ditriflate could also be used similarly. The bromo and particularly the iodo complexes are fairly labile, and revert to the chloro and/or hydroxo complexes upon standing in chloroform solution [26,43]. Gouterman and co-workers also noted that SnBr$_2$ and SnI$_2$ cannot be used for the direct synthesis of Sn(Etio I)Br$_2$ and Sn(Etio I)I$_2$ from the free base [26], so the dihydroxide, either directly or via the perchlorate or triflate, is the starting material of choice to prepare the heavier halo complexes.

#### *3.3.2. Hydroxo and alkoxo complexes*

The dihydroxo complexes Sn(P)(OH)$_2$ are of primary importance as they can be used for the preparation of most other Sn(IV) porphyrin species. The hydroxo ligand can be replaced readily using acids HX, as long as the p$K_a$ of HX is lower than that of water. Even alcohols will work, forming alkoxo complexes, but anhydrous conditions must be employed to obtain pure products (see below). The hydroxo complexes are usually prepared by base treatment of the dichloro complexes, and one convenient method is that of Wöhrle, who treated Sn(TPP)Cl$_2$ with concentrated ammonia in pyridine [77]. The product was precipitated with water, filtered and chromatographed on deactivated alumina. We found that the TAP dihydroxo complexes can be isolated conveniently using a one-pot procedure in which H$_2$(P) and hydrated SnCl$_2$ are heated in pyridine, followed directly by the ammonia treatment [42]. It is also possible to form the hydroxo complexes by treatment of Sn(P)Cl$_2$ with alkali [19a,26,76] or simply by stirring with basic alumina (usually deactivated, e.g. activity IV or V) [42,43,47].

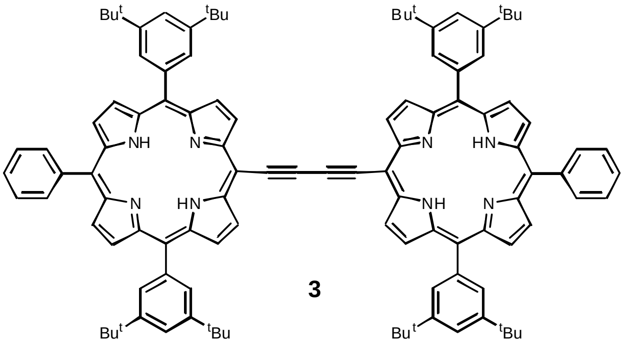
Recently, Sanders and co-workers used this method on Sn(THxTMeDPP)Cl$_2$, this time with activity I basic alumina [69]. In another case, the authors noted that the hydrolysis was rather slow, and two successive treatments with deactivated alumina over two days were required to form the tetrahydroxo Sn(IV) complex of a cavity porphyrin trimer (**2**) [20].



**2**

The inward-directed chlorides were presumably more difficult to hydrolyse than the more exposed ones. Others working in the field of multiporphyrin receptors have had difficulty obtaining clean replacement of all Sn-bound chlorides by hydroxides [78]. Webb and Sanders reported a phenomenon also noticed by us, namely that use of chloroform containing ethanol stabiliser in this procedure results in the formation of variable amounts of ethoxo complexes [20] (these are easily identified by the presence of multiple β-pyrrole resonances and the signals of the highly shielded ethoxy protons to high field of 0 ppm). For most subsequent reactions, for example displacements by acids, this does not matter, as alkoxo complexes are equally useful in this regard. Crossley et al. [21] recently reported a new method of preparation of hydroxo complexes of very lipophilic porphyrins, including angular Tröger's base and laterally-extended quinoxalino and diaryldiacetylene bis(porphyrins). These authors reported that treatment of the dichloro complexes with $K_2CO_3$ in refluxing THF/$H_2O$ gave good yields of Sn(P)$(OH)_2$. In other cases, they used $K_2CO_3$ in refluxing dichloromethane/methanol (4:1). The crude products were chromatographed over deactivated neutral alumina. It was presumed that methoxo complexes were intermediates in the latter case but these are known to be very labile to hydrolysis in the absence of excess methanol (see below). In a new development, Crossley et al. [21] reported that dicarboxylato complexes, e.g. Sn(TPP)$(OCOR)_2$ (R = Me, Ph), could be hydrolysed to Sn(TPP)$(OH)_2$ in high yield by refluxing for 2 h with $K_2CO_3$ in THF/$H_2O$ (4:1). Usually, this reaction is run in the opposite direction, i.e. the formation of carboxylato complexes from the dihydroxide.

In a recent experience of tin porphyrin chemistry, we attempted the hydrolysis of the bis($SnCl_2$) complex of butadiyne-linked bis(porphyrin) **3**, but this species seemed particularly intractable to all the above methods, and clean removal of all four chlorides was not achieved, the products comprising mixed chloro/methoxo/hydroxo complexes [22]. Even wet silver oxide at room temperature did not remove all the chlorides. Whether this is an intrinsic problem due to the particular electronic properties of this conjugated bis(porphyrin) is unknown, but new workers in this field should be aware that the methods that work very well for, say, TPP or TpTP complexes, may not be applicable for more elaborate systems.



**3**

Unfortunately, there have been no quantitative studies of the basicity (or acidity) of the OH ligands on Sn(P)$(OH)_2$. Indeed there are very few mechanistic studies of its reactions, apart from the work of Sanders on the formation of carboxylato complexes and the qualitative comparisons of the reactivity of phenols by the groups of Langford [66] and Maiya [52] (see Section 3.4). It is clear that dinuclear μ-oxo products are formed under basic conditions from hydroxo and methoxo complexes. Indeed, Crossley et al. [21] observed the apparent formation of oxo-bridged condensation products under MALDI-MS conditions. Other postulated examples are mentioned in Sections 3.4 and 3.5 below. It is well known that dinuclear and trinuclear oxo-bridged condensation products are formed in aqueous solutions from Sn(IV) complexes of natural porphyrins, as these have been characterised by NMR spectroscopy [48,79]. However, no examples have been unambiguously prepared, isolated and structurally characterised.

Alkoxo complexes Sn(P)$(OR)_2$ are also known [19a,43, 61,80,81,82]. These are not easy to study in pure form unless rigorous precautions are taken to avoid their facile hydrolysis to Sn(P)$(OH)_2$. The first one reported was Sn(OEP)$(OMe)_2$, described by Buchler et al. in his pioneering studies of the metal complexes of OEP [19a]. It was prepared by crystallising Sn(OEP)$(OH)_2$ from methanol. Wöhrle et al. prepared Sn(TPP)$(OCH_2CH_2OH)_2$ from Sn(TPP)$(OH)_2$ in refluxing ethylene glycol, and then converted the former into a stable polymer by heating to 300 °C [77]. There were no other reports of alkoxides until our preparation of Sn(TPP)$(OMe)_2$ in 1986 [43]. We found that nearly pure product can be obtained by passing Sn(TPP)$Cl_2$ (not TTP as stated [43]) or Sn(TPP)$(OH)_2$ [42] in dry methanol through basic alumina, activity I, and concentrating under vacuum until crystals form. The product must be protected from atmospheric water. Chen et al. followed this work by preparing more examples, namely Sn(P)$(OMe)_2$ [P = TPP, TpTP, TpOMePP] and determining the crystal structure of the last of these [61,80,81]. Woo's group formed Sn(TpTP)$(OMe)_2$ by methanolysis of complexes with more strongly basic axial ligands (see Sections 3.3.6 and 3.3.7) [71]. As mentioned above, the presence of ethanol as stabiliser in chloroform solutions of Sn(P)$(OH)_2$ will result in the formation Sn(P)$(OEt)_2$ and/or Sn(P)(OH)(OEt) to some extent [20]. Overall, so far the alkoxo complexes have been of rather minor interest compared to their far more useful and tractable aryloxo analogues to be discussed in the next section.

### 3.3.3. *Aryloxo complexes*

These complexes have been part of a resurgence of interest in tin porphyrins because of the opportunity to use the coordination of aryloxide ligands to build arrays of more than one porphyrin. It is easy to make aryloxo complexes of Sn(IV) porphyrins; either Sn(P)$Cl_2$ or Sn(P)$(OH)_2$ can be reacted with the free phenol. The p$K_a$ differences are such that the aryloxo complexes are relatively stable to hydrolysis, unlike the alkoxides described above. Buchler prepared Sn(OEP)$(OPh)_2$ by heating Sn(OEP)$Cl_2$ in neat phenol for 2 h at 220 °C [19a]. The product was isolated in 72% yield after column chromatography on activity IV alumina. Nimri and Keiman prepared bis(1-naphthoxo) complexes of TpTP, TCPP and TpBrPP by treating Sn(P)$Cl_2$ with a large excess of 1-naphthol, and determined the crystal structure of one derivative, namely Sn(TpTP)(O-1-Nap)$_2$ [62]. They were studying these complexes as transition state analogues of metalloporphyrin sulfoxidation catalysts, and also reported the formation and some NMR details of the mixed ligand complex Sn(TCPP)(O-1-Nap)Cl [62].

We found that aryloxo complexes are conveniently prepared using the dihydroxo complex and only a small excess of the phenol. Thus we prepared Sn(TPP)$(OC_6H_4\text{-}4\text{-}Me)_2$ complexes by refluxing Sn(TPP)$(OH)_2$ with a modest excess

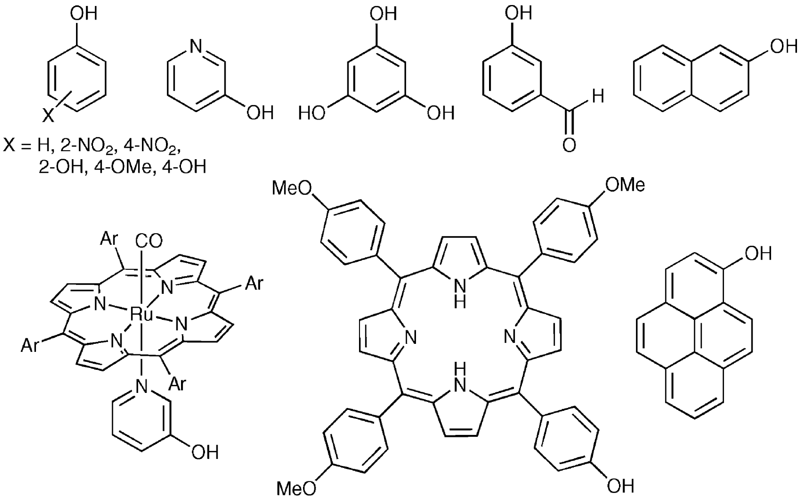


Fig. 5. Structures of phenols used by Langford et al. to prepare aryloxo Sn(IV) porphyrin complexes [65,66].

of *p*-cresol in benzene for 1 h [43]. Later, we also prepared Sn(TPP)($OC_6H_4$-4-Br$)_2$ and Sn(TPP)($OC_6H_4$-4-$NO_2)_2$, using Sn(TPP)$(OH)_2$ and the phenol in a 1:2.5 molar ratio in $CDCl_3$ in NMR tubes for our $^{119}$Sn NMR studies. The compounds were subsequently isolated by evaporation of the solvent and trituration with ether [39]. This method is the most convenient as it avoids the undesirable solvent benzene and large excesses of the phenols (which can be difficult to remove, even by recrystallization). This may be another reflection of the tendency of acids to H-bond to O-bound axial anions (see below).

Langford et al. have recently made detailed studies of bis(aryloxo) complexes, including determining several crystal structures [63–66,83]. They have now studied quite a variety of phenols (Fig. 5). They confirmed the formation of mono- and bis(aryloxo) complexes and referred to this acidolysis as a “recognition”, in the same sense used by Sanders et al. in studies of carboxylate coordination [84,85]. The expected phenomenon of the upfield shift of the axial ligand protons was emphasised again in this paper with the statement “this observation offers the likelihood of Sn(IV) porphyrins acting as shift reagents for phenolic species” [66]. This point has been made before [42] and the analogous Ge(IV) porphyrin complexes were highlighted in this regard by Kenney as long ago as 1973 [86]. Langford’s work led to the proposal of a mechanism for the substitution reaction (see Section 3.4 below) [66]. In related structural studies, this group has also published crystal and molecular structures of two bis(aryloxo) complexes that form molecular sieve-like channels in the crystal [64] – these will be discussed in Section 3.5 below. The complexes were all prepared from Sn(TpTP)$(OH)_2$ and the corresponding phenol in chloroform, and were purified by column chromatography on neutral alumina. This confirms again the stability of aryloxo complexes to hydrolysis.

On the other hand, the group of Maiya have used the benzene method to prepare several bis(aryloxo) complexes [52]. In a paper dealing only with monoporphyrin structures, they described the preparation, visible, fluorescence, NMR and mass spectra and redox potentials of Sn(TpTP)$(OAr)_2$ [Ar $= C_6H_5$, $C_6H_4$-4-Me, $C_6H_4$-4-$NO_2$, $C_6H_3$-3,4-$Me_2$ and $C_6H_4$-4-$OC_6H_3$-2,4-$(NO_2)_2$] [52]. The products were formed by refluxing Sn(TpTP)$(OH)_2$ with a large excess of the phenol in benzene for 2 h, and crude products were chromatographed on activity I neutral alumina. Pure products were obtained in yields of 60–70%. Reddy and Maiya also emphasised the shielding effects of the porphyrin on the protons of the coordinated ligands. The authors pointed out that apart from loss of the OAr fragment in the FAB-MS measurements, the aryloxo ligands showed no tendency to dissociate during any synthetic manipulations or spectroscopic measurements [52]. Maiya’s group have used axial aryloxo coordination to build multiporphyrin arrays (see Section 3.5) [87,88], and their work, together with that of Langford et al., has illustrated well the convenient properties of these aryloxo complexes.

### 3.3.4. Carboxylato complexes

Tin(IV) bis(carboxylates) are readily prepared and are very stable and tractable compounds. For this reason, they are ideal for use as building blocks for multiporphyrin arrays, as described by Webb and Sanders [20]. From the relative p$K_a$ values of phenols and carboxylic acids, the carboxylates are expected to be even more stable to hydrolysis than are the aryloxides. We also found that carboxylate ligands on tin are useful for defining the NMR shielding zones of the porphyrin ligand and for studying the effects of other axial ligands on the properties of the tin coordination sphere [42]. Carboxylato complexes have featured with respect to the use of Sn(IV) porphyrins as active cationic components in ion-selective electrodes of the polymeric membrane type. These membranes detect the clinically-relevant anion salicylate in a super-Nernstian fashion [49,89]. This aspect will be described in Section 3.4 below, as will the studies of Sanders et al. on carboxylic acid recognition mechanisms.

As mentioned above, use of acetate-containing metallation media, e.g. $SnCl_2$/acetic acid/sodium acetate, is generally not a good method for preparing pure diacetato complexes. Therefore, we used excess silver acetate in acetic acid to ensure the removal of chloride from $Sn(TPP)Cl_2$. The product retained acetic acid, but this could be removed by grinding and vacuum drying at 70 °C [43]. We later found that the complexes are easily prepared by acidolysis of the dihydroxo complexes in dichloromethane or chloroform and we published this method in the form of an undergraduate experiment whose aim is to illustrate aromatic ring current effects on NMR spectra [42]. This technique was suggested by the work of Gouterman et al., who prepared $Sn(Etio\ I)(OBz)_2$ by the reaction of $Sn(Etio\ I)(OH)_2$ in chloroform with a saturated aqueous solution of benzoic acid [26]. The crystal structure of $Sn(TPP)(OAc)_2$ was determined by Chen et al. on a sample prepared by a similar method. Although the sample for crystallography was grown from dichloromethane/hexane, it still retained two molecules of acetic acid per porphyrin unit [68]. Brothers and co-workers reported the preparation and crystal structure of $Sn(TpClPP)(OCOEt)_2$, prepared from propionic acid and the dihydroxo complex (not isolated, but prepared by chromatography of the dichloride) [67]. We prepared several other bis(carboxylato) complexes, namely $Sn(TPP)(OCOAr)_2$ (Ar = phenyl, 2-hydroxyphenyl, 2-acetoxyphenyl), by the acidolysis of $Sn(TPP)(OH)_2$ in chloroform and determined their crystal structures (see Section 3.2 above) [57].

The diformato complexes $Sn(P)(OCOH)_2$ (P = TPP, TpTP) are readily prepared by treatment of $Sn(P)(OH)_2$ with formic acid [41]. There are very few well-documented examples of mixed-ligand Sn(IV) porphyrins, i.e. Sn(P)(X)(Y), but by using one equivalent of formic acid, Sn(TPP)(OH)(OCOH) was isolable [41]. The mixed-ligand complexes are not stable in solution and tend to undergo symmetrisation to yield mixtures with the dihydroxo and diformato species [41]. Indeed, we found it convenient to study the unsymmetrical complexes Sn(TPP)(OCOH)X formed in situ by mixing $Sn(TPP)(OCOH)_2$ and $Sn(TPP)X_2$ and allowing them to reach equilibrium in $CDCl_3$ solution (Eq. (1)) [40].

$$Sn(P)(OCOH)_2 + Sn(P)X_2 \rightleftharpoons 2Sn(P)(OCOH)X \qquad (1)$$

The rates and equilibrium constants of these redistributions vary widely depending on the nature of $X^-$, but we did not study these processes quantitatively. The ready availability of a series of complexes with formate as one axial ligand and a variety of anions in the *trans* position enabled us to study the *trans* influences of the anions $X^-$ [40]. The chemical shifts of the formate proton and the coupling constants $^3J(SnH)$ correlate with each other over a wide range of ligands, and furthermore the coupling constants correlate with the $pK_a$ of *trans* O-bound ligands [40]. Weaker bases exhibit stronger Sn–formate bonding, as shown by their large $^3J(SnH)$ values. The wide range of $J$ values (22–71 Hz) makes this a sensitive measure of the *trans* influence. As also found for various other estimates of *trans* influences, the halides do not fit the relationship seen for the O-bound ligands [40]. However, the bonding situation does not seem to be entirely explained by proton basicity, since amongst the most deviant of points from the $J$ versus $pK_a$ correlation were the other carboxylates. It would probably be very informative to obtain a crystal structure of a mixed bis(carboxylato) complex, but special precautions (perhaps crystallisation at very low temperatures) may be required to avoid the precipitation of mixtures or the displacement of the redistribution equilibrium away from the unsymmetrical complex.

### 3.3.5. Other O-bound complexes

Under this heading we describe complexes of oxyanions that are more weakly basic than carboxylates. These are most readily obtained by the simple procedure of acidolysis of the dihydroxo complexes. We prepared $Sn(TPP)X_2$ ($X = ClO_4$, $CF_3SO_3$ and $NO_3$) by this method. One convenient procedure is to treat $Sn(P)(OH)_2$ with HX (neat or aqueous) in dichloromethane at room temperature followed by the addition of a drying agent such as an anhydrous salt [40,42]. The reactions of $Sn(P)(OH)_2$ with these strong acids are virtually instantaneous. Kadish et al. made $Sn(TpTP)(ClO_4)_2$ and $Sn(TmTP)(ClO_4)_2$ by acidolysis of $Sn(P)Cl_2$ in dichloromethane [76]. Our original preparation of $Sn(TPP)(ClO_4)_2$ involved precipitation of chloride from $Sn(TPP)Cl_2$ using $AgClO_4$ in dry benzene [43]. We also prepared $Sn(TPP)(CF_3SO_3)_2$ (or the diaqua complex) using $AgCF_3SO_3$ in THF [57]. This method is not recommended when compared with the acidolysis route. We prepared the perchlorato complex in order to obtain a very weakly ligated system for subsequent anion replacements [43], but nowadays the bis(triflate) complex is recommended. We do not have any specific evidence of an explosion hazard with $Sn(P)(ClO_4)_2$, but obviously it is better not to use perchlorate when triflate is available. Both these complexes behave differently to all other $Sn(P)X_2$ in the presence of coordinating solvents. We noted in our early papers [43,57] that both $Sn(TPP)(ClO_4)_2$ and $Sn(TPP)(CF_3SO_3)_2$ have low solubility in chloroform, but are readily soluble in THF and acetone unlike all other complexes in this series. It is clear that ligands such as THF, water and acetone displace the anionic ligands to generate [Sn(TPP)(Solv)(X)]X or $[Sn(TPP)(Solv)_2]X_2$ (Solv = neutral solvent, $X = ClO_4$, $CF_3SO_3$). This was shown also by Kadish et al. in their electrochemical studies of $Sn(P)(ClO_4)_2$ [76]. In the crystal structure determination of "$Sn(TPP)(CF_3SO_3)_2$", we found that in the crystal actually analysed, water had coordinated during slow crystallisation from THF/pentane [57]. However, the crystal structure of $Sn(TPP)(ClO_4)_2$ determined by Chen and co-workers revealed ordered O-bound perchlorates [70]. It is clear that both $Sn(TPP)(ClO_4)_2$ and $Sn(TPP)(CF_3SO_3)_2$ are very labile species and particularly the latter offers an ideal starting material for reaction with anions under very mild conditions. We have prepared the dinitrato complex by both the Sn(TPP)$Cl_2$/$AgNO_3$/benzene and Sn(TPP)$(OH)_2$/$HNO_3$/$CH_2Cl_2$ routes and determined its structure crystallographically [38]. The weakly-bound nitrate is ordered and monodentate, and this complex is well-behaved in chloroform solution. It would probably also be a useful starting material for anion displacements, but we are not aware that it has been employed as such.

### *3.3.6. N-Bound complexes*

There are relatively few complexes of Sn(IV) porphyrins with axial N-bound ligands. The earliest example was Sn(TPP)$(NCS)_2$ prepared from Sn(TPP)$(ClO_4)_2$ and KSCN in acetone [43]. The IR spectrum and comparison of NMR coupling constants indicated that the axial ligands in this complex are N-bound [43]. The diazido complexes Sn(P)$(N_3)_2$ (P = OEP, TpTP, TmTP) were prepared by Guilard et al. by treating Sn(P)$Cl_2$ with a large excess of $NaN_3$ in 1,2-dichloroethane [90]. It is possible that the last two complexes were contaminated with some of the corresponding chlorin complexes, as the authors reported absorption bands at 627 nm. Such bands were not reported for the OEP complex nor for the corresponding germanium derivatives. We prepared Sn(TPP)$(N_3)_2$ from the corresponding diperchlorate and sodium azide in acetone, and did not observe an absorption band near 627 nm [24]. The diazido complexes were used by Guilard et al. to prepare N-bound bis(phenyltetrazolato) complexes Sn(P)$(N_4CPh)_2$ (P = OEP, TpTP, TmTP) using cycloaddition of the bound azides to benzonitrile [91]. These complexes were characterised by a range of spectroscopic measurements. It is not clear from this report whether these complexes are readily hydrolysed, but the authors did use Schlenk techniques.

More recent work by Chen and Woo resulted in the characterisation of derivatives of more basic amide anions [71]. Thus they prepared N-bound amido complexes Sn(TpTP)$(NHPh)_2$, Sn(TpTP)$(NPh_2)_2$ and Sn(TpTP)[*o*-$C_6H_4(NH_4)_2]_2$ by metathesis of Sn(TpTP)$Cl_2$ with excess of the corresponding lithium amides in toluene. Precipitation with hexane gave crystalline products. The handling of these very basic derivatives required dry box conditions. The *o*-phenylenediamine derivative was shown, as expected, to have the *cis* chelated geometry. Chen and Woo also studied the exchange of amido ligands, for example the reactions of Sn(TpTP)$(NHPh)_2$ with *p*-toluidine, 2,3,5,6-tetrafluoroaniline and *o*-phenylenediamine gave the respective amide exchange products. Reaction of Sn(TpTP)$Cl_2$ with the bulky reagent lithium (2,4,6-tri-*tert*-butylphenyl)amide, even at low temperature, generated only the reduction product Sn(TpTP) [71]. The high basicity of the amido ligands was shown by reaction with methanol, which rapidly and quantitatively generated Sn(TpTP)$(OMe)_2$ [71,81]. The authors stated the conclusion that has been demonstrated in almost all studies of Sn(IV) porphyrins, that ease of protolytic substitution of axial anions correlates qualitatively with anion basicity (see Section 3.4 below).

### *3.3.7. C-Bound complexes*

To extend the range of axial anions into the very strongly basic region, various authors have prepared organometallic Sn(IV) porphyrins. It has been noted that organometallic porphyrins are well-known for similar metalloporphyrins such as M(P)R (M = Al, Ga, In, Tl) and M(P)$R_2$ (M = Si, Ge), but are rather rare for Sn(IV). This is probably a consequence of both the ease of reduction of Sn(IV) porphyrins and the photosensitivity of the tin-carbon bond in Sn(P)$R_2$ complexes.

Cloutour et al. reported the first experiments in this field in a series of papers from 1977 to 1984 [44,92–94]. These authors studied the reaction of M(TPP)$Cl_2$ (M = Ge, Sn) with Grignard reagents and the photooxidation of the dialkyl derivatives M(TPP)$R_2$ (for M = Sn, R = $CH_2SiMe_3$, Et) [44,93]. Later, they also reported the reactions of Sn(TPP)$(OH)_2$, Sn(TPC)$(OH)_2$ and Sn(TPiBC)$(OH)_2$ with a range of Grignard reagents, namely ethyl, propyl, isopropyl, isobutyl, *sec*-butyl and *tert*-butyl [94]. These alkyl derivatives of Ge(IV) and Sn(IV) porphyrins are very light-sensitive and are readily decomposed in the presence of light and oxygen to alkylhydroperoxo complexes M(P)$(OOR)_2$ [44,93]. Only $Me_3SiCH_2MgX$ gave pure products for tin; EtMgX led to incomplete alkylation [92]. Cloutour et al. showed that when alkylation does not take place on the metal, the primary attack is at the periphery of the macrocycle, leading to one-electron reduction and thence addition of the alkyl group to the ring [92]. This type of reaction and Senge's alkyllithium alkylations of porphyrins and metalloporphyrins would appear to be quite similar [95]. In the comparative reactions with the dihydroxo complexes, the most sluggish alkylation at tin (and most ring addition) occurred with the branched alkyl groups and the porphyrin complex. For the TPiBC complex, alkylation was exclusively at the metal. The authors then showed that transition metal impurities in the magnesium used for the Grignard reagent preparation favoured the electron transfer reactions, and so Sn(TPP)$Et_2$ could be formed exclusively using very pure magnesium [94]. It seems interesting that the dihydroxo complexes could be used in these reactions without complications from deprotonation of bound OH groups. As stated elsewhere in this review, no quantitative studies of the basicity of Sn-bound OH groups have been reported, although it is clear that μ-oxo bridged diporphyrins can be formed from Sn(P)$(OH)_2$ under certain conditions.

The first organometallic Sn(IV) porphyrins to be isolated as pure solids were reported in 1992 by Kadish et al. [45], who used the elegant method of oxidative addition of methyl iodide to tin(II) porphyrins in THF to prepare Sn(P)(Me)I (P = OEP, TpTP, TmTP, TMP). These complexes required handling under anaerobic, anhydrous conditions, but were fully characterised by CHN analysis, spectroscopy and electrochemistry. This method circumvented the problems experienced earlier by Cloutour et al. [44,92–94]. Using cyclic voltammetry, Kadish et al. demonstrated the displacement of the *trans*-iodide by coordinating solvents, namely PhCN and THF, and also found evidence for the *trans*-dimethyl species Sn(P)$Me_2$ [45].

In 1996, J. Arnold and co-workers prepared *trans*-Sn(P)$Ph_2$ (P = TPP, TpTP) by reaction of the dichlorides with diphenylmagnesium [50]. These authors also prepared for the first time the *cis*-diaryl complexes Sn(P)$Ph_2$ (P = TpTP, TBPP, OEP) by the novel method of insertion of the $SnPh_2$ fragment as $SnPh_2Cl_2$ into $Li_2(DME)_2$(P). These *cis* complexes were isolated in good yields and characterised spectroscopically, and the crystal structure of the TBPP complex was determined (see Section 3.2 and Fig. 1). The authors also demonstrated the formation of Sn(TpTP)(Ph)Cl by stirring Sn(TpTP)$Ph_2$ in chloroform in ambient light [50].

In association with their work on amido complexes mentioned in Section 3.3.6, Chen and Woo prepared several *trans*-dialkyl and for the first time, *trans*-dialkynyl complexes Sn(TpTP)$R_2$ (R = Et, $CH_2CMe_3$, $C_2Ph$, $C_2SiMe_3$) [71]. These were prepared by conventional metathesis of Sn(TpTP)$Cl_2$ with $ZnEt_2$ or alkyl- or alkynyllithiums. They confirmed the applicability of the $Li_2(THF)_2$(TpTP) + $SnR_2X_2$ method for making *cis* complexes by using $SnMe_2Br_2$ in toluene to make *cis*-Sn(TpTP)$Me_2$. Remarkably, in $CH_2Cl_2$ the same reaction gave *trans*-Sn(TpTP)(Me) Br. As an illustration of the stabilisation conferred by less basic organic anions, Chen and Woo showed that the dialkynyl complexes Sn(TpTP)$(C_2R)_2$ (R = Ph, $SiMe_3$) were remarkably robust, being inert even in the presence of light, and surviving aerobic conditions in benzene solutions for three days [71]. On the other hand, one or both phenylacetylides readily underwent methanolysis to form Sn(TpTP)($C_2Ph$)(OMe) and thence Sn(TpTP)$(OMe)_2$ [81]. From the above examples, it is apparent that the chemistry of organometallic Sn(IV) porphyrins has not been developed very extensively, and there are opportunities for broader studies. It has been noted by several authors in this field, that the photoreactivity of these species is a potential therapeutic tool, especially because various Sn(IV) porphyrinoids (e.g. tin Etiopurpurin) exhibit favourable photodynamic behaviour. However, the air- and water-sensitivity of the alkyl and aryl derivatives seems to conspire against such applications.

### 3.3.8. *Miscellaneous complexes*

There are a few other complexes with uncommon axial ligands whose chemistry is collected here. Among the Sn(IV) complexes, there are only two types of five-coordinate complex reported, namely the sulfides and selenides Sn(P)S and Sn(P)Se (P = TPP, TpTP, TmTP, TMP, OEP). These were prepared by the Guilard/Kadish group by reacting the tin(II) porphyrins with $Cp_2TiS_5$ or $Cp_2TiSe_5$ [96]. All except the OEP complexes were fully characterised by CHN analysis, spectra, voltammetry and spectroelectrochemistry. In particular, the NMR spectra showed facial non-equivalence as expected for square-pyramidal geometry. IR bands in the ranges 426–437 and 292–300 $cm^{-1}$ were observed respectively for the sulfides and selenides, and these confirm the Sn=X bonding situation. Interestingly, the selenides and Sn(TMP)S showed an extra Q band at 630–643 nm [96]. Woo's group also prepared Sn(TpTP)S and Sn(TpTP)Se by the above method, and showed that these complexes transfer the chalcogen atom from tin to molybdenum according to Eq. (2) (X = S, Se) [97].

$$\begin{aligned}&\mathrm{Mo(TpTP)(PhC_2Ph) + Sn(TpTP)X}\\&\quad\rightarrow \mathrm{Mo(TpTP)X + Sn(TpTP) + (PhC_2Ph)}\end{aligned}\qquad(2)$$

Inoue et al. reported the existence of cationic complexes containing triphenylphosphine and its oxide, prepared in situ by substitution of bound water molecules on $[Sn(TPP)(H_2O)_2]^{2+}$ [98]. The latter was formed by addition of water to solutions of Sn(TPP)$Cl_2$ in dry acetonitrile. An increase in fluorescence intensity and a small blue shift of the Soret band were taken as evidence of coordination of neutral ligands. On the other hand, addition of hydroxide or phosphine oxide to the diaqua complex caused modest ($\frac{3}{4}$ 2 nm) red-shifts. Although the authors showed these changes did affect the photophysical behaviour, more definitive data, namely intensity ratios of the Q bands and NMR spectra, were not provided, so it is difficult to assess the validity of the structural proposals. It is clear, therefore, that complexes of neutral Lewis bases on Sn(IV) porphyrins are really rather rare and not many examples have been unambiguously defined.

Finally, there are a few complexes containing axial ligands derived from metal carbonyls, mostly analogous to those of other main group metals such as Ge and In. The first of these involved reaction in refluxing 1,2-dichlorobenzene of Sn(TPP)$Cl_2$ with $Re_2(CO)_{10}$ to form Sn(TPP)$[Re(CO)_3]_2$ in 23% yield [99]. This complex was characterised by UV-Vis and vibrational spectra. Conducting the reaction at the lower temperature of 160 °C led instead to an unusual dicarbido complex Sn(TPP)$[CRe(CO)_3]_2$, whose structure was proved by X-ray crystallography [74]. In 1996, Guilard et al. reported a re-investigation of this reaction [100]. They isolated two types of cationic Sn–Re bonded species, namely $\{Sn(P)[Re(CO)_5]\}(BF_4)$ (A) and $\{[Sn(TPP)]_2Re(CO)_4\}(BF_4)$ (B) (P = TpTP, TmTP). These species were fully characterised by FAB mass spectra, and IR, UV-Vis and NMR spectra, as well as electrochemical measurements [100]. On the basis of all the data, the authors assigned the structures of complexes (A) as hybrids of $[Sn(IV)–Re(–I)]^+$ and $[Sn(II)–Re(I)]^+$ limiting forms, and those of (B), as hybrids of $[Sn(IV)–Re(–I)–Sn(II)]^+$ and $[Sn(II)–Re(I)–Sn(II)]^+$ [100]. The (A) complexes are therefore analogous to the 18-electron $Fe(CO)_4$ complexes previously studied by these authors. The latter species, namely Sn(P)$[Fe(CO)_4]$ (P = OEP, TpTP, TmTP), were prepared by treatment of Sn(P)$Cl_2$ with $Na_2Fe(CO)_4$ in THF. They were characterised spectroscopically, crystallographically {for Sn(OEP)$[Fe(CO)_4]$ [54]} and electrochemically [101]. The data, including Mössbauer measurements, supported structures having "carbenoid" bonding of Sn(II)(P) to a formally zerovalent iron carbonyl fragment [54]. This group also later characterised similar complexes of tetraarylporphyrins with appended fatty acid amido substituents [102].

A more extended M–M framework has also been attached to a tin porphyrin. Complexes Sn(TPP)–$Mn(CO)_4$–Hg–$Mn(CO)_5$ and Sn(TPP)–$Co(CO)_3$–M–$Co(CO)_4$ (M = Hg, Cd, Zn) were prepared by reacting $Sn(TPP)Cl_2$ with $Hg[Mn(CO)_5]_2$ or $M[Co(CO)_5]_2$ in THF [75]. The crystal structure of the Sn–Mn–Hg–Mn complex was determined, and this showed a tin(II) porphyrin attached to the Mn fragment in a *cis* orientation to the Hg-$Mn(CO)_5$ moiety. The tin atom lay out of plane by 0.85 Å [75]. Although the ligand on tin is rather unusual, the nature of the Sn–Mn bonding is completely analogous to that in the Guilard compounds described above.

### 3.4. Mechanisms of axial substitution reactions

There have been surprisingly few attempts to study substitution reactions of tin(IV) porphyrins from a quantitative mechanistic viewpoint. Asadi et al. studied the kinetics and mechanism of the apparent displacement of chloride ligands by amines, namely $BuNH_2$, *sec*-$BuNH_2$, *tert*-$BuNH_2$, $Bu_2NH$ and $Bu_3N$, in DMF solution [103]. The kinetic data were obtained from the decay of an absorption band at 626 nm, but it is very likely that this is due to the presence of chlorin complex as an impurity in the $Sn(TPP)Cl_2$, and the reaction being followed was a (photo)oxidation of the chlorin. The proposed associative mechanism seems unusual for a saturated main group metal centre, particularly given the fact that Sn(IV) seems so comfortable in its six-coordinate state with bond lengths near ideal for a planar porphyrin ligand. Kadish and collaborators have studied the mechanisms of displacement reactions that occur during electrochemical measurements, and these have been summarised in detail in tables of data in ref. [12]. As mentioned above in Section 3.3.4, we used the redistribution/symmetrisation equilibrium to prepare mixed-ligand complexes [40], and this type of reaction would be an interesting one to study rigorously from both kinetic and thermodynamic viewpoints.

The type of reaction that has been most studied, at least semi-quantitatively, is the acidolysis of O-bound ligands, e.g. $Sn(P)(OH)_2$ with carboxylic acids and phenols and $Sn(P)(OMe)_2$ with water. From the descriptive chemistry outlined above, it is clear that stronger acids will readily displace weaker acids, so the dihydroxo complexes will react well with any acid stronger than water (conversely, under basic/nucleophilic conditions, anions of weak acids are readily displaced, e.g. halides will displace perchlorate or triflate). The only detailed kinetic studies of protolysis reactions are those by Chen and co-workers of the hydrolysis of the dimethoxides $Sn(P)(OMe)_2$ (P = TPP, TpOMePP) in $CDCl_3$ under conditions of controlled addition of water [80,81]. The hydrolysis occurs by a competitive, consecutive second-order reaction via the mixed complex Sn(P)(OH)(OMe). We had previously observed this sequence qualitatively by NMR, but the Taiwanese workers studied it quantitatively and obtained kinetic parameters at 28 °C for the reactions (3) and (4) [P = TpOMePP] [81].

$$\mathrm{Sn(P)(OMe)_2 + H_2O \rightarrow Sn(P)(OMe)(OH) + MeOH} \\ k_1 = (6.63 \pm 0.66) \times 10^{-3}\,\mathrm{M^{-1}\,s^{-1}} \tag{3}$$

$$\mathrm{Sn(P)(OMe)(OH) + H_2O \rightarrow Sn(P)(OH)_2 + MeOH} \\ k_2 = (3.55 \pm 0.35) \times 10^{-3}\,\mathrm{M^{-1}\,s^{-1}} \tag{4}$$

This yielded $K = k_2/k_1 = 0.54 \pm 0.11$, similar to that obtained for the hydrolysis of $Sn(TPP)(OMe)_2$ (0.43) [80]. However, the authors justifiably did not speculate on the details of the mechanism, in the absence of activation energy or entropy measurements and isotope studies. The mechanism of the similar reaction of $Ge(TPP)(OH)_2$ with ethanol, phenols and thiophenol was studied by Meyer and Wöhrle who concluded that these reactions involve initial protonation of the coordinated OH group followed by unimolecular dissociation to a five-coordinate cation. This is attacked by neutral ROH and deprotonation yields the substitution product [104]. This $S_N1$-like mechanism certainly seems the most likely for all similar acidolysis reactions.

Sanders' group presented the first detailed study of the acidolysis mechanism for carboxylic acids, using NMR spectroscopy [84]. These authors also commented in some detail about the relative stabilities and reactivities of various Sn(IV) porphyrin complexes [20]. The major conclusions were as follows. The rate and extent of complex formation from $Sn(P)(OH)_2$ increases with acid strength, e.g. reaction with propionic acid is much slower than with dichloroacetic acid. The carboxylate complexes are in slow exchange (NMR timescale) with excess free carboxylic acid. As we noted in our formate studies [40,41], it is possible with weaker acids or less than two equivalents of stronger acids, to observe formation of Sn(P)(OH)(OCOR). In addition, stronger carboxylic acids will displace weaker ones, but anthracene-9-carboxylic acid displays anomalously "strong" behaviour due to specific π–π interactions with the porphyrin ring. A very interesting observation was that hydrogen-bonded outer-sphere complexes form immediately on mixing $Sn(P)(OH)_2$ with acids, e.g. propionic acid. Using the crowded weak acid adamantane-1-carboxylic acid and reducing the temperature to −53 °C, the H-bonded species was the exclusive product, and an apparent association constant of ca. $10^4\,dm^3\,mol^{-1}$ was derived. From this evidence, the authors postulated the mechanism shown in Fig. 6 [84].

It should be noted that the first suggestion of outer-sphere interaction between carboxylic acids and ligands on tin(IV) porphyrins came from the studies of Meyerhoff et al. on ion-selective electrodes [49]. They found that in polymeric membranes or THF/water solutions, chlorides dissociate from $Sn(TPP)Cl_2$ to form the bis(aquo) dication (a process that does not occur for the dihydroxo complex). The response to salicylate and other aromatic carboxylates was

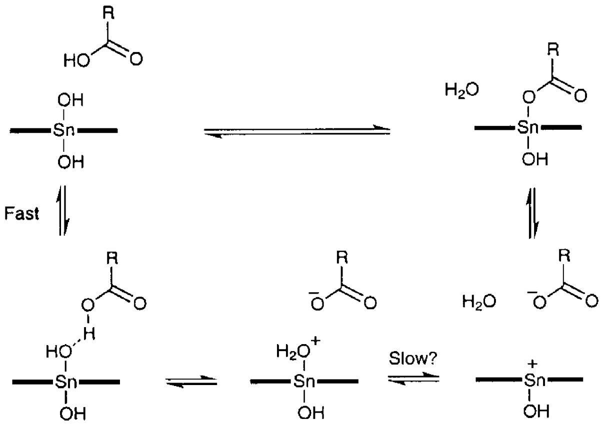


Fig. 6. Proposed mechanism for the acidolysis of dihydroxo complexes by carboxylic acids (also applicable to phenols, etc.). From ref. [84]—reproduced by permission of The Royal Society of Chemistry.

consistent with outer-sphere coordination of the anions to the Sn-bound water molecules, followed by displacement within the membrane. Conductometric measurements implied the involvement of three salicylate ions per porphyrin unit [49]. However, in the most recent discussion of membranes with high porphyrin loadings or containing tetraarylborate additives, the authors ascribe the super-Nernstian salicylate response as being due to a monoporphyrin-diporphyrin equilibrium involving two tin porphyrins bridged by a single hydroxide ion [89a], so the status of the earlier results is unclear. The interesting point noted by Webb and Sanders [20] is that the unusual response is actually for the arylcarboxylates that have internal H-bonds, namely salicylate and 2-hydroxybenzhydroxamate.

Langford and co-workers reported phenol recognition and aryloxide coordination by phenolysis of Sn(TpTP)(OH)$_2$ [65,66]. The rate of substitution was dependent on the substituent in the order phenol $\gg$ 4-methoxyphenol $>$ 4-nitrophenol. This rather anomalous lack of p$K_a$ dependence was noted. The authors also studied the exchange between free and complexed phenols by NMR. In order to compare the complexation behaviour of phenols with that of carboxylic acids (see Section 3.3.4), the possibility of outer-sphere interactions of free phenols with the bound hydroxides was probed using a sterically-hindered phenol, 6-hydroxy-2-methoxy-2,5,7,8-tetramethylchroman. Upon mixing ArOH with Sn(TpTP)(OH)$_2$, NMR changes suggested H-bonding of the type Sn–O(H)... H-OAr. The mixture of Sn(TpTP)(OC$_6$H$_4$-4-OMe)$_2$ with two equivalents of 3-hydroxypyridine at 50 °C caused formation of a statistical mixture of the three possible phenolato complexes within 10 min [66]. This seems to contrast with the observation of Webb and Sanders that addition of excess CD$_3$CO$_2$H to Sn(TPP)(OCOCH$_3$)$_2$ led to no observable deuterium exchange after 5 h [20]. The time is certainly ripe for rigorous quantitative studies to delineate these mechanisms, including measurements of rates and equilibria for ligands whose p$K_a$s span those of other ligand types, i.e. strongly acidic phenols versus carboxylic acids. It could be argued, of course, that chemists are doing quite well anyway in preparing elaborate compounds without this knowledge.

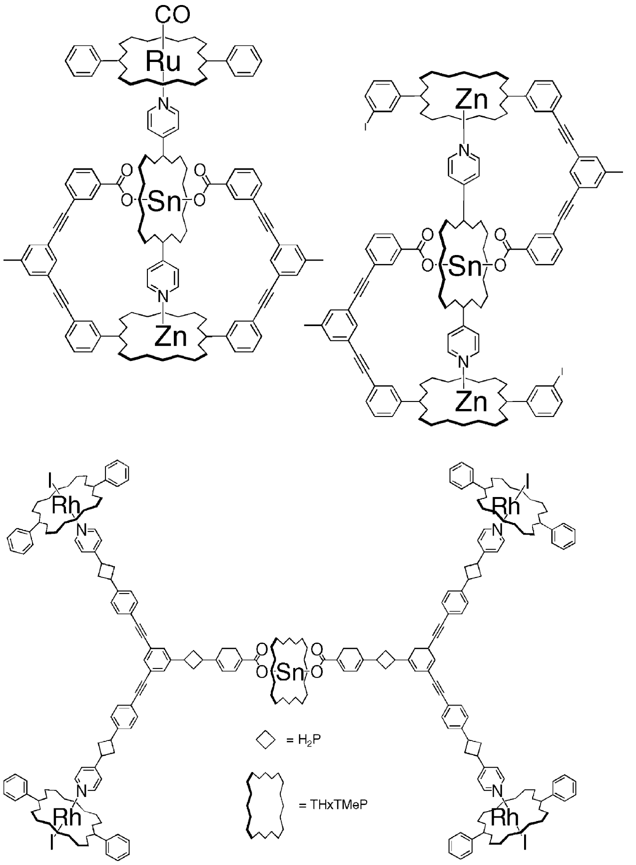
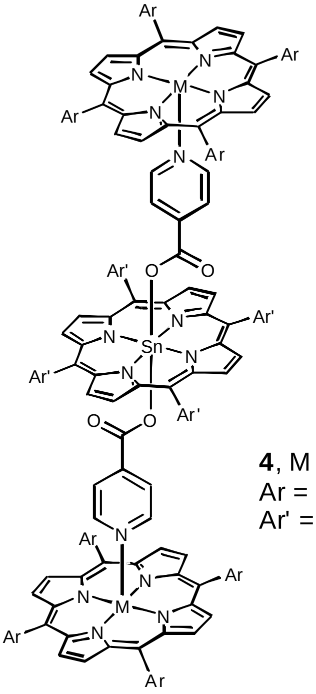


Fig. 7. Some of the Sn(IV) carboxylate-linked multiporphyrin arrays prepared by Sanders and co-workers (peripheral substituents removed for clarity) [69,105].

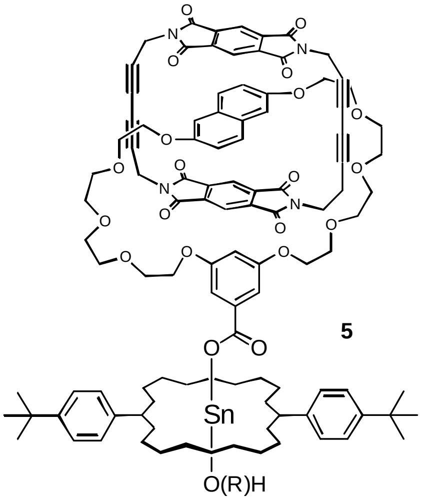
### 3.5. Supramolecular arrays based on Sn(IV) porphyrins

The strong preference of Sn(IV) porphyrins for coordination to carboxylates and phenolates has been used by several authors to construct neutral coordination arrays comprising up to eleven porphyrin nuclei [20,65,69,83,85–88,105–108]. Using carboxylate binding to Sn(IV) components coupled with complementary binding of pyridines to Zn(II), Ru(II) and Rh(III) porphyrins, Sanders et al. prepared trimeric stacks as well as higher arrays generated by linking porphyrin units covalently through aryl alkynes [20,69,85,105]. Some examples are shown in Fig. 7. The original authors have reviewed these elegant studies in “The Porphyrin Handbook” [106a] and have now published a full paper on this work [106b].

The favourable NMR properties of the Rh(III) and Sn(IV) porphyrins, coupled with slow exchange kinetics and tight ligand binding allow detailed NMR studies of the structures of the arrays [20,69,85,105–107]. Triporphyrin cavities and other similar cyclic arrays were constructed using arylacetylene linkers and Zn and Ru porphyrin building blocks [20,105]. In addition, chiral cavities were generated by employing chiral carboxylates on the Sn(IV) centres, but unfortunately the resulting molecules were not capable of inducing enantioselective catalysis [20]. However, this work has clearly demonstrated the utility of the selective coordination of carboxylates to Sn(IV) porphyrins as a tool for multiporphyrin construction. Maiya, Sanders and co-workers showed that the fluorescence of the trimeric stack **4** was significantly quenched compared to the emission from its monomeric components, a fact interpreted in terms of photo-induced electron transfer from the axial Ru(II) porphyrin to the excited state of the central Sn(IV) porphyrin [107]. This demonstrated the additional possibilities of using such arrays for directed electron transfer by virtue of the favourable photoredox properties of Sn(IV) porphyrins. Sanders and co-workers also employed an Sn(IV) porphyrin in a highly original manner as a novel "supramolecular protecting group" attached to a crown ether carboxylate to favour catenane formation through the crown ring by apparently modifying the conformation of the crown component [108]. The ring current shifts induced by the porphyrin facilitated analysis of the NMR spectra of the catenane. Interestingly, the authors were able to cleave the tin porphyrin from the catenane carboxylate **5** by simple treatment with a large excess of methanol for 30 min [108].



**4**, M = Ru(CO),
Ar = p-tolyl,
Ar' = 3,5-di-tBuPh



**5**

The groups of Langford [65,83] and Maiya [87,88] recently used the alternative aryloxide coordination motif to generate multiporphyrin aggregates. The former group has prepared a number of complexes $Sn(P)(OAr)_2$ and characterised their supramolecular interactions in the solid state using X-ray crystallography [64]. They found a common structural result for several derivatives comprising tight helical channels dominated by hydrophobic cavities – a result of weak but significant nonclassical H-bonds of the C–H. . . O type between the Sn(IV) oxygen of one porphyrin in one layer and two hydrogen atoms of the *meso*-tolyl substituent of another layer (e.g. Fig. 8). The authors further suggested that appropriate substituents on the aryloxo rings could be used to design active materials with functional channels [64]. Trinuclear Ru–Sn–Ru and Zn–Sn–Zn stacks were prepared using the complementary binding principle, using phenolate binding to the Sn(IV) centre combined with pyridine binding to Ru(CO)(TpTP) or Zn(TpTP) units (see structure **6**). The Ru-containing trimer was conveniently generated by simple self-assembly and was isolated in the remarkable yield of 95% after chromatography, while the $Zn_2$ complex was characterised in situ due to its lability [65].

Maiya and co-workers prepared a variety of trinuclear arrays using either phosphorus(V) or Sn(IV) porphyrin phenoxides as the central components, e.g. **7** [87,88]. These compounds were conveniently characterised, as usual, by

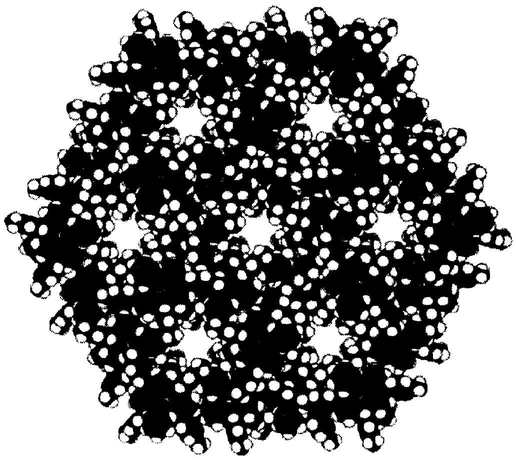
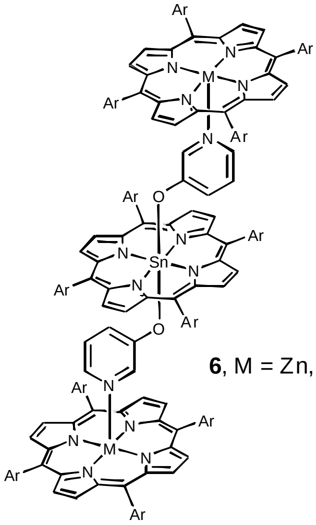
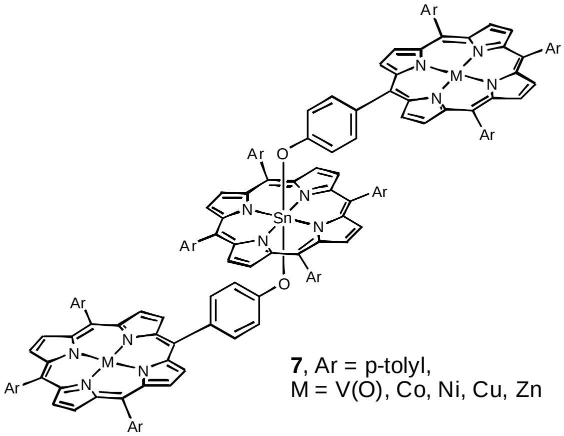


Fig. 8. Hexagonal molecular sieve-like structure adopted by Sn(IV) porphyrin bis(aryloxides) in the solid state. Reprinted in part from ref. [64]. Copyright 2002 American Chemical Society.



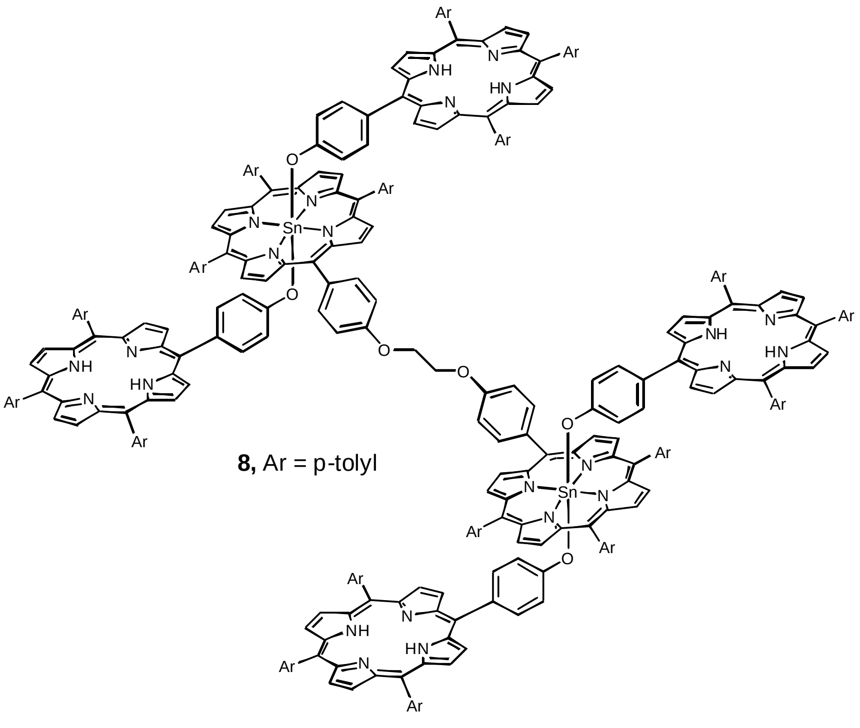
**6**, M = Zn, Ru(CO)

NMR and other techniques, including electrochemistry and fluorescence. The measurements enabled the authors to postulate the mechanisms of photoinduced energy and electron transfer in the complexes having either free base or Zn(II) porphyrins as the axial partners [87]. This group recently extended this building block principle to make hexanuclear and nonanuclear constructs, comprising Sn(IV) porphyrin bis(phenolate) triple stacks linked laterally through ethers in the *para* positions of *meso* aryl substituents, e.g. **8** [88]. To attach the axial porphyrins, they reacted the $Sn(P)(OH)_2$ lateral dimer or trimer and the porphyrinylphenol in boiling benzene. Once more, the authors investigated the interesting energy and electron transfer properties of these arrays [88].



**7**, Ar = p-tolyl,
M = V(O), Co, Ni, Cu, Zn

A recent imaginative use of bis(carboxylato) Sn(IV) porphyrins for construction of a complex nanostructure was reported by Zimmerman et al., who reacted the $SnCl_2$ complex of an alkene-terminated porphyrin dendrimer with succinic acid and silver oxide to form a columnar oligomer linked through the coordination at tin [109]. The terminal units were subjected to Grubbs' olefin metathesis to form a porphyrin-filled tube. The core was then removed almost completely by transesterification with sodium methoxide to release mononuclear Sn porphyrin, leaving nanotubular oligomers [109]. Finally, the work of Fuhrhop and co-workers on chiral Sn(IV) porphyrin assemblies highlights the potential for coordination at tin to generate very complex staircase and lateral aggregates [110]. These structures used porphyrins of the natural substitution pattern, namely proto-, meso- and deuteroporphyrin in the form of D-gluconylhydrazides. By controlling the pH, the



**8,** Ar = p-tolyl

compounds were induced to form either μ-oxo stacks or lateral assemblies that led to fibres or leaflets of monomolecular thickness in water. H-bonding between the axial ligands holds the stacks together—at pH 0 by Cl. . . H. . . Cl interactions or at pH 5 by using cyanate ligands. The supramolecular binding types were delineated by absorption spectral changes and electron microscopy. The chirality and stacking were studied by circular dichroism spectroscopy and the structures exhibited the expected exciton coupling between adjacent porphyrin chromophores [110a].

## 4. Conclusions and outlook

It is clear that the full potential of main group metalloporphyrins as components of multiporphyrin supramolecular arrays and nanostructures is yet to be realised, but the favourable properties of Sn(IV) porphyrins, i.e. planarity, six-coordination and robust binding of oxyanions, suggest that many interesting structures could be made. Weaker supramolecular interactions involving the axial ligands and adjacent CH or other units in the solid state will extend the possibilities. Overall, there are several aspects of Sn(IV) porphyrins that are yet to be fully developed. The medical applications of Sn(IV) porphyrinoids will continue to attract interest, especially in the areas of photoinactivation of pathogens and photodynamic therapy. The complexes with enforced *cis* coordinated ligands have yet to be studied in detail, e.g. dicarboxylates, catecholates and diolates. It is possible that Sn=O oxo complexes may be attainable, by analogy with Group 4 metalloporphyrins, and that these may have uses as oxidation catalysts. The Lewis acidity of Sn(IV) porphyrins has been exploited a few times for catalysis [111], so further developments may be anticipated, especially in the area of solid-supported catalysts [112]. The remarkable anodic shifts of porphyrin reduction potentials caused by coordination to Sn(IV) may allow the isolation of interesting radical anions; for example, we were able to observe for the first time, the electronic absorption spectra of the *triply*-reduced bis($SnCl_2$) complex of ligand **3** [22]. The exploitation of the favourable reduction and electron-transfer properties of Sn(IV) porphyrins for photocatalysis, such as water splitting, will continue. There are several avenues for investigation of fundamental preparative, mechanistic, and structural properties and the complexes of neutral ligands are almost unknown. Quantitative measurements of the $pK_a$ of the Sn(IV)-coordinated hydroxo ligand would be informative, as would rigorous studies of rate and equilibrium constants for axial substitutions. However, we urge anyone contemplating such work to characterise their products and intermediates as fully as possible by the measures that we have highlighted above.

We hope that this review will stimulate further research into the chemistry and spectroscopy of tin porphyrins. There has been a resurgence of interest in tin porphyrins as shown by the recent chemistry described above, but there seems also to have been a tendency for rediscovery of matters described by past workers. We have tried to bring some of these points to the fore in the hope that progress may be facilitated in areas that are really novel. We look forward to further developments in coordination chemistry as well as a continuation of the steady increase in applications of these interesting and attractive complexes.

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