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Self-Assembly and X-Ray Crystal Structures of Novel Sn(IV)Porphyrin Phenolates *

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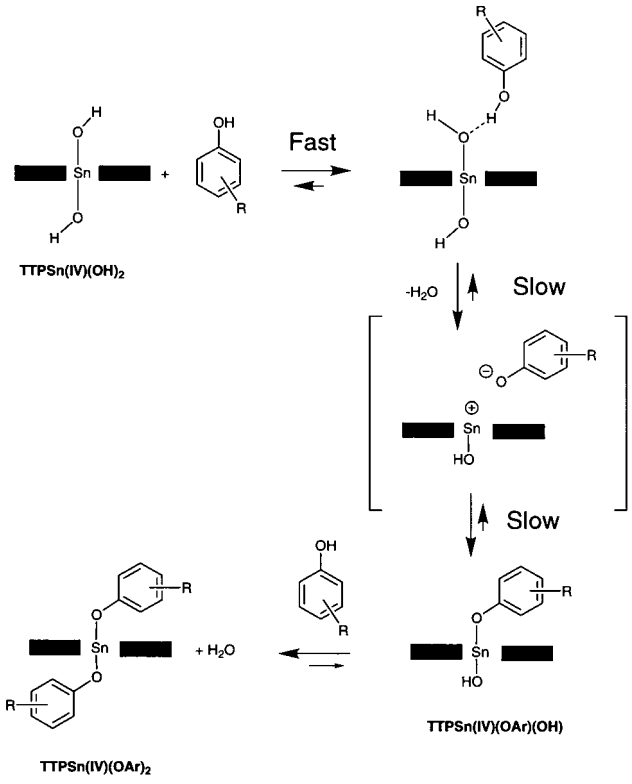
Abstract

A series of complexes of the type [Sn(TTP)L_2] have been prepared by the condensation of [Sn(TTP)OH_2] (TTP = *meso*-tetratolylporphyrin) with a range of substituted phenols. The resulting complexes were characterised using ^{1}H NMR and single crystal X-ray diffraction techniques. In each case, the condensation of the phenols with the Sn(IV)porphyrin in $CDCl_3$ solution is slow (h) but essentially quantitative. The slow kinetics of the formation of the diaxial phenolate complexes allows for the identification, by ^{1}H NMR spectroscopy, of three independent complexes within this process, namely an outer-sphere (H-bonded) complex as well as two independent phenolate complexes. The rate of condensation is in the order phenol $\gg$ 4-methoxyphenol $>$ 4-nitrophenol and suggests a steric rather than pKa dependency.

Introduction

Conclusive evidence from variable temperature ^{1}H NMR [1, 2] and X-ray crystallographic studies [3] indicating that carboxylic acids bind strongly to the metal centres of tin(IV) porphyrins in an axial fashion has renewed interest in their use as structural motifs for supramolecular chemistry [4, 5]. Variable temperature ^{1}H NMR studies [2] on the formation of such complexes revealed that the rate and extent of complex formation is dependent on acid strength and that the process is stepwise. This dependence on acid strength caused us to postulate that phenols (pKa 7–11) might not only bind well but provide suitable structural and recognition roles for the assembly of a new family of sensors and mimics. The inherent simplicity and flexibility in choice of phenolic ligand could be employed in the design and fabrication of more elaborate assemblies and arrays that may mimic portions of the photosynthetic reaction centre or that generate new classes of sensors based on the electronic characteristics of the porphyrin macrocycle. In this paper, we report on the generality of recognition of phenols (Figure 1) and provide direct evidence for the stepwise formation of the bisphenolates of Sn(IV)TTP [6] shown in Scheme 1.



Scheme 1.

* Supplementary Data relating to this article are deposited with the British Library as Supplementary Publication No. SUP 82294 (40 pages).

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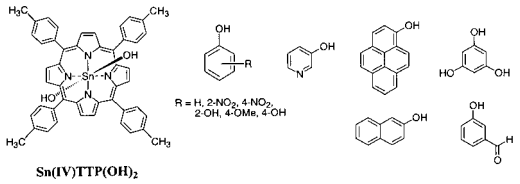


Figure 1. Structures of porphyrinic and phenolic components.

Experimental

General procedures

(5,10,15,20-Tetratolylporphyrinato)tin(IV) dihydroxide was synthesised by literature methods [7]. All phenols were purchased from Aldrich and used as received. ^{1}H and ^{13}C NMR spectra were recorded using the Brüker 300DPX spectrometer operating at 300 and 75 MHz, respectively, and referenced against residual solvent. X-ray crystallographic measurements were carried out using a Nonius KappaCCD diffractometer with graphite monochromatised MoKα radiation [λ(MoKα) = 0.71069 Å] and a $\omega/2\theta$ scan mode to 2θ = 56.6° at 173.0 ± 1 K. The cell constants and the orientation matrices for data collection were obtained from a least squares refinement using setting angles of reflections in the range $0 < 2\theta < 56.6°$. The data were corrected for Lorentz and polarisation effects. Data were collected and processed using Nonius software [8, 9].

General condensation procedure

Sn(IV)TTP(OH)$_2$ (1×10^{-2} mmol) was added to the desired phenol(2×10^{-2} mmol) in based washed $CDCl_3$ (1 mL). *Selected spectroscopic data*: **Sn(IV)TTP(4-OC$_6$H$_4$NO$_2$)$_2$**: ^{1}H NMR: δ_H ($CDCl_3$) 9.18 (s, 8H), 8.01 (d, J = 7.9 Hz, 8H), 7.65 (d, J = 8.2 Hz, 8H), 6.60 (d, J = 9.2 Hz, 4H), 2.75 (s, 12H), 1.84 (d, J = 9.2 Hz, 4H). ^{13}C NMR: δ_C ($CDCl_3$) 162.6, 147.8, 139.1, 137.7, 135.0, 133.2, 128.5, 123.4, 122.6, 117.7, 21.9. **Sn(IV)TTP(OC$_6$H$_5$)$_2$**: ^{1}H NMR: δ_H ($CDCl_3$) 9.12 (s, 8H), 8.10 (d, J = 7.9 Hz, 8H), 7.63 (d, J = 7.7 Hz, 8H), 5.74 (t, J = 1.2 Hz, 2H) 5.65 (t, J = 1.6 Hz, 4H), 2.76 (s, 12H), 1.87 (d, J 7.3 Hz, 4H). ^{13}C NMR: δ_C ($CDCl_3$) 147.7, 138.6, 138.3, 135.2, 132.6, 127.9, 126.5, 122.0, 117.9, 116.7, 21.9. **Sn(IV)TTP(OC$_5$H$_4$)$_2$**: ^{1}H NMR: δ_H ($CDCl_3$) 9.15 (s, 8H), 8.08 (d, J = 3.9 Hz, 8H), 7.62 (d, J = 8.1 Hz, 8H), 7.00, d, J = 1.3 Hz, 2H), 5.57 (m, 2H), 3.25 (d, J = 2.7 Hz, 2H), 2.71 (s, 12H), 2.17 (m, 2H). ^{13}C NMR: δ_C ($CDCl_3$) 213.0, 147.7, 138.7, 138.0, 137.8, 133.2, 128.2, 124.2, 122.4, 121.3, 113.4, 21.9.

Results

^{1}*H NMR study*

Figure 2 shows the time dependent ^{1}H NMR spectra of [Sn(IV)TTP](OH)$_2$ taken at 300 K in $CDCl_3$ after the addition of 2.2 equivalents of 4-methoxyphenol (pKa 10.2). Initial mixing gives: (1) [Sn(IV)TTP](OH)$_2$ (□), (2) resolved 4-methoxyphenol (♦), (3) a set of resonances judged to be a 1:1 complex (■), and (4) a significantly smaller proportion of the 2:1 complex (●). The signals attributed to the uncomplexed [Sn(IV)TTP](OH)$_2$ resonate at the same δ values as they do in the ^{1}H NMR spectra of that individual component. This situation is clearly one of slow kinetics at 300 MHz and 300 K. Over time (*ca.* 120 min) the proportion of each component in solution changes until the only species in solution can be attributed to the excess phenol, water and the bis-phenolate complex. The stoichiometry of the complex formed is readily determined as 1:2 by integration of relevant probe protons on both the host and guest species. In terms of the characteristic porphyrin resonances, subtle changes brought about by the phenol ring system are also seen. In particular, that part of the AA′XX′ system attributable to the *meso*-aryl protons *ortho* to the porphyrin ring are shifted further downfield than the corresponding *meta* protons. Complete control of the three-step condensation process shown in the Scheme is possible through simple heating and cooling. At 253 K, the process is essentially halted while warming a solution containing both components to 333 K completes the recognition process in minutes.

In order to probe the scope of this recognition, we investigated the changes ($\Delta\delta$) of selected resonances in the ^{1}H NMR spectra for phenol (pKa = 10.0), 4-methoxyphenol (pKa = 10.2), 2-nitrophenol and 4-nitrophenol (pKa = 7.2), and a range of other phenols shown in Figure 1. In each of these cases, very large chemical shift changes were observed for the protons *ortho* to the phenol group bound to the Sn(IV) centre (Figure 3), as a result of the time-averaged orientation and proximity of these nuclei to the porphyrin ring. This observation offers the likelihood of Sn(IV)porphyrins acting as shift reagents for phenolic species. The rate of condensation is substituent dependent with the initial order for the conversion of the monophenolate and hence the formation of the bisphenolate complex being phenol ≫ 4-methoxyphenol > 4-nitrophenol (Figure 4). Surprisingly, this result indicates that the mechanism is not governed by a pKa dependency but is more likely influenced by steric factors due to interactions between the substituents on the phenol group with the porphyrins meso aryl groups. The condensation of 3-hydroxybenzaldehyde with Sn(IV)TTP indicates that this method is mild and also selective for phenols and carboxylic acids.

The fact that in all cases, resonances attributed to the aromatic protons of the complexing phenol were instantaneously and unexpectedly shifted upfield ($\Delta\delta$ *ca.* 0.5) and that the set of resonances attributed to the *ortho* phenol protons appear slightly broader than the other phenolic resonances caused us to investigate whether one or more other processes were also occurring. Direct irradiation of the signals attributed to the phenol complex failed to give rise to any residual effects on the signals responsible for the free phenol through an exchange mechanism. However, variable temperature ^{1}H NMR studies over the range 333 K to 253 K (Figure 5) suggested that the unexpected shift of phenol resonances was indeed due to an exchange process. The dramatic changes (> 2 p.p.m.) in the chemical shift of these probe protons indicate a time-averaged interaction

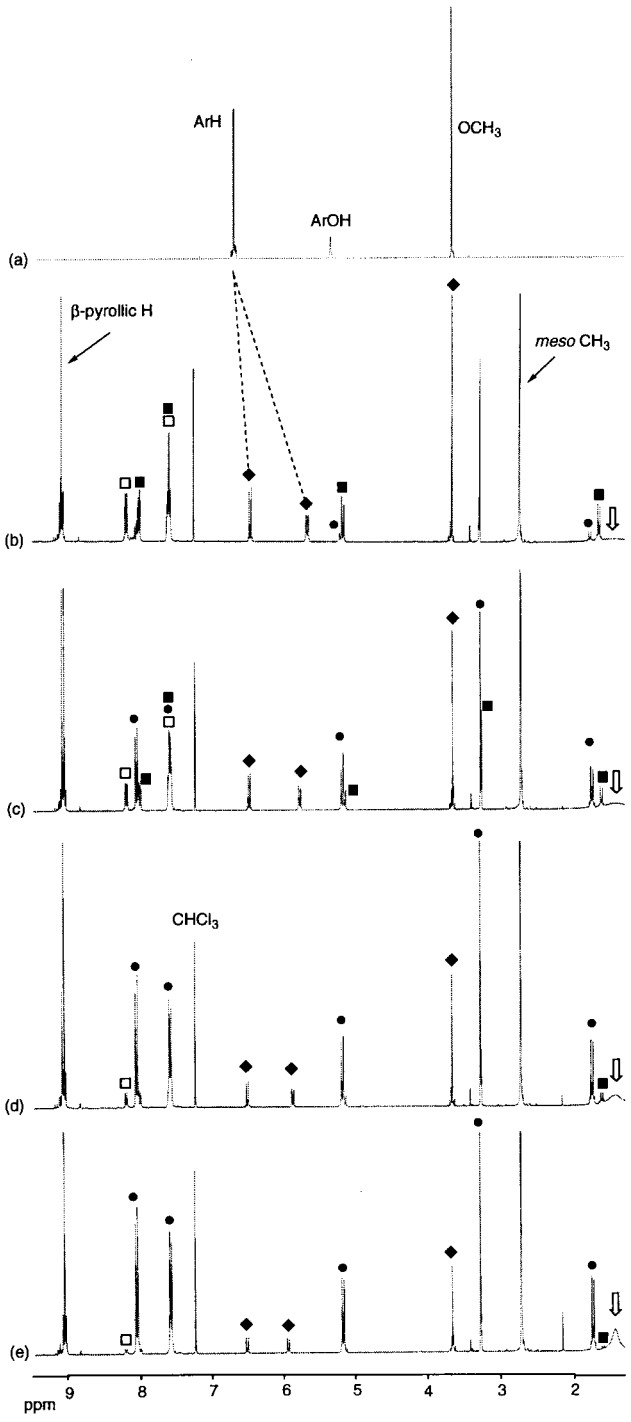


Figure 2. (a) 300 MHz ^{1}H NMR spectrum of 4-methoxyphenol. Time-dependent ^{1}H NMR spectra of 18 mM [Sn(TTP)OH2] recorded in $CDCl_3$ solution at 25 °C after the addition of 2.2 equiv. 4-methoxyphenol (b) 6 min, (c) 26 min, (d) 110 min, (e) 8 h.

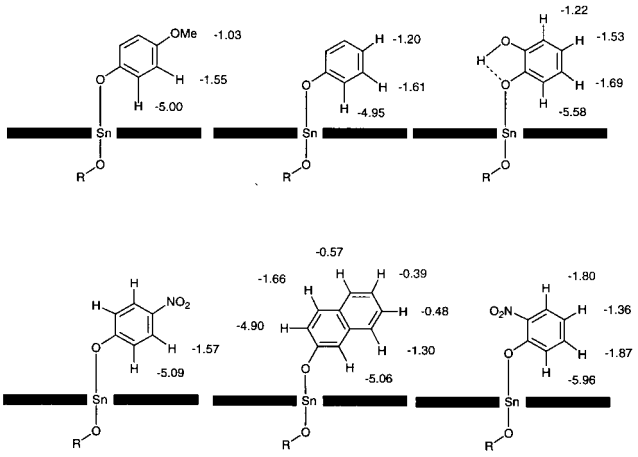


Figure 3. Porphyrin-induced chemical shifts (300 MHz) for some Sn(IV)(TTP) diphenolate complexes observed at 300 K. In each case, $\Delta\delta = \delta$(complex) $- \delta$(free phenol).

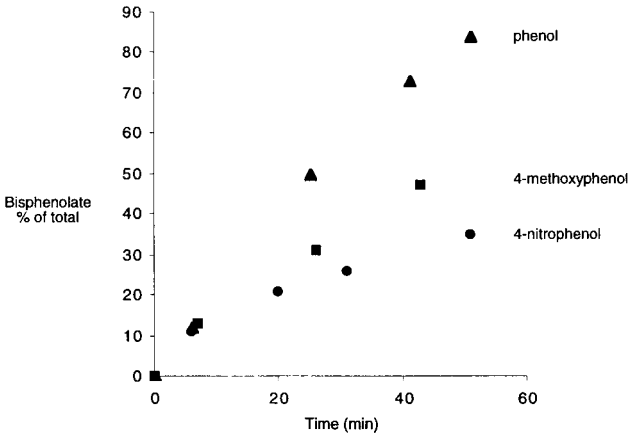


Figure 4. Graph of composition (% of total) of bisphenolate vs time for the phenols 4-nitrophenol (pKa = 7.2), 4-methoxyphenol (pKa = 10.2) and phenol (pKa = 10.0). In each case [Sn(IV)TTP$(OH)_2$] = mM, [phenol] = mM.

between both phenol and porphyrin components consistent with the exchange of one "free" phenol for a bound (Scheme). In order to verify this set of observations, two experiments were performed. In the first, [Sn(IV)TTP$(OH)_2$ (1 mol%) was added to a solution of 4-methoxyphenol in $CDCl_3$. As expected, the phenol resonances underwent the same chemical shift changes, suggesting that an exchange process was likely. To rule out a general porphyrin effect, the same experiment was conducted with ZnTTP (1–30 mol%) with no effect. In the second experiment, a solution of the Sn(IV)TTP bis-4-methoxyphenolate in $CDCl_3$ was mixed with two equivalents of 3-hydroxypyridine. After 10 minutes of warming at 50 °C, the ^{1}H NMR spectrum displayed signals attributable to a statistical mix of the three possible phenolate complexes as well as signals attributed to both exchanging phenols in solution.

In order to confirm the existence of an outer-sphere complex as recently reported for similar complexations involving carboxylic acids [2] and to probe its usefulness to resolve NMR resonances, we mixed [Sn(IV)TTP$(OH)_2$ with two equivalents of the sterically-hindered phenol 6-hydroxy-2-methoxy-2,5,7,8-tetramethylchroman [10], a vitamin e precursor, and observed changes in the 300 MHz ^{1}H NMR spectrum (Figure 6). Almost instantaneously, the two unresolved methyl resonances at δ 2.16 disperse and become fully resolved at 300 MHz. Accompanying this change is the extreme broadening of the otherwise sharp ArOH singlet at δ 4.24, also consistent with the likelihood of an exchange process through hydrogen bonding between the phenol and

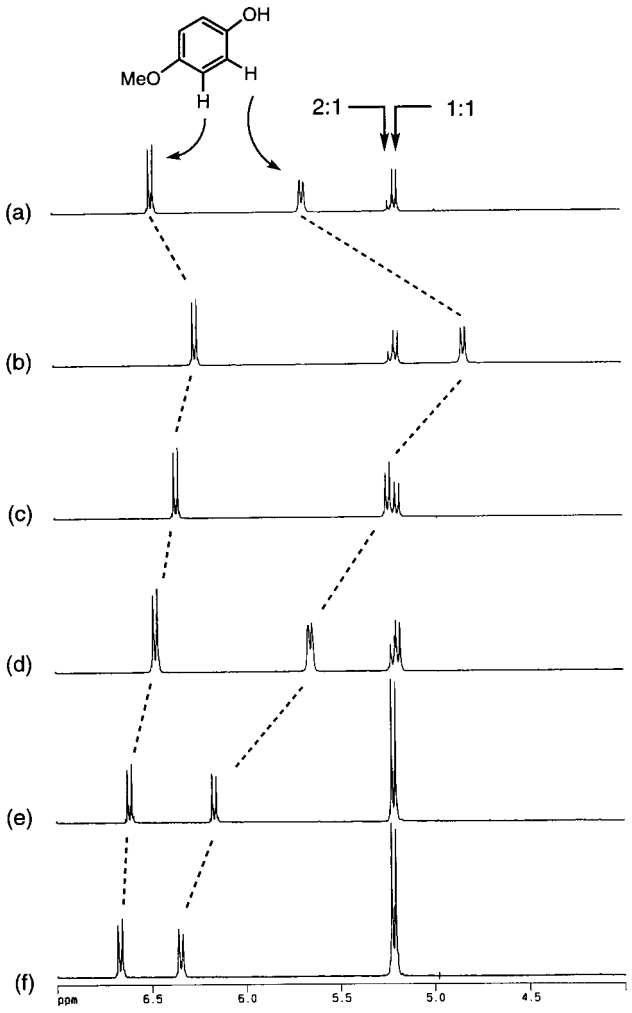


Figure 5. The temperature-dependent behaviour of "free" phenol indicates the presence of a weaker outer-sphere complex. Partial 400 MHz ^{1}H NMR spectra of a $CDCl_3$ solution of 4-methoxyphenol and [Sn(IV)TTP(OH_2)] at (a) 300 K, (b) 263 K, (c) 233 K, (d) 300 K, (e) 313 K, and (f) 333 K.

Sn—OH group. The presence of the methyl groups around the aromatic ring did not allow the reaction to proceed further.

X-ray crystallography

Red single crystals of size 0.38 × 0.18 × 0.14 mm (Sn(IV)TTP(OC_6H_3)$_2$) and 0.27 × 0.25 × 0.08 mm (Sn(IV)TTP(4-$OC_6H_4NO_2$)$_2$) and of suitable quality for X-ray analysis were obtained by slow vapour diffusion of hexane into a dichloromethane solution of the respective complexes. The crystal data are presented in Table 1 and molecular structures and numbering schemes for both complexes are shown in Figure 7. In the crystalline state, both complexes adopt a diaxial and *anti* arrangement of the phenol groups, attached to an octahedral Sn(IV) centre. The Sn—O distances of 2.055 Å and 2.083 Å for Sn(IV)TTP(OC_6H_3)$_2$ and Sn(IV)TTP($4OC_6H_4NO_2$)$_2$ respectively are similar to those found for Sn—O distances in carboxylate complexes. The porphyrin macrocycles are essentially planar showing little distortion due to the effect of the phenol groups. The average Sn—O—C bond angles of 126° and 121° for

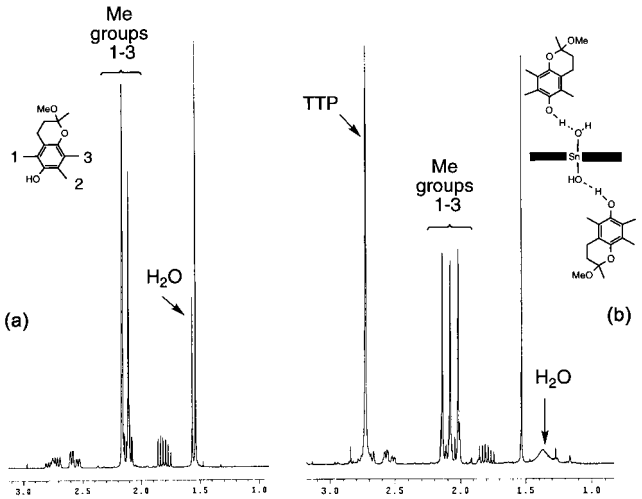
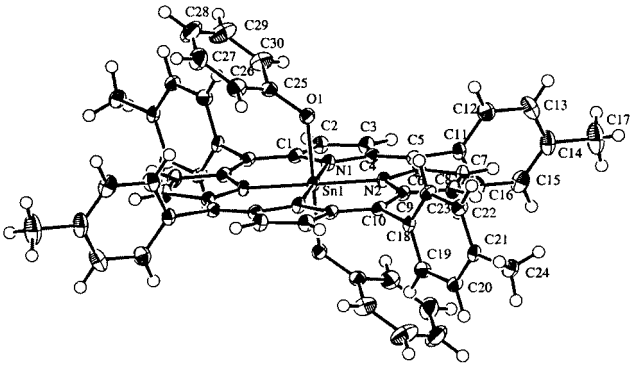
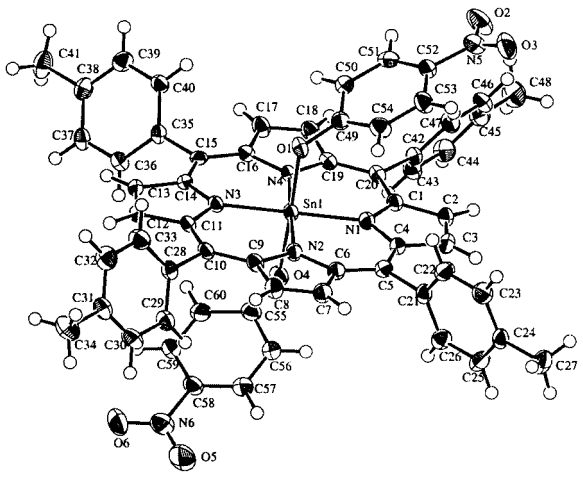


Figure 6. Partial ^{1}H NMR spectra of 6-hydroxy-2-methoxy-2,5,7,8-tetramethylchroman (a) before and (b) after the addition of [Sn(TTP)OH_2] illustrating the separation of aromatic methyl signals.



a



b

Figure 7. Molecular conformations and the crystallographic numbering scheme of Sn(IV)TTP(OC_6H_5)$_2$ (a) and Sn(IV)TTP(4-$OC_6H_4NO_2$)$_2$ (b). Anisotropic displacement ellisoids are drawn at the 50% probability level.

Table 1. Crystal data and structure refinement for Sn(IV)TTP(4-$OC_6H_4NO_2)_2$ and Sn(IV)TTP$(OC_6H_5)_2$

Compound	Sn(IV)TTP(4-$OC_6H_4NO_2)_2$	Sn(IV)TTP$(OC_6H_5)_2$
Formula	$C_60H_{44}N_6O_6Sn$	$C_60H_{44}N_6O_6Sn$
M	1063.73	973.74
T, K	123 ± 1	123 ± 1
Crystal system,	Monoclinic	Trigonal
space group	$P2_1/n$	R3
a/Å	9.7461(1)	36.7789(3)
b/Å	22.9161(3)	
c/Å	21.8754(3)	9.4742(3)
β/°	94.4377(9)	
V/Å^3	4871.06(9)	11098.7(3)
Z	4	9
D_c/g cm^{-3}	1.450	1.311
μ/mm^{-1}	0.586	0.565
F (000)	2176.00	4500.00
Crystal size, mm	$0.27 \times 0.25 \times 0.08$	$0.38 \times 0.18 \times 0.14$
Theta range for data collection, deg	56.6	56.6
Reflections collected	57340	53475
Independant reflections	12194 ($R_{int} = 0.050$)	6109 ($R_{int} = 0.048$)
Completeness to theta, %		
Absorption correction	0.848–0.954	0.7823–0.9587
DData/restraints/parameter	6543/0/658	4128/0/304
GOF on F^2	1.12	1.05
Final R_1, wR_2	0.034, 0.044	0.024 , 0.034
Largest diff. peak and hole/e Å^{-3}	0.62, −0.51	1.99, −0.41

Sn(IV)TTP$(OC_6H_3)_2$ and Sn(IV)TTP(4-$OC_6H_4NO_2)_2$ respectively are likely causes for the canting of the *meso* phenyl groups from being orthogonal to the porphyrin plane. In the case of the smaller phenol, the canting values are 83.6° and 110.2° for C5 and C10 respectively. The more pronounced canting for the *p*-nitro derivative (values of 101.7°, 118.1°, 121.4° and 117.8° for C5, C10, C15 and C20) are consistent with the results seen for the rate of formation (Figure 4), namely there exists greater steric effects in the substituted cases. Interestingly, in both cases the canting is biased towards the phenolic groups. We attribute this phenomena to a mix of crystal packing forces and a relaxation of the steric hindrance brought about by the close contacts with the ArH groups of both phenol and *meso* groups. In this case, the two phenol groups are also biased to the same half of the porphyrin macrocycle with a "slip" angle of 27.3°.

Conclusions

We have demonstrated that Sn(IV)porphyrins are useful for the recognition of a range of phenol units. At the simplest level, the dispersity of the phenol signals attributed to the porphyrin ring current in the ^{1}H NMR spectrum should allow tin(IV) porphyrins to act as shift reagents. This is complementary to the recognition of carboxylic acids [2]. We have also shown that the rate of complexation of phenols is independent of pH as a result of substitutent effects. We are at present investigating whether this process can be used to prepare one-dimensional mixed metal porphyrin assemblies involving phenolic linkers.

Acknowledgements

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