

Synthesis and Hydrogen-Bonded Supramolecular Assembly of trans-Dihydroxotin(IV) Tetrapyriddyloporphyrin Complexes

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trans-Dihydroxo[5,10,15,20-tetrakis(*n*-pyridyl)porphyrinato]tin(IV) (*n* = 3 and 4) complexes have been synthesized and fully characterized. X-ray structural analysis of trans-dihydroxo[5,10,15,20-tetrakis(4-pyridyl)porphyrinato]tin(IV) reveals that the supramolecular hydrogen bondings between the hydroxotin(IV) porphyrins and lattice water molecules form a hydrogen-bonded two-dimensional network. The hydrogen bonding mode between the tin(IV) porphyrins and the water molecules closely resembles that of the hydrogen-bonded outer-sphere intermediate in the acidolysis of dihydroxotin(IV) porphyrins.

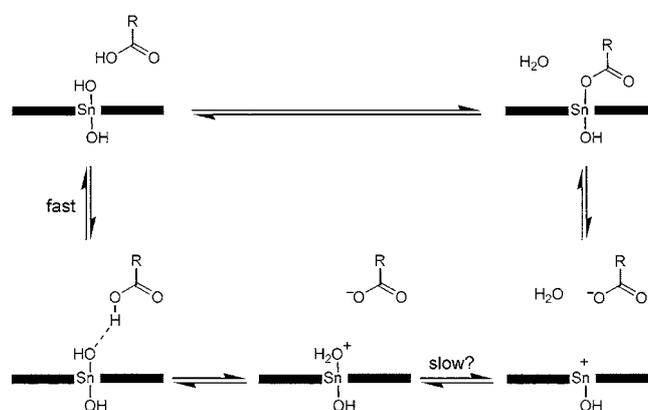
Key Words : Tin(IV), Porphyrins, Hydroxo ligands, Hydrogen bonds, Supramolecular assembly

Introduction

Tin(IV) porphyrins have drawn recent attention in the architectures of supramolecular porphyrin arrays¹⁻³ because of their useful coordination properties conferred by the highly charged main group metal center. Tin(IV) porphyrins readily form stable six-coordinate complexes with the two *trans* axial ligands of oxyanions due to the oxophilic nature of the tin(IV) center.⁴ The hydroxotin(IV) porphyrins are of primary importance because they preferentially recognize carboxylic acids or alcohols in the preparation of most other tin(IV) porphyrins (Scheme 1).⁵ When this strong preference of the tin(IV) porphyrins is in harmony with the mutually non-interfering binding properties of the peripheral groups, it becomes possible to assemble elaborate multiporphyrin arrays.⁶ In addition, tin(IV) porphyrins have appealed as interesting candidates for useful applications such as photocatalysis⁷ and photodynamic therapy.⁸ The ditopic porphyrins such as dihydroxotin(IV) tetrapyriddyloporphyrins, possessing the mutually non-interfering binding sites in their axial and peripheral positions, have thus great potential for the construction of functional multiporphyrin supramolecular arrays and nanostructures. Here we report the synthesis and supramolecular assembly of trans-dihydroxotin(IV) tetrapyriddyloporphyrins. The crystallographic analysis of trans-dihydroxo[5,10,15,20-tetrakis(4-pyridyl)porphyrinato]tin(IV) reveals that the supramolecular hydrogen bondings between the hydroxotin(IV) porphyrins and lattice water molecules form a hydrogen-bonded two-dimensional network. It also affords a crystallographic evidence for the hydrogen-bonded outer-sphere intermediate³ in the acidolysis of dihydroxotin(IV) porphyrins.

Experimental Section

All chemicals were of reagent grade and were used without further purification. 5,10,15,20-Tetrakis(*n*-pyridyl)-



Scheme 1. Proposed mechanism for the acidolysis of dihydroxotin(IV) porphyrins by carboxylic acids.^{5a}

porphyrin (*n* = 3 and 4)⁹ and trans-dichloro[5,10,15,20-tetrakis(4-pyridyl)porphyrinato]tin(IV) **1a**¹⁰ were prepared by literature procedures. UV-vis and IR spectra were recorded on a Scinco S-1150 photodiode array and a Jasco FTIR-460 Plus spectrophotometer, respectively. ¹H and ¹³C NMR spectra were obtained on a Bruker DRX-500 spectrometer. Electrospray ionization (ESI) mass spectra were recorded on a Waters ZQ 2000 LC/MS spectrometer. Elemental analyses were performed on a ThermoQuest EA 1110 analyzer.

Syntheses. (a) **trans-Dichloro[5,10,15,20-tetrakis(3-pyridyl)porphyrinato]tin(IV) 1b.** **1b** was synthesized by the same method as for **1a**¹⁰ and a typical procedure is as follows. 5,10,15,20-Tetrakis(3-pyridyl)porphyrin (0.800 g, 1.30 mmol) was dissolved in pyridine (250 mL) and SnCl₂·2H₂O (0.586 g, 2.60 mmol) was added. The reaction mixture was heated at reflux until the reaction was complete. The progress of the reaction was monitored by UV-vis spectroscopy and thin layer chromatography. After 9 h, the solvent was removed *in vacuo*. The residue was dissolved in CH₂Cl₂ and filtered through a Celite pad. The solvent of the filtrate was evaporated under reduced pressure to give a crude product. It was then recrystallized from CH₂Cl₂/*n*-

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hexane solution to afford crystalline solids of *trans*-dichloro[5,10,15,20-tetrakis(3-pyridyl)porphyrinato]tin(IV) **1b**. Yield: 0.992 g (95%). ¹H NMR (500 MHz, CDCl₃): δ 9.59 (s, 4H, py), 9.26 (s, 8H, β-pyrrolic H), 9.16 (d, *J* = 3.8 Hz, 4H, py), 8.65 (s, 4H, py), 7.86 (t, *J* = 5.8 Hz, 4H, py). ¹³C NMR (CDCl₃): δ 153.9, 150.4, 146.7, 141.5, 136.4, 133.3, 122.7, 118.1. UV-vis (CH₂Cl₂, nm): λ_{max} (log ε) 422 (5.02), 521 (3.42), 560 (3.96), 599 (3.80). MS (ESI): *m/z* 769.69 [(*M*-Cl)⁺ requires 769.08]. Anal. Calcd. for C₄₀H₂₄N₈Cl₂Sn: C, 59.59; H, 3.00; N, 13.90. Found: C, 59.82; H, 3.28; N, 13.71.

(b) *trans*-Dihydroxo[5,10,15,20-tetrakis(4-pyridyl)porphyrinato]tin(IV) **2a**. A mixture of *trans*-dichloro[5,10,15,20-tetrakis(4-pyridyl)porphyrinato]tin(IV) **1a** (0.450 g, 0.558 mmol) and potassium carbonate (1.14 g, 8.89 mmol) in tetrahydrofuran (400 mL) and water (100 mL) was heated at reflux for 4 h. The solution was concentrated on a rotary evaporator to remove the tetrahydrofuran, and then allowed to cool in a refrigerator for a day. The produced microcrystalline solid of *trans*-dihydroxo[5,10,15,20-tetrakis(4-pyridyl)porphyrinato]tin(IV) **2a** was filtered, washed with cold water and dried under vacuum. Yield: 0.365 g (85%). ¹H NMR (500 MHz, DMSO-*d*₆): δ 9.12 (s, 8H, β-pyrrolic H), 9.11 (d, *J* = 3.7 Hz, 8H, py), 8.30 (d, *J* = 3.7 Hz, 8H, py), -6.06 (s, 2H, OH). ¹³C NMR (DMSO-*d*₆): δ 148.43, 148.38, 145.3, 132.8, 129.5, 118.6. IR (KBr, cm⁻¹): ν_{OH} 3587. UV-vis (DMSO, nm): λ_{max} (log ε) 423 (4.93), 523 (3.34), 561 (3.78), 599 (3.59). MS (ESI): *m/z* 751.23 [(*M*-OH)⁺ requires 751.12]. Anal. Calcd. for C₄₀H₂₆N₈O₂Sn·2H₂O: C, 59.64; H, 3.75; N, 13.91. Found: C, 59.28; H, 3.67; N, 13.59.

(c) *trans*-Dihydroxo[5,10,15,20-tetrakis(3-pyridyl)porphyrinato]tin(IV) **2b**. **2b** was synthesized in 87% yield by the same procedure as for **2a** using *trans*-dichloro[5,10,15,20-tetrakis(3-pyridyl)porphyrinato]tin(IV) **1b**. ¹H NMR (500 MHz, DMSO-*d*₆): δ 9.43 (s, 4H, py), 9.13 (d, *J* = 3.7 Hz, 4H, py), 9.10 (s, 8H, β-pyrrolic H), 8.71 (s, 4H, py), 7.99 (t, *J* = 5.8 Hz, 4H, py), -6.08 (s, 2H, OH). ¹³C NMR (DMSO-*d*₆): δ 153.0, 149.6, 145.9, 141.0, 136.7, 132.6, 122.6, 117.6. IR (KBr, cm⁻¹): ν_{OH} 3604. UV-vis (CH₂Cl₂, nm): λ_{max} (log ε) 422 (4.99), 521 (3.40), 560 (3.94), 599 (3.78). MS (ESI): *m/z* 751.01 [(*M*-OH)⁺ requires 751.12]. Anal. Calcd. for C₄₀H₂₆N₈O₂Sn·H₂O: C, 61.01; H, 3.58; N, 14.23. Found: C, 61.31; H, 3.30; N, 13.82.

X-ray crystal structure determination. Single crystals suitable for X-ray work were grown by slow cooling of a hot DMSO solution of **2a**. A crystal covered with Paratone-N hydrocarbon oil on a glass fiber was mounted on a Siemens SMART diffractometer equipped with a graphite monochromated Mo Kα (λ = 0.71073 Å) radiation source and a CCD area detector. Data collection was performed at 223K. Crystal data and structure refinement for **2a**·2H₂O are summarized in Table 1. The intensity data were corrected for Lorentz and polarization effects. Empirical absorption correction was applied (SADABS). The structures were solved by a combination of Patterson and difference Fourier methods and refined initially by full-matrix least-squares method (SHELXTL). All non-hydrogen atoms were refined

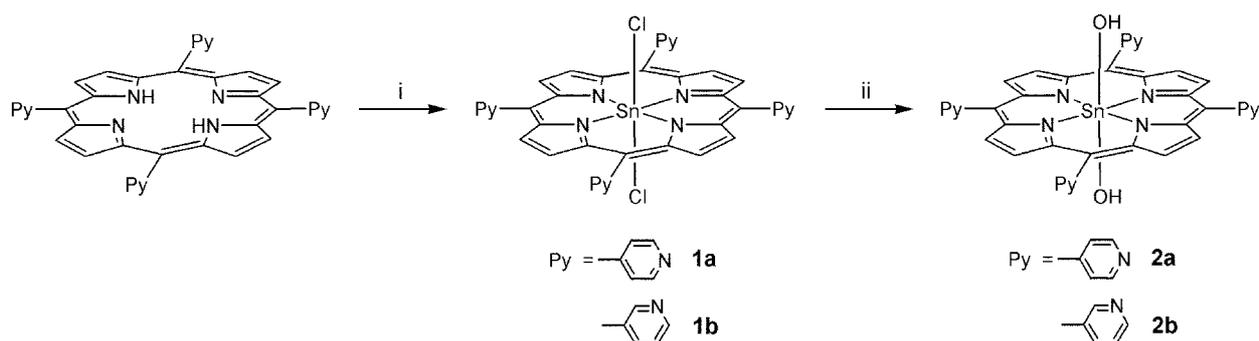
Table 1. Crystal data and structure refinement for **2a**·2H₂O

Empirical formula	C ₄₀ H ₂₆ N ₈ O ₂ Sn·2H ₂ O	
Formula weight	805.41	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	<i>P</i> 2 ₁ / <i>n</i>	
Unit cell dimensions	<i>a</i> = 11.286(3) Å	α = 90°
	<i>b</i> = 12.708(3) Å	β = 112.822(4)°
	<i>c</i> = 12.481(3) Å	γ = 90°
Volume	1649.9(6) Å ³	
<i>Z</i>	2	
Density (calculated)	1.621 mg/m ³	
Absorption coefficient	0.833 mm ⁻¹	
<i>F</i> (000)	816	
Crystal size	0.15 × 0.15 × 0.2 mm ³	
Theta range for data collection	2.39 to 28.30°.	
Index ranges	-12 ≤ <i>h</i> ≤ 14, -15 ≤ <i>k</i> ≤ 16, -16 ≤ <i>l</i> ≤ 16	
Reflections collected	9746	
Independent reflections	3918 [R(int) = 0.0464]	
Completeness to theta = 28.30°	95.5%	
Absorption correction	SADABS	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data/restraints/parameters	3918/0/250	
Goodness-of-fit on <i>F</i> ²	1.004	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	R1 = 0.0436, ωR2 = 0.1050	
<i>R</i> indices (all data)	R1 = 0.0642, ωR2 = 0.1170	

anisotropically. The hydrogen atoms of the Sn-OH moieties and the water molecules were located from the difference Fourier maps and refined isotropically. Other hydrogen atoms of **2a** were included in calculated positions with isotropic thermal parameters 1.2 times those of attached atoms. Final block-diagonal matrix least-squares refinement on *F*² with all 9746 reflections and 250 variables converged to R1 (*I* > 2σ(*I*)) = 0.0436, ωR2 (all data) = 0.1170, and GOF = 1.004.

Results and Discussion

Tin is commonly inserted into porphyrins by using tin(II) chloride to give the dichlorotin(IV) porphyrins, which are then hydrolyzed under basic conditions to the corresponding dihydroxotin(IV) porphyrins. The dichlorotin(IV) tetrapyrrolylporphyrins **1a** and **1b** were similarly prepared by the reported procedure,¹⁰ the reaction of free-base porphyrins with tin(II) chloride in refluxing pyridine under aerobic conditions. To hydrolyze **1a**, we had tried a mild technique employing basic deactivated alumina.¹¹ Unfortunately, we could hardly extract dihydroxotin(IV) tetrapyrrolylporphyrins **2a** from the adsorbed alumina surface due to their poor solubility. We have thus adopted an alternative route, the treatment with K₂CO₃ in the mixed solution of THF-H₂O at reflux.¹² In this reaction condition, **2a** became precipitated during the reaction progress. After further precipitation at



Scheme 2. Synthesis of dichlorotin(IV) and dihydroxotin(IV) porphyrins. *Reagents and conditions:* i) $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, pyridine, reflux; ii) K_2CO_3 in $\text{THF-H}_2\text{O}$, reflux.

low temperature, **2a** was readily isolated in high yields by simple filtration. **2b** was also yielded by the same procedure. The synthetic route of dihydroxotin(IV) tetrapyrridylporphyrins from the free-base porphyrins is summarized in Scheme 2. All products were fully characterized by various spectroscopic methods and elemental analyses. In the ^1H NMR spectra of **2a** and **2b**, the resonances of the hydroxo protons appear as a singlet at -6.06 ppm for **2a** and -6.08 ppm for **2b**, respectively. The significant upfield shifts of these resonances due to the strong shielding by the porphyrin ring support the formation of axially oriented Sn-OH bonds. The hydroxo ligands in **2a** and **2b** were also identified by weak IR absorption band at 3587 and 3604 cm^{-1} , respectively. The ESI mass spectrum of **2a** exhibits a parent ion peak at $m/z = 751.73$ resulting from the loss of one hydroxo ligand although the molecular ion peak was not observed. Similar ligand lability of tin(IV) porphyrin complexes in the mass spectrometry has been observed.¹²

The structure of **2a** has been confirmed by X-ray crystallography. The X-ray structure of **2a** reveals that the central tin(IV) ion adopts an octahedral geometry with the porphyrin occupying the square base and axial coordination of two hydroxo ligands, as shown in Figure 1. The tin(IV) ion lies on an inversion center, so that the two hydroxo ligands lie in an exact *trans* orientation with respect to each other. The average Sn-N bond distance is estimated to be 2.101 Å and the Sn-O bond distance is $2.014(3)$ Å, which

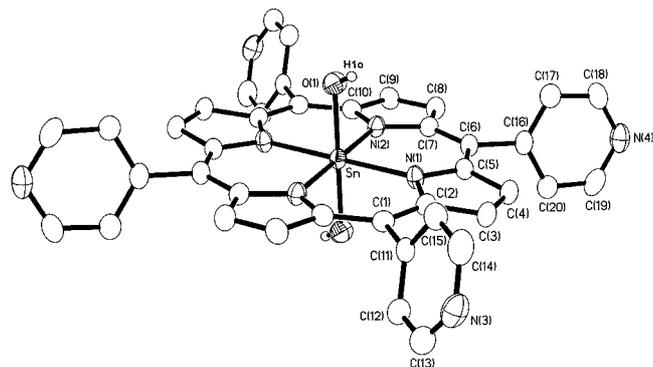


Figure 1. Molecular structure of **2a**. The hydrogen atoms of the porphyrin ligand are omitted for clarity.

are comparable to those of $(\text{TPP})\text{Sn}(\text{OH})_2$ (TPP = tetraphenylporphyrinato dianion).¹³ In comparison with the reported structure of dichlorotin(IV) porphyrin **1a**,¹⁰ it should be noted that the average Sn-N bond distance for **2a** (2.101 Å) is longer than that of **1a** (2.081 Å). This is probably attributed to the higher basicity of hydroxo ligand than that of chloro ligand in the tin(IV) porphyrins. The correlation of ligand basicity with Sn-N bond distance has been established; tin(IV) porphyrins with axial ligands of higher basicity have longer Sn-N bonds.^{4a}

The basic nature of the hydroxo ligands along with that of the peripheral pyridyl groups in **2a** affects the supramolecular interactions in the crystal lattice. One lattice water molecule, presumably originated from residual water in the solvent, is found in the crystallographic asymmetric unit. The water molecules are hydrogen-bonded with the hydroxo ligands in one porphyrin (2.934 Å for $\text{Sn-O}1 \cdots \text{O}2\text{w}$) as well as with the peripheral pyridyl groups in adjacent porphyrins (2.929 Å for $\text{N}4 \cdots \text{O}2\text{w}$). More specifically, the water hydrogen atoms, which were located from the difference Fourier maps, are hydrogen-bonded to the oxygen atom of the hydroxo ligand and the nitrogen atoms of the pyridyl group giving the

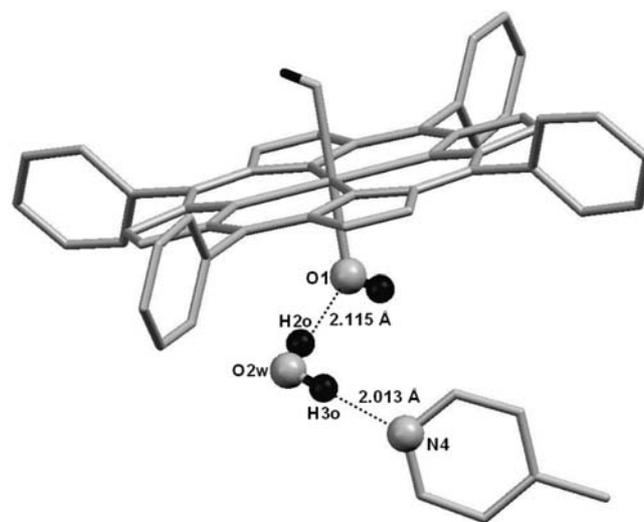
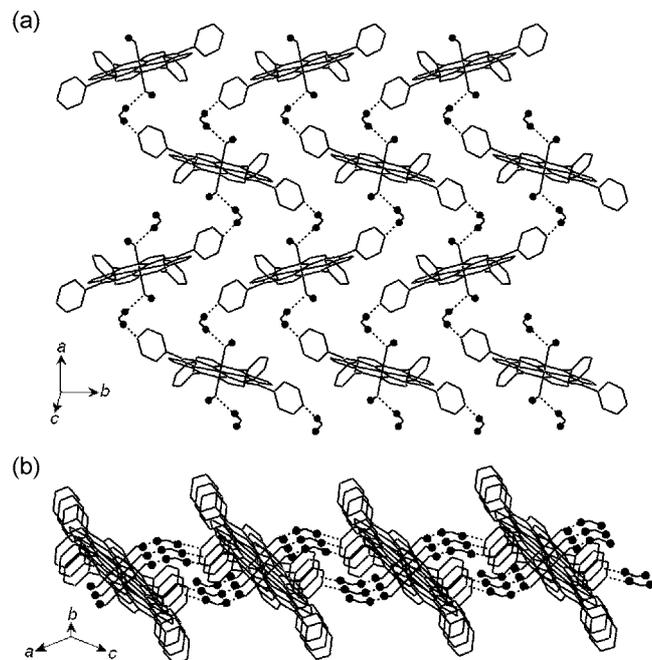


Figure 2. Intermolecular hydrogen bonding interactions between **2a** and the lattice water molecule in the crystal of $\text{2a} \cdot 2\text{H}_2\text{O}$.

Table 2. Selected bond distances (Å) and angles (°) associated with hydrogen bonds

D-H...A	D-H	H...A	D...A	∠ D-H...A
O2w-H2o...O1	0.828	2.115	2.934	169.98
O2w-H3o...N4	0.933	2.013	2.929	166.93

D = donor atom, A = acceptor atom

**Figure 3.** Hydrogen-bonded 2D network in the crystal of **2a**·2H₂O. Filled circles represent hydrogen atoms attached at oxygen atoms of the hydroxo ligands and the lattice water molecules.

distances of 2.115 Å (Sn-O1...H2o) and 2.013 Å (N4...H3o), respectively (Figure 2). The structural parameters associated with hydrogen bonds are summarized in Table 2. Interestingly, the two in *trans* of four pyridyl groups in **2a** participate in hydrogen bonding interactions with the lattice water molecules. **2a** can be regarded as a building block having two orthogonal H-accepting sets consisting of the hydroxo ligands pair and the pyridyl pair. One set of the hydroxo ligands in any one porphyrin is linked to the other set of the pyridyl groups in neighboring porphyrins by hydrogen bonding bridges of the lattice water molecules. Such supramolecular hydrogen bonds between **2a** and the water molecules lead to the formation of hydrogen-bonded two-dimensional network in the crystal of **2a**·2H₂O, as illustrated in Figure 3.

On the other hand, the hydrogen bonding mode in the crystal of **2a**·2H₂O, in which the hydroxo ligands act as H-acceptor and the water molecules as H-donor, is essentially identical to that of the hydrogen-bonded outer-sphere intermediate in the proposed mechanism for the acidolysis of dihydroxotin(IV) porphyrins by carboxylic acids or alcohols (Scheme 1). To our knowledge, such hydrogen bonding mode of the dihydroxotin(IV) porphyrins has never

been characterized by X-ray crystallography, although it has been proved in solution state by NMR spectrometry.^{5a}

Conclusion

We have synthesized and fully characterized the dihydroxotin (IV) tetrapyrridylporphyrins as well as the corresponding dichlorotin(IV) porphyrins. X-ray structural analysis of *trans*-dihydroxo[5,10,15,20-tetrakis(4-pyridyl)porphyrinato]tin(IV) reveals that the hydroxo ligands are sufficiently basic to act as a hydrogen bonding acceptor and the hydroxotin (IV) porphyrins are supramolecularly assembled to form a two-dimensional network by hydrogen bonding interactions with the lattice water molecules. It also provides a crystallographic evidence for the hydrogen-bonded outer-sphere intermediate in the acidolysis of dihydroxotin(IV) porphyrins.

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Supplementary material. Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC 250002). The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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