trans-Dihydroxotin(IV) Tetrapyridylporphyrin 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) tetrapyridylporphyrins, 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) tetrapyridylporphyrins.

Experimental Section

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

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

porphyrin (n = 3 and 4)9 and trans-dichloro[5,10,15,20-tetrakis(4-pyridyl)porphyrinato]tin(IV) 1a10 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. $^1$H and $^{13}$C 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 1a10 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 SnCl$_2$·2H$_2$O (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 CH$_2$Cl$_2$ 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 CH$_2$Cl$_2$/n-
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): λmax (log ε) 422 (5.02), 521 (3.42), 560 (3.96), 599 (3.59). MS (ESI): m/z 769.69 [M-CI]+ requires 769.08. Anal. Calcd. for C40H26N8O2Sn·2H2O: C, 61.01; H, 3.58; N, 14.23. 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-d6): 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-d6): δ 148.43, 148.38, 145.13, 132.8, 129.5, 118.6. IR (KBr, cm−1): νOH 3587. UV-vis (DMSO, nm): λmax (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-d6): δ 8.93 (s, 4H, py), 9.13 (d, J = 3.7 Hz, 4H, py), 9.10 (s, 8H, β-pyrrolic H), 8.71 (s, 2H, OH), 7.99 (t, J = 5.8 Hz, 4H, py), -6.08 (s, 2H, OH). 13C NMR (DMSO-d6): δ 153.0, 149.6, 145.9, 141.0, 136.7, 132.6, 122.6, 117.6. IR (KBr, cm−1): νOH 3564. UV-vis (CH2Cl2, nm): λmax (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 C40H28N8O2Sn·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 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 F2 with all 9746 reflections and 250 variables converged to R1 (I > 2σ(I)) = 0.0436, wR2 = 0.1050. R indices (all data) R1 = 0.0642, wR2 = 0.1170.

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) tetrapyridylporphyrins 1a and 1b were similarly prepared by the reported procedure, 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. Unfortunately, we could hardly extract dihydroxotin(IV) tetrapyridylporphyrins 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. In this reaction condition, 2a became precipitated during the reaction progress. After further precipitation at
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) tetrapyridylporphyrins 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 are comparable to those of (TPP)Sn(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.\(^{3a}\)

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 Sn-O1···O2w) as well as with the peripheral pyridyl groups in adjacent porphyrins (2.929 Å for N4···O2w). 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

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

**Figure 2.** Intermolecular hydrogen bonding interactions between 2a and the lattice water molecule in the crystal of 2a·2H\(_2\)O.

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**Scheme 2.** Synthesis of dichlorotin(IV) and dihydroxotin(IV) porphyrins. Reagents and conditions: i) SnCl\(_2\)·2H\(_2\)O, pyridine, reflux; ii) K\(_2\)CO\(_3\) in THF-H\(_2\)O, reflux.
Table 2. Selected bond distances (Å) and angles (°) associated with hydrogen bonds

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<tr>
<th>D-H···A</th>
<th>D-H</th>
<th>H···A</th>
<th>D···A</th>
<th>≪ D-H···A</th>
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<tbody>
<tr>
<td>O2w-H2o···O1</td>
<td>0.828</td>
<td>2.115</td>
<td>2.934</td>
<td>169.98</td>
</tr>
<tr>
<td>O2w-H3o···N4</td>
<td>0.933</td>
<td>2.013</td>
<td>2.929</td>
<td>166.93</td>
</tr>
</tbody>
</table>

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) tetrapyridylporphyrins 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 Load, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

References

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