Influence of position of methoxy groups in Zn-methoxyphenylporphyrins

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Abstract. The crystal structure of the compound, Zn(II) 5,10,15,20-tetrakis(*meta*-methoxyphenyl)porphyrin chloroform trisolvate, [ZnT(*m*-OCH₃)PP]·3CHCl₃ **1** reveals that it forms a weak one-dimensional chain structure through interaction between Zn of porphyrin and the oxygen atom of the methoxy group of a neighbouring porphyrin. The zinc–oxygen interaction observed in compound **1** is compared with Zn(II) 5,10,15,20-tetrakis(*para*-methoxyphenyl)porphyrin [ZnT(*p*-OCH₃)PP] **2** and Zn(II) 5,10,15,20-tetrakis(3,4,5-tri-methoxyphenyl)porphyrin [ZnT(3, 4, 5-triOCH₃)PP] **3** to understand the preferred methoxy-position of interaction. The strength of the non-covalent zinc–oxygen (methoxy group of a neighboring porphyrin) interaction in compound **1** is in between that of similar interactions observed in compounds **2** and **3**. The Mulliken charge analysis using theoretical calculation at the DFT level shows that the *meta*-methoxy oxygen has a higher probability of binding to the metal than the *para*-methoxy oxygen. In the presence of nucleophiles, the formation of one-dimensional chain structure stops due to the binding of the nucleophiles to the metal zinc. The photoluminescence and differential scanning calorimetric studies were also performed for compound **1**.

Keywords. Porphyrin; coordination polymer; zinc; UV-Visible spectra; X-ray crystallography.

1. Introduction

In the last few decades, non-covalent interaction have been of great interest in inorganic chemistry.^{1–4} Porphyrins are very attractive molecules for studying non-covalent interactions and have been used to construct supramolecular assemblies due to their macrocyclic structure.⁵ In addition to that, porphyrin non-covalent interactions have significant interest in various biological processes because it provides specificity and flexibility which is required for the biological processes such electron transfer, oxygen transport, etc.^{6–10} On the other hand, a coordination polymer is formed when a ligand bridges between metal ions, and each metal is bonded to more than one linker (ligand) to form an extended arrangement of metal ions. Porphyrin, the broadly found biological ligand is a beautiful building block for the formation of coordination polymer due to its rigid structure and the metalation site.^{11,12} Coordination polymers of porphyrin

molecules have demand due to their bio-mimetic model of electron transfer in photosynthesis, catalysis and as sensors.¹³ The 5,10,15,20-tetra(4-pyridyl)porphyrin (H₂TPyP), 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (H₆TCPP) and Zn(II)1,2-bis(*meso* octaethylporphyrin)ethane are the most common porphyrin ligands used for formation of coordination polymers¹⁴ and metal-organic frameworks due to their additional metal binding site at pyridyl and carboxylate groups.¹⁵ Zn-5,10,15,20-tetra(4-pyridyl)porphyrin is reported to form J-type aggregation through Zn–N axial coordination.¹⁶ There are others reports of porphyrin coordination polymers and metal organic framework due to its bridging ligand capability.¹⁷ Coordination polymers and metal-organic frameworks with different carboxylates and metal ions are known.¹⁸ The zinc(II) 5,15-di-(2-methoxymethylphenyl)-porphyrin forms three dimensional coordination polymer through the interaction of methoxy-oxygen atoms of one porphyrin peripheries to the metal centers of two neighbouring identical

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Figure 1. The chemical drawings of compound **1**, **2** and **3**.

porphyrins.¹⁹ An another porphyrin Zn(II)1,2-bis(*meso*-octaethylporphyrin)ethane is reported to form an one-dimensional coordination polymer with *N,N*-bispyridine-4-yl-methylene ethylenediamine by forming a dimer and the same forms a sandwich structure with 1,2-diaminobenzene.²⁰

We have recently shown that the 5,10,15,20-tetrakis(3,4,5-tri-methoxyphenyl)porphyrinato, {T(3,4, 5-triO-CH₃)PP} is a beautiful ligand to form diverse coordination polymers.^{21,22} This ligand has three methoxy groups in the peripheral phenyl rings at 3, 4 and 5 position and can form 1D coordination polymer through binding of different methoxy groups to a neighbouring metal of the adjacent porphyrin. We observed the formation of 1D coordination polymer of MgT(3,4,5-triOCH₃)PP and ZnT(3,4,5-triOCH₃)PP through *meta*-oxygen (oxygen atom from the *m*-methoxy group of an adjacent porphyrin)–metal bonds.²¹ To understand whether the *m*-methoxy group is only special position to form a 1D coordination polymer, here in this work we studied the zinc–oxygen interaction in zinc(II) (5,10,15,20-tetrakis(3-methoxyphenyl)) porphyrin, [ZnT(3-OCH₃)PP] (**1**) and compared with Zn(II) 5,10,15,20-tetrakis(4-methoxyphenyl)porphyrin [ZnT(4-OCH₃)PP] **2**²³ and Zn(II) 5,10,15,20-tetrakis-(3,4,5-tri-methoxyphenyl)porphyrin [ZnT(3,4, 5-triOCH₃)PP] **3** (Figure 1). The crystal structure of **1** reveals that it has an interaction similar to MgT(3,4,5-triOCH₃)PP and ZnT(3,4,5-triOCH₃)PP between trans metal oxygen (oxygen atom from the *m*-methoxy group of an adjacent porphyrin) bonds. The aggregation mode of porphyrins determines several biological properties of porphyrin.²⁴ We have studied the interaction of **1** with various nucleophiles to understand the stability of the chain structure and its aggregation. The differential scanning calorimeter (DSC) studies for compound **1** was performed to understand the thermal properties. The thermal stability of 5,10,15,20-tetrakis-(4-methoxyphenyl)porphyrin, (T(4-OCH₃)PP) was reported to higher than 5,10,15,

20-tetrakis(3-methoxyphenyl) porphyrin, (T(3-OCH₃)PP).²⁵

2. Experimental

2.1 Materials and methods

Solvents like dichloromethane, hexane, chloroform and *N,N*-dimethylformamide were purchased from Merck Life Science Private Ltd. 3-Methoxybenzaldehyde and pyrrole were purchased from Spectrochem Private Ltd.

2.2 Physical Measurements

Electronic absorption spectral measurements for both solid and solution samples were recorded in a Perkin-Elmer (Lamda 35) spectrophotometer. Luminescence spectral measurements were carried out using an Aligent Cary Eclipse Fluorescence Spectrophotometer. Elemental analysis for carbon, hydrogen and nitrogen were checked with Leco CHNOS 948 carbon hydrogen nitrogen oxygen and sulfur determination. Infrared spectra were recorded on a Shimadzu FT-IR spectrophotometer as pressed KBr disks in the IR region. DSC measurement was carried out with Shimadzu DSC-60 at a scan rate of 5 °C/min.

2.3 X-ray structural analysis

The diffracted crystal was glued to a glass fiber and mounted on BRUKER SMART APEX diffractometer. The instrument was equipped with CCD area detector and data were collected using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at room temperature (293 K). The crystallographic data, conditions retained for the intensity data collection and some features of the structure refinements are listed Table S1 in Supplementary Information. All empirical absorption corrections were applied using the SADABS program. All data were collected with SMART 5.628 (BRUKER, 2003), and were integrated with the BRUKER SAINT program. The crystal structure was solved using SIR97 and refined using SHELXL-97. The space group of the compound was obtained based on the lack of systematic absence

and intensity statistics. Full matrix least squares/difference Fourier cycles were performed which located the non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The structural figures were drawn with the Ortep2 program.²⁶

2.4 Synthesis of ligand 5,10,15,20-tetrakis-(*meta*-methoxyphenyl)porphyrin, $H_2T(m-OCH_3)PP$

The ligand 5,10,15,20-tetrakis(3-methoxyoxyphenyl) porphyrin, $H_2T(3-OCH_3)PP$ was synthesized by refluxing 7.5 mL pyrrole (144 mmol) and 13.13 mL *m*-anisaldehyde (144 mmol) in 250 mL propionic acid following the reported procedure.²⁷ The yield of the compound was found as 20%. The molecular formula of the ligand is $C_{48}H_{38}N_4O_4$. Molecular weight 734. UV/Visible bands are at λ_{max}/nm (in $CHCl_3$, 10^{-6} M) 419 ($560000\text{ Lmol}^{-1}\text{cm}^{-1}$), 514 ($23000\text{ Lmol}^{-1}\text{cm}^{-1}$), 553 ($7000\text{ Lmol}^{-1}\text{cm}^{-1}$), 590 ($5000\text{ Lmol}^{-1}\text{cm}^{-1}$) and 646 ($4200\text{ Lmol}^{-1}\text{cm}^{-1}$), respectively. IR analysis gave characteristics peaks at 3603, 3402, 2939, 1805, 1705, 1589, 1465, 1165, 1041, 979, 910, 794, 726, 648, 462 cm^{-1} , respectively.

2.5 Synthesis of compound $[ZnT(m-OCH_3)PP] \cdot 3CHCl_3$ **1**

A sample of 0.6 g (0.81 mmol) of the porphyrin $H_2T(m-OCH_3)PP$ was taken in a 50 mL of DMF in a round bottom flask followed by addition of 0.255 g of $ZnCl_2$ (1.875 mmol) and was refluxed for 1 h. The mixture was dried in a water bath to remove the solvent. The dried compound was dissolved in dichloromethane then filtered and evaporated. The compound **1** was finally isolated and purified by column chromatography using dichloromethane and hexane as solvent. The compound was re-crystallized using chloroform and petroleum-ether mixture. The yield of the compound **1** was 95%. Molecular Formula: $C_{51}H_{39}Cl_9N_4O_4Zn$; Molecular Weight 1155.5; UV/Vis (in $CHCl_3$) λ_{max}/nm (ϵ): 423 ($380000\text{ Lmol}^{-1}\text{cm}^{-1}$), 550 ($15000\text{ Lmol}^{-1}\text{cm}^{-1}$), 593 ($5000\text{ Lmol}^{-1}\text{cm}^{-1}$); IR analysis gave characteristics peaks at 2928, 2840, 1649, 1587, 1470, 1328, 1273, 1173, 1007, 926, 790, 704, 667 cm^{-1} , respectively.

3. Result and Discussion

3.1 Crystal structure of compound $[ZnT(m-OCH_3)PP] \cdot 3CHCl_3$ **1**

The complex **1** crystallizes in a triclinic system with P-1 space group. The crystallographic data for the compound **1** is given in Table S1 in Supplementary Information. The crystal structure of complex **1** consists of two unique Zn(II) ions, Zn1 and Zn2 situated in special positions, and two crystallographically independent molecules of the porphyrin ligand tetra

Figure 2. The perspective view of compound **1**.

meta-methoxyphenylporphyrin (first porphyrin ligand is with pyrrole nitrogens N1N2 and second is N3N4) and three chloroform solvent molecules. Figure 2 shows the perspective view of the chemical surroundings of one of the unique Zn (Zn1) ions. The perspective view of compound **1** with the both Zn(II) ions and symmetry codes of nitrogen and oxygen atoms is shown in Figure S1 in Supplementary Information. The metal zinc is in the plane of the porphyrin ring. The Zn–N(py) bond length was found to be in the range from 2.028 Å to 2.055 Å. The metal Zn1 makes two long bonds at 2.674 Å with O4 of *meta* methoxy group of the adjacent porphyrin (both are O4 and are trans because Zn1 is on an inversion centre) while Zn2 makes two long bonds at 2.604 Å with *meta* methoxy group of the adjacent porphyrin (both are O1). The extended structure with this weak interaction of the compound **1** is shown in Figure 3 and Figure S2 (Supplementary Information). The Zn1–O4 and Zn2–O1 distances in compound **1** is too long to be considered as true Zn–O bonds; hence compound **1** is not a coordination polymer but forms a weak one-dimensional chain structure through this bond (Figure S2). The Zn–O bond distance (2.604 and 2.674 Å) in complex **1** is slightly longer than reported the longest six coordinate Zn–O bond distance of $Zn(THF)_2$ complex.²⁸

We recently reported the formation of 1D coordination polymer of $ZnT(3,4,5\text{-triOCH}_3)PP$ and $MgT(3,4,5\text{-triOCH}_3)PP$ through *meta*-oxygen (oxygen atom from

Figure 3. Illustration of the one-dimensional infinite chain due to the weak zinc (metal)–oxygen (methoxy) interaction.

the *m*-methoxy group of an adjacent porphyrin)–metal bonds.²¹ We have compared the Zn–O bond of complex **1** of with reported crystallographic data of zinc(II) (5,10,15,20-tetrakis(4-methoxyphenyl))porphyrin [ZnT(*p*-OCH₃)PP] **2** and zinc(II) (5,10,15,20-tetrakis(3,4,5 tri-methoxyphenyl))porphyrin, [ZnT(3,4, 5-triOCH₃)PP] **3**. Interestingly, in *p*-methoxy analogue Zn(T(4-OCH₃)PP), the Zn–O bond distance is 2.69 Å much longer than the Zn–O bond distance of complex **1** and **3**.²³ This indicates that the metal oxygen interaction through *para* position is very weak. In an another work, we recently reported that metal zinc in complex **3** in the acetone-dichloromethane-water medium does not bind to methoxy oxygen of adjacent porphyrin instead binds with a water molecule. Similarly, it is reported that compound **2** binds to the water molecule in the phenol-water solvent system instead of the oxygen atom of the methoxy group.

3.2 Synthetic aspects, electronic spectra of complexes

The metal Zn was inserted into the tetra *meta*-methoxyphenylporphyrin, [T(*m*-OCH₃)PP] following known procedure²⁹ in DMF medium using ZnCl₂ as salt and was purified by using column chromatography. The suitable crystal for diffraction was found from chloroform and petroleum ether mixture. The UV-visible spectrum of the compound **1** shows a typical Soret band at 423 nm

Figure 4. Electronic spectral change of compound **1** (in chloroform) upon addition of 2.0×10^{-5} M imidazole.

and Q band in the range 550–600 nm due to well-known porphyrin π – π^* electronic transition.³⁰ To understand the stability of the 1-D weak structure of complex **1**, we have studied the reaction of compound **1** with some nucleophilic ligands like imidazole. The change of electronic spectra of compound **1** on the addition of imidazole is shown in Figure 4. On addition of imidazole, a red shifting of the Soret and Q band was observed indicating the binding of imidazole.³¹

The change in the electronic spectrum of **1** with the addition of imidazole in chloroform medium is

consistent with previously reported results.^{31–33} The coordination of zinc porphyrin with imidazole and pyridine ligand has been widely studied and it is reported that zinc pentacoordinate is the usual binding mode in solution except in some cases due to chelate effect.^{32,33} Iron complexes of isoporphyrin (a tautomer of porphyrin) undergo ring opening in the presence of nucleophiles.³⁴ Similarly on the addition of ethanol the electronic spectrum changes, which is due to the coordination of ethanol as an axial ligand which resists the formation of Zn–O(OCH₃) bond. Furthermore, we have performed solid state UV-Visible spectral studies of different zinc methoxyphenylporphyrins **1**, **2**, and **3** (Table 1). The Soret band for all the studied porphyrins were observed at around 420 nm. The intensity of the Soret band for all the porphyrins was observed to be decreased in the solid state as compared to the solution.

The number of Q bands in the solid-state spectrum is the same as in the solution state spectrum (Table 1). The solid-state UV-Visible spectra of 4-bromo-2,6-bis[5-(4-aminophenyl)-10,15,20-triphenylporphyrin]phenol and its metal complex are known. Authors observed fewer numbers of Q bands in the solid state than in the solution state.³⁵ The solid-state UV-Visible spectrum of the compound **1** is shown in Figure S3 in Supplementary Information. The IR spectroscopy can provide some information about the structure of metalloporphyrins. The IR spectra of the free base porphyrin and compound **1** are given in Figures S4 and S5 in Supplementary Information. The bands observed in the IR spectrum of **1** agree well with those of similar compounds reported in the literature.^{36,37} For example, in the IR spectrum of compound **1**, aromatic $\nu(\text{C-H})$ vibrates at 2928 cm^{−1}, $\nu(\text{C-N})$ at 1328 cm^{−1}, $\nu(\text{C=C})$ at 1649 cm^{−1}, $\nu(\text{C=N})$ at 1587 cm^{−1}, and methoxy group at the *meta*-position vibrates at 2840 cm^{−1} for $\nu(\text{C-H})$, 1007 cm^{−1} for $\nu(\text{C-O-C})_{\text{sym}}$, respectively.

3.3 Fluorescence properties and DSC studies of compound **1**

The luminescence spectra of compounds **1**, **2** and **3** measured at excitation wavelength $\lambda_{\text{ex}} = 420$ nm are shown in Figure 5. The luminescence spectra of the synthesized zinc methoxyphenylporphyrins are similar with the luminescence spectrum of ZnTPP (Figure 5). Fluorescence maximum of the synthesized zinc methoxyphenylporphyrin **1** and **2** was localized at 660 nm and a slightly weaker maximum was observed at 620 nm at a dilute solution (10^{−6} M). Compound **2** displays emission maximum at 612 nm and a weaker

Table 1. Electronic spectral data and selected bond length, Zn—O (OCH₃), Å in Zn porphyrins.

Compound	No	λ_{max} (nm)	Powder (solid state) samples, λ_{max} (nm)	Space group	Distance, Zn—O (OCH ₃) (Å)	Reference
[ZnT(<i>m</i> -OCH ₃)PP]·3CHCl ₃	1	423, 550, 590 (in CHCl ₃)	421, 553, 599	P-1	2.674(5), 2.604(5)	This work
[ZnT(<i>p</i> -OCH ₃)PP]·2CH ₂ Cl ₂	2	425, 554, 597 (in CH ₂ Cl ₂)	422, 546, 593	P2 ₁ /c	2.694(2)	23
[ZnT(3,4,5 tri-OCH ₃)PP]	3	422, 550, 588 (in CH ₂ Cl ₂)	423, 549, 596	C2/c	2.519(5)	21

Figure 5. Luminescence spectra of compound **1**, **2**, **3** and ZnTPP in DCM (10^{-6} M). Excitation wavelength, $\lambda_{\text{ex}} = 420$ nm.

maximum at 665 nm in dilute solution (10^{-6} M). In concentrated solution, porphyrin emission is remarkably decreased due to the known π - π stacking.³⁸ The luminescence properties of magnesium analogue of compound **3** is known.³⁹

The thermal studies of several porphyrins are known.^{40,41} We have performed the differential scanning calorimetric studies for the compound **1** at a scan rate of $5^\circ\text{C}/\text{min}$ up to 250°C . At that rate, the compound **1** showed one weak endothermic peak at onset temperature 136°C (Figure S6, Supplementary Information). The endothermic peak at 136°C is most probably due to loss of solvent chloroform molecules as for the heated sample (at 130°C for 2 h) we did not observe any significant peak in that region.

3.4 Theoretical calculations

To understand the reason behind the formation of a coordination chain through the preferred *meta*-methoxy group we have performed the theoretical calculations using the Gaussian 03 package.⁴² The frontier MOs of the compound **1** with their energy is shown in Figure 6 and of compound **3** is shown in Figure S7 (Supplementary Information). The energy difference between HOMO and HOMO-1 is 0.126 eV and the LUMO and LUMO+1 MOs is 0.265 eV. The HOMO-LUMO gap is 6.41 eV. The HOMO-2 orbital has distinct contributions from *m*-methoxy oxygen atom. The Mulliken charge of compound **3** is shown in Figure S8 (Supplementary Information). The Mulliken charge of *meta*-methoxy oxygen atom is more negative than the *para*-methoxy oxygen atom (Figure S8, Supplementary Information). This result suggests that

Figure 6. Frontier molecular orbital energy level diagram of compound **1**.

the *meta*-methoxy oxygen has a higher probability of binding to the metal than the *para*-methoxy oxygen.

4. Conclusions

The complex Zn(II) 5,10,15,20-tetrakis(*meta*-methoxyoxyphenyl)porphyrin, **1** shows one-dimensional chain structure through secondary interaction (albeit weak) of zinc with oxygen atoms of a *meta*-methoxy group of the neighbouring porphyrins. The zinc-oxygen interaction observed in compound **1** is found to be stronger than similar interaction present in the compound [ZnT(*p*-OCH₃)PP] **2**, *p*-analogue of compound **1**, but weaker than similar interaction present compound [ZnT(3,4,5-triOCH₃)PP] **3**. The theoretical calculation at the DFT level corroborates the higher probability of the binding of *meta*-methoxy oxygen than the *para*-methoxy oxygen to the metal in Zn-methoxyphenyl porphyrins. Nucleophilic solvents or nucleophiles resist the formation of this weak Zn-O(OCH₃) bond and forms nucleophiles coordinated compounds.

Supplementary Information (SI)

CCDC 1817617 contains the supplementary crystallographic data for complex **1**. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The synthesis of compounds **1**, **2** and **3**, UV-Visible, fluorescence, IR spectra, and DSC spectrum are available as Supplementary Information for this article at www.ias.ac.in/chemsci.

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