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Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

Publication details, including instructions for authors and subscription information:

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Accepted author version posted online: 31 Jul 2015.



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To cite this article: Joshua A. Obaleye, Adedibu C. Tella, Gabriel K. Obiyenwa, Nzikahyel Simon & Margaret D. Olawale (2015): Zinc(II) complex of meso-tetraphenylporphyrin with 4-methoxyaniline: Crystal structure and antimicrobial activities of 4-methoxyaniline-5, 10, 15, 20-tetraphenyl-porphyrinatozinc (II), *Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry*, DOI: [10.1080/15533174.2014.988813](https://doi.org/10.1080/15533174.2014.988813)

To link to this article: <http://dx.doi.org/10.1080/15533174.2014.988813>

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Zinc(II) complex of *meso*-tetraphenylporphyrin with 4-methoxyaniline: Crystal structure and antimicrobial activities of 4-methoxyaniline-5, 10, 15, 20-tetraphenyl-porphyrinatozinc (II)

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Abstract

4-methoxyaniline-5,10,15,20-tetraphenylporphyrinatozinc(II),[(ZnTPP(MOAN))]**1** was synthesized (MOAN = 4-methoxyaniline) and characterised by elemental analysis and spectroscopic techniques. The molecular structure of **1** was determined by single crystal X-ray crystallography. The structure revealed a triclinic crystal system and the space group *P1* with the central metal adopting slightly distorted square pyramidal geometry with 4-methoxyaniline in the axial position. The antimicrobial activities were carried out using well diffusion method and the zone of inhibition of four bacteria and two fungi was measured.

Keywords : Porphyrin, 4-methoxyaniline, crystal structure, spectra, antimicrobial activity.

Introduction

Porphyrin and chlorin derivatives are among the most important tetrapyrrolic macrocycle. Synthetic porphyrins and metalloporphyrins have been applied in chemotherapy particularly in cancer treatment by boron neutron capture therapy (BNCT) and photodynamic therapy (PDT) [1,2]. PDT technique is considered an alternative to cytostatics and radiotherapy. It is indeed preferred because of its selectivity. Photosensitizers selectively localise themselves in the affected cancerous tissue which cause death of tumour cells or damage the neoplastic tissue [3,4]. Relationship exists between cancer and metals as acknowledged by recent developments in the field of metal-based anticancer agents [5]

Porphyrins and their metal complexes function as photosensitizers in PDT. Their efficiency in the technique is due to energy transfer from the porphyrin triplet state to the oxygen ground state. They have high singlet oxygen quantum yields with apparent lack of toxicity. It has been reported that a long-life triplet state is required for efficient photosensitization and incorporation of diamagnetic metals such as zinc into the porphyrin macrocycles aids this process [6]. Similarly, it was discovered that porphyrins bearing methoxy group on *meso*-phenyl group enhance photophysical properties of a photosensitizer [7]. 4-Methoxyaniline readily forms Schiff bases which coordinate metals to form complexes with various biological activities [8-11]. This work focuses on preparing metalloporphyrins containing methoxy substituent and a diamagnetic metal as potential photosensitizers in photodynamic therapy for cancer treatment. In order to contribute further towards synthesis and structural determination of metal complexes with application in chemotherapy [12,13], we hereby report the synthesis of [ZnTPP(MOAN)]**1**

complex containing 4-methoxyaniline ligand which is expected to contribute to the coordination chemistry of porphyrin.

EXPERIMENTAL

Materials

Propionic acid, pyrrole, and benzaldehyde were purchased from Sigma-Aldrich. Pyrrole was distilled on an oil bath immediately before use. Synthesis grade triethylamine was purchased from Scharlau Chemie S.A. while chloroform and 4-methoxyaniline were from M&B Laboratory. Dichloromethane was from Koch Light Laboratories and distilled over K_2CO_3 before use. Zinc chloride ($ZnCl_2$) was obtained from British Drug House Chemical Limited, Poole, England.

Physical measurements

Elemental analysis (C,H and N) was performed on Thermo Flash 1112 CHNSO elemental analyser. Electronic spectra of the ligands and their complexes were recorded in dichloromethane solution and on Jenway 6405 UV-Visible spectrophotometer in the range 200-1100 nm. The IR spectra were recorded on Shimadzu 8400S FTIR spectrophotometer as KBr pellets in the range 4000-400 cm^{-1} . The 1H and ^{13}C NMR spectra were recorded on NMR spectrometer, Mercury Varian BB 200 using deuterated chloroform as solvent and tetramethylsilane (TMS) as the internal standard.

Synthesis of 5, 10, 15, 20-Tetraphenylporphyrin (TPPH₂).

TPPH₂ was synthesized from pyrrole and benzaldehyde using previously described method Adler-Longo^[14,15] (see Electronic supplementary Information, Scheme 1)

Synthesis of 5, 10, 15, 20-Tetraphenylporphyrinatozinc(II) (ZnTPP).

ZnTPP was synthesized using known method reported by Terazono, et al^[16] and Sapien and Grazynski^[17] and some modifications were adopted for the synthesis (see Electronic supplementary Information, Scheme 2)

Synthesis of 4-Methoxyaniline-5, 10, 15, 20-tetraphenylporphyrinatozinc (II) (ZnTPP(MOAN)1).

4-Methoxyaniline (0.0688 g, 0.5386 mmol) dissolved in 12.5 ml of chloroform (yellowish-brown solution) was slowly added to a reddish-pink solution of ZnTPP (0.0854 g, 0.126 mmol) in hot chloroform (15 ml). The mixture was boiled under reflux for 1hr to obtain a purple solution after which the stirring continued for 11 hours at room temperature. The resulting red-purple solution was allowed to evaporate slowly. After 11 days a reddish-purple crystalline residue was obtained. A bright red-purple solution of the residue in dichloromethane gave a single spot on TLC plate. The crude product was recrystallized from toluene to give blue-purple single crystals suitable for X-ray crystallographic studies.

Yield = 87.22% (0.1345 g). Melting point: 342 °C.801.281; Anal. Calcd. for ZnC₅₁H₃₇N₅O (%): C, 76.45; H, 4.65; N, 8.74. Found: C, 75.72; H, 4.86; N, 8.53. UV-vis (CH₂Cl₂): λ_{max} (nm) 330, 350, 415, 425, 550, 584. IR (KBr, cm⁻¹): 3371, 3308, 3104, 3024, 2832, 1595, 1483, 1512, 1439, 1389, 1339, 1298, 1242, 1204, 1067, 1040, 1001, 750, and 702.

X-ray Crystallography of 1

A blue-purple crystal of [ZnTPP(MOAN)]**1** was on a glass fiber and mounted on a crysloop with Paratone-N oil and data collected using Bruker D8 Venture Dual Source diffractometer equipped with a CMOS-detector using graphite-monochromated Mo K α ($\gamma = 0.71073 \text{ \AA}$) radiation at 293K.

The structure of **1** was solved by direct methods using (SHELXS-86, Sheldrick, G.M., 1990)^[19] and completed by iterative cycles ΔF synthesis, using the (SHELXL-97 packages, Sheldrick, G.M., 1997)^[20]. The structure was solved by Charge Flipping using SUPERFLIP^[21] (Superflip, 2007) and refined by full-matrix least-squares methods based on F^2 using SHELXL (Sheldrick, G.M., 2008)^[22] Details of the crystal parameters, data collection and refinements are listed in Table 4.). Molecular graphics or complete structure solution, refinement and analysis program was achieved using OLEX2 (Dolomanor et al,^[23] . Table 5 lists selected bond length describing the zinc atom coordination with the porphyrin core and the 4-methoxyaniline ligand.

Antibacterial and antifungi susceptibility tests

The *in vitro* biological effects of the investigated compounds were tested against important bacteria and fungi strains by well diffusion method^[24] . Cloxacillin was used as reference drug for bacteria. The drug, 4-methoxyaniline and the metal complex [ZnTPP(MOAN)] **1** were screened in-vitro activity against one Gram-positive bacteria, *Staphylococcus aureus*, three Gram-negative bacteria, *Proteus vulgaris*, *Escherichia coli* and *Klebsiella pneumonia*, and two fungi species, *Candida albican* and *Aspergillus niger*. The media used for this test were nutrient agar, nutrient broth and potato dextrose agar. *Proteus vulgaris* was obtained from University

College Hospital, Ibadan, Nigeria. *Staphylococcus aureus*, *Escherichia coli* and *Klebsiella pneumoniae* were collected from University of Ilorin Teaching Hospital, Nigeria. The fungi were obtained from the Microbiology Department University of Ilorin, Nigeria.

Solutions (0.2 ml) of each compound (16 mg) under test in 10 ml of dimethylsulphoxide (DMSO) containing 320 μ g were pipetted into the bored media wells and allowed to disperse evenly. The plates were then incubated for 24 hours at 37 °C in the case of bacteria and at room temperature (about 28 °C) for 72 hours in the case of fungi. After incubation zones of clearance were observed and diameter of these inhibition zones was measured.

RESULTS AND DISCUSSION

Formation and characterization of zinc (II) complex

Insertion of zinc into the ligand TPPH₂ was achieved by dissolving ZnCl₂ in methanol and refluxing the resulting solution with a chloroform solution of the ligand. Four coordinate ZnTPP was formed. The progress of the reaction was conveniently followed by electronic spectroscopy. The second ligand MOAN was thereafter introduced to ZnTPP to obtain [ZnTPP(MOAN)]**1**, a five coordinate complex.

The percentage yield of the complex was excellent (above 80%) and greater than that of ZnTPP from which it was prepared. This shows that MOAN readily react with the metalloporphyrin and coordinate with metal ions. In fact, 4-methoxyaniline and its structural isomers form many Schiff bases and their metal complexes ^[10,11]. The use of the chloroform as solvent for both metalloporphyrin and the organic compound during the synthesis might have also enhanced the metallation process as suggested by Adler et al ^[25]. C, H, N analysis shows a good agreement

with the theoretical percentage of each of the elements. The coordination number of zinc increased to five as suggested by the analytical results.

UV-Visible Spectra

Table 1 shows the results of UV-vis spectral data and their assignments. The effect of axial ligation on the electronic absorption spectral properties of ZnTPP was also investigated. The bands observed in the spectra of [ZnTPP(MOAN)] **1** was as a result of π to π^* electronic transitions in the porphyrin and 4-methoxyaniline ring systems. The two organic molecules (MOAN and TPPH₂) contain highly conjugated π electrons which masked any d-d transition in the metal ion orbitals. Unlike most transition metal complexes, the colour of metalloporphyrins are attributed to absorption within the porphyrin ligand involving excitation of electrons from π to π^* of porphyrin ring orbital. This can be explained by considering the four frontier orbitals (HOMO and LUMO orbitals). According to Gouterman's four-orbital model^[26], the transition $a_{1u}(\pi) \rightarrow e_g(\pi^*)$ and $a_{2u}(\pi) \rightarrow e_g(\pi^*)$ are largely responsible for the Soret and Q (α and β) bands of metalloporphyrins. The dxz and dyz ($d\pi$) orbitals of normal metalloporphyrins (d^0 or d^{10}) are of relatively low energy and have very little effect on the porphyrin $\pi \rightarrow \pi^*$ energy gap in porphyrin^[27]. The peaks observed in the mixed ligand complexes were quite different from those of metalloporphyrin reactants. These peaks experienced blue shifts and two new peaks at 482 and 510 nm were observed as Q bands in the zinc complex. Small bathochromic shifts have been reported to characterise the addition of oxygen donor axial ligands to ZnTPP by Narda and Dawson^[28]. The hypsochromic shift suggested that MOAN was not an oxygen donor but a nitrogen donor toward the metal in ZnTPP. The spectral changes can be attributed to the

coordination of metal ions by MOAN so as to form more stable geometry by expanding their coordination spheres. B bands or Soret peaks however did not experience any appreciable shift. Square-pyramidal geometry was reported to be common to pentacoordinate zinc (II) porphyrins [16].

Infrared spectrum of [ZnTPP(MOAN)]1

Table 2 displays the spectral bands of [ZnTPP(MOAN)]1 compared with those of the metalloporphyrin ZnTPP on one hand and those of TPPH₂ and MOAN on the other. Stretching and deformation bands of C-H of methoxy group were present in the mixed ligand complexes and in the spectrum of MOAN as expected which indicate the presence of p-anisidine in them. Similarly, C-O_{str} frequency bands appeared in the complexes which did not undergo significant shift compared to the bands in MOAN. This suggests that methoxy group of MOAN was not involved in the coordination with the metal ion. In the spectra of ZnTPP(MOAN), N-H_{str} and C-N_{str} bands were present and shifted to lower frequencies when compared to the same band in MOAN. This shift can be attributed to the utilization of N-H group for coordination. The metal-nitrogen [29] stretching bands around 1000 cm⁻¹ were found present in the mixed ligand complex but experienced red shift from the band of ZnTPP as a result of coordination with MOAN through the nitrogen atom. It had been reported that ZnTPP usually take up only one axial ligand resulting in five-coordinated zinc atom [28,30] and peripheral phenyl groups in the complex do not create any steric hindrance to coordination of bases [31]. The finding in this work further confirmed the above report by previous workers. The addition of molar excess of MOAN to

ZnTPP (4:1 mole ratio) only produced a complex of 1:1 stoichiometry as revealed by analytical and spectroscopic results.

Crystal and molecular structure of [ZnTPP(MOAN)]1

The structure of the compound has been studied by X-ray diffraction. Crystallographic parameters and refinement results for **1** are shown in Table 3. Three views of the complex are shown in Figure S1. Selected bond lengths and angles are presented in Tables 4 and 5 respectively. The zinc is five-coordinate zinc (II) porphyrin. The Zn-N_{porphyrin} distance (average 2.0596 Å) is comparable with the distance found for similar bonds in five-coordinate zinc-porphyrin complexes (Zn-N = 2.057(1)-2.076(9)Å) [33, 34,35] (Table 4) but are longer than Zn-N distance (2.036 Å) in four coordinate ZnTPP [36]. Thus, the complex possesses a moderately expanded porphyrin core (2.052 Å). The equatorial Zn-N_{porphyrin} bond distance is smaller than axial Zn-N5 bond distance (2.2053 Å). The 4-methoxyaniline molecule is weakly bound to the zinc atom by comparison with the much shorter Zn-N_{pyridyl} bond distance of 2.140(8) Å estimated in the pyridine adduct of [5, 10, 15, 20-tetrakis(heptafluoropropyl)porphinato]zinc (II) [37]. The Zn-N_{pyrrolic} bond distances (2.0556-2.0665 Å) are, however, within the range of that reported for similar complexes (2.052-2.076 Å) [38].

The four Zn-N bonds (Zn-N1 to Zn-N4) are non-equivalent as shown in Table 4. This could be caused by in-plane elongation of the porphyrin core due to steric strain enforced by the peripheral substituents. The mechanism of the core is explained by repulsion of the pyrrolic β-β substituents that push the meso-phenyl groups towards the unsubstituted pyrroles [39].

The primary amino group did not become deprotonated on coordination as suggested by the results of infrared spectroscopy. It implies that a lone pair of electron on the nitrogen atom was utilized for coordination with zinc metal. The crystal structure is shown in figure 1.

Antibacterial and antifungal tests

Cloxacillin was used as reference drug for bacteria. The inhibition zones developed at the concentration of 1600 $\mu\text{g/L}$ (1.6mg/ml) in DMSO are shown in Table 8. The complex formed by ZnTPP with MOAN inactivates the organic compound 4-methoxyaniline against *E. coli*. The presence of the metalloporphyrin which is not well known to be biologically active compared to the reported activities of metal complexes of MOAN. $[\text{ZnTPP}(\text{MOAN})]\mathbf{1}$ displayed no activity against all other bacteria species tested. Compound 1 is comparable in activity with 4-methoxyaniline against *Candida albican* fungi at the concentration used. This activity may have been imparted on the complex by the axial ligand. This is not unexpected since porphyrins and metalloporphyrins were not reported as having significant antimicrobial activity. They were, however, found to act as photosensitizers in photodynamic therapy.

Conclusion

In summary, we reported the first Zinc-porphyrin complex containing 4-methoxyaniline. Spectroscopic and X-ray crystal studies of $[\text{ZnTPP}(\text{MOAN})]$ revealed that the complex contains 4-methoxyaniline in the axial position and coordinate the central metal through the nitrogen atom without loss of hydrogen atoms of the primary aromatic amine while leaving methoxy group unbound. The Zn-N_{porphyrin} distance is comparable with the distance found for similar bonds in five-coordinate zinc-porphyrin complexes. Antimicrobial investigations of the compound

indicate that it is moderately effective against *Candida albican* but showed no activity against the four bacteria selected for the test. The presence of methoxy group and the diamagnetic zinc may make the new compound a better photosensitizer in photodynamic therapy for the treatment of cancer.

Supplementary Material.

Supplemental data is available at the publisher's website. CCDC 968549 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the Cambridge crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ; fax +441223336033). Electronic supplementary Information ESI available.

Acknowledgement

We are grateful for the support from the World Bank Science and Technology Education Post-Basic Project (STEP-B), Department of Chemistry University of Ilorin, Nigeria and Markus Neuburger for help with the crystal structure determination during the Zurich School of Crystallography 2012 at the University of Zurich, Institute of Organic Chemistry, Winterthurerstrasse 190 CH-8057, Zurich. We thank Prof. Mino Caira of the University of Cape Town, South Africa for supplying the various views of ZnTPP(MOAN)

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Table 1. Electronic absorption bands of TPPH₂ and its Zinc complexes

Compound	Visible absorption bands (nm)		Assignment
	B band (Soret)	Q bands	
TPPH ₂	415	515, 550, 590, 650	$\pi \rightarrow \pi^*$
ZnTPP	425	545, 585	$\pi \rightarrow \pi^*$
[ZnTPP(MOAN)] 1	429	482, 510, 541, 584	$\pi \rightarrow \pi^*$
MOAN	435	360, 405	$\pi \rightarrow \pi^*$

Table 2. Infrared spectra results of 5, 10, 15, 20-Tetraphenylporphyrin and its metal complexes

IR Band Assignment (KBr, cm ⁻¹)				
	TPPH ₂	ZnTPP	MOAN	ZnTPP(MOAN)
N-H _{str} (arom. amine)	3317m	3435w	3424s, 3349m	3371m
C-N _{str} (arom. amine)	1350s	1338m	1333w	1339s, 1298w
M-N _{str}	-	995s	-	1001s
C-O _{str}	-	-	1275m, 1234s, 1032s	1242m, 1204w, 1067s, 1040m

Table 3 . Crystallographic parameters and refinement results for **1**

molecular formula	$C_{51}H_{37}N_5OZn$
molecular weight:	801.23
space group	<i>P1</i>
temperature (K):	293
colour:	Purple-blue
crystal system	Triclinic
unit cell dimensions:	
<i>a</i> (Å)	10.580(5)
<i>b</i> (Å)	10.702(5)
<i>c</i> (Å)	18.305(5)
α (°)	79.492(5)
β (°)	86.445(5)
γ (°)	78.066(5)
<i>V</i> (Å ³)	1993.2(14)
<i>Z</i>	2
<i>D</i> _{calc} (Mgm ⁻³)	1.335
μ (mm ⁻¹)	0.66
<i>F</i> (000)	832
Radiation	M_o K α ($\lambda = 0.71073$ Å)

θ range	2.1-27.5°
h, l, k collected	$\pm 13, \pm 13, \pm 23$ (fine-focus sealed tube graphite)
reflections with $I > 2\sigma(I)$	7515
no of reflections collected	44978
no of independent reflections	9107 [$R_{int} = 0.055$]
R_w (F^2)	0.120
slope of normal prob plot	1.13
Largest diff. peak/hole/e \AA^{-3}	0.39/-1.01

Table 4 . Bond Lengths (Å) Describing the Zinc Atom Coordination, the Porphyrin Core, and the MOAN Ligand

Zn1-N1	2.0567 (18)
Zn1-N2	2.0556 (18)
Zn1-N3	2.0597 (18)
Zn1-N4	2.0665 (18)
Zn1-N5	2.2053 (18)
N3-C5	1.374 (3)
N3-C8	1.378 (3)
N2-C13	1.376 (3)
N2-C10	1.377 (3)
N5-C45	1.432 (3)
N4-C20	1.372 (3)
N4-C3	1.377 (3)
N1-C15	1.374 (3)
N1-C18	1.376 (3)

Table 5 . Bond Angles (deg) Describing the Zinc Atom Coordination, the Porphyrin Core, and the MOAN Ligand

N2-Zn1-N1	89.31 (7)
N2-Zn1-N3	89.55 (7)
N1-Zn1-N3	166.81 (7)
N2-Zn1-N4	167.34 (7)
N1-Zn1-N4	89.08 (7)
N3-Zn1-N4	89.16 (7)
N2-Zn1-N5	97.34 (7)
N3-C5-C4	125.66 (18)
N3-C5-C6	109.42 (17)
N1-Zn1-N5	98.24 (7)
N3-Zn1-N5	94.93 (7)
N4-Zn1-N5	95.32 (7)

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C5-N3-C8	106.62 (17)
C5-N3-Zn1	126.49 (13)
C8-N3-Zn1	126.45 (14)
C13-N2-Zn1	126.60 (14)
C10-N2-Zn1	126.09 (14)
C45-N5-Zn1	114.67 (13)
C20-N4-Zn1	126.70 (14)
C3-N4-Zn1	125.69 (13)
N4-C3-C4	125.77 (18)
N4-C3-C2	109.44 (17)
N1-C18-C19	125.63 (18)
N1-C18-C17	109.17 (18)
N4-C20-C19	125.30 (18)
C15-N1-C18	106.76 (16)
C15-N1-Zn1	126.10 (13)
C18-N1-Zn1	126.58 (14)

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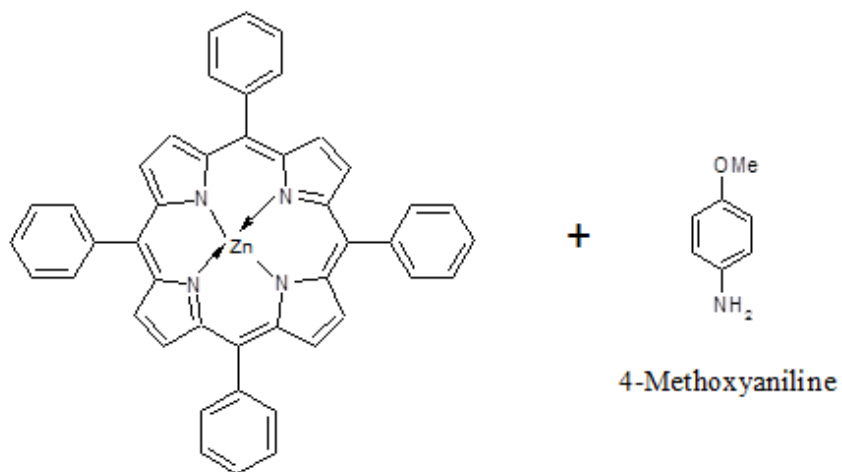
N1-C15-C14	126.01 (19)
N1-C15-C16	109.51 (18)
N4-C20-C1	109.58 (17)
N2-C13-C14	125.47 (18)
N2-C13-C12	109.39 (18)
N3-C8-C9	125.18 (19)
N3-C8-C7	109.58 (18)
N2-C10-C9	125.80 (19)
N2-C10-C11	109.21 (18)

Table 6 . Comparative Structural Analysis of Zinc Porphyrins ^[40]

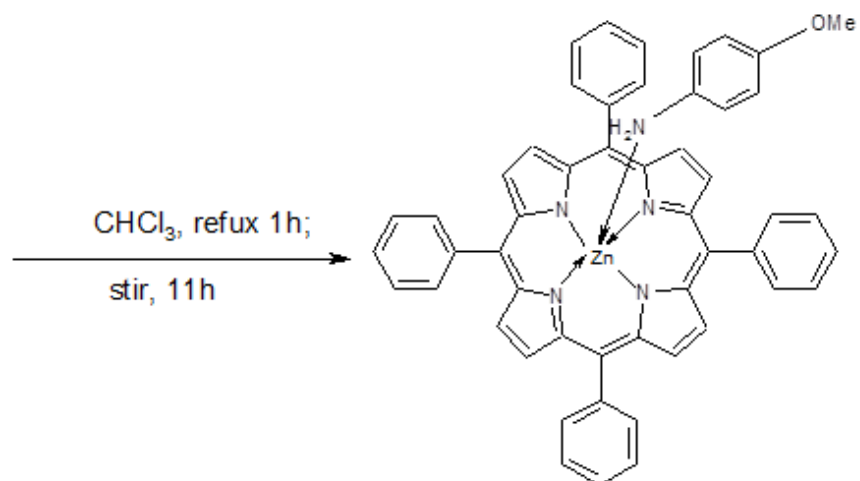
zinc-porphyrin complex	(Zn-N) _{av} (Å)	Ref
ZnTPP(ANSD)	2.0596(18)	this work
ZnTPP(ClO ₄)	2.076 (9)	32
ZnTPP.2C ₆ H ₅ CH ₃	2.036 (6)	33
ZnOEP(py)	2.067 (6)	34
Zn(TPyP)(py)	2.073 (8)	35
ZnTPP(THF) ₂	2.057 (1)	39

Table 7. Zones of inhibition of bacteria and fungi by Cloxacillin and ZnTPP(MOAN) at 1.6mg/ml (DMSO)

Organism/ Compounds	<i>Staphylococ cus aureus</i>	<i>Klebsiella pneumoniae</i>	<i>Escherichia coli</i>	<i>Proteus vulgaris</i>	<i>Candida albican</i>	<i>Aspergillus niger</i>
Zones of Inhibition (mm)						
Cloxacillin	15	Inactive	Inactive	Inactive	17	Inactive
MOAN	Inactive	Inactive	30	Inactive	15	Inactive
[ZnTPP(MOAN)]	Inactive	Inactive	Inactive	Inactive	15	Inactive



5,10,15,20-Tetraphenylporphyrinatozinc (II) (ZnTPP)

4-methoxyaniline-5,10,15,20-tetraphenylporphyrinatozinc (II) [ZnTPP(MOAN)] **1****Scheme 3.** Synthesis of [ZnTPP(MOAN)] **1**

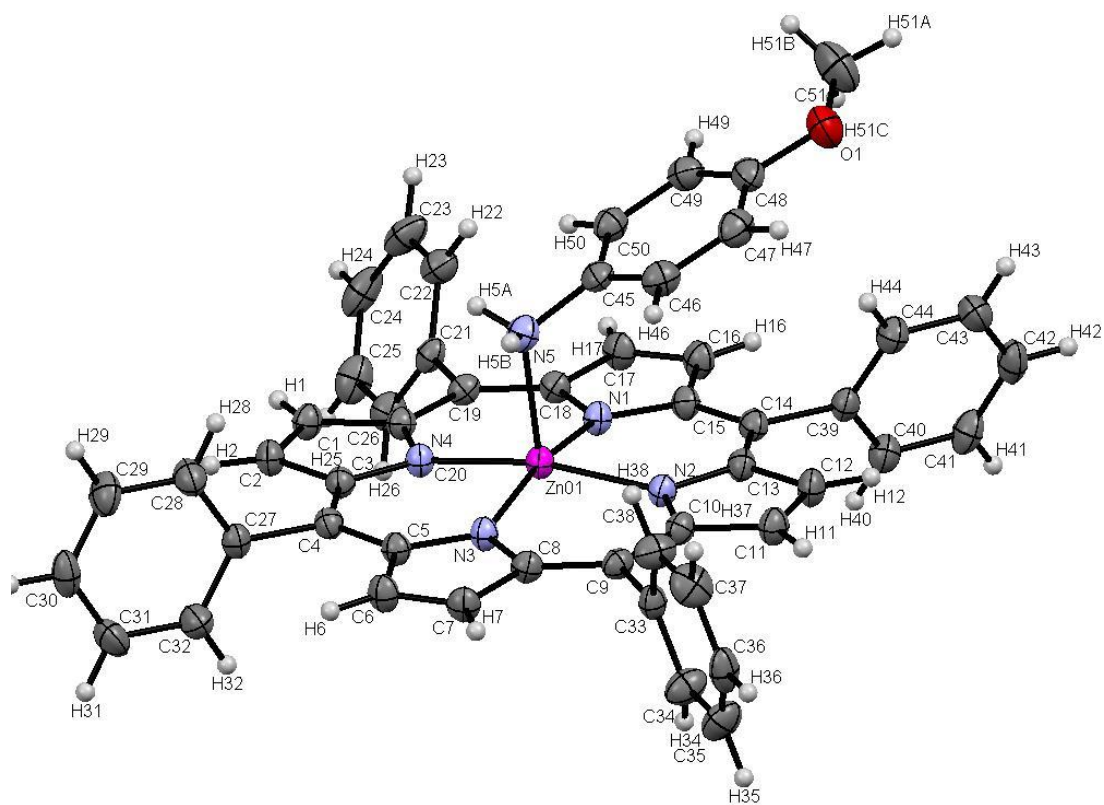


Figure 1. Thermal ellipsoid plot of ZnTPP(MOAN)1