# Synthesis and Spectroscopic Studies of Zirconium(IV) Porphyrins with Acetylacetonate and Phenolates at Axial Positions

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## ABSTRACT

Reaction of p-methoxy-meso-tetraphenylporphyrin(p-OCH$_3$H$_2$TPP) with Zirconium(IV) acetylacetonate(Zr(acac)$_4$) and phenols at 200-220°C results in the formation of correspondimg axially ligated Zirconium(IV)-p-methoxy-mesotetraphenylporphyrin [Zr(p-OCH$_3$TPP)(Y)(X)] [Y=acac and X=different phenolates]. The separation and isolation of these compounds have been achieved through chromatographic methods and characterized by ^{1}HNMR, Electronic absorption spectra, IR spectra, elemental analysis and mass spectroscopy. Inseration of metal ion in the porphyrin ring is confirmed by absorption spectroscopy which shows normal two Q bands i.e., Q(0,0), Q(1,0) and one shoulder Q(2,0). The ^{1}H NMR spectra of Zr(IV)porphyrins show upfield(shielded) compared to meso-tetraphenylporphyrin(H$_2$TPP). IR spectra confirm the appearance of Zr-N at 457-502cm^{-1}, Zr-O at 649-680cm^{-1} and also the incorporation of (acac)(C$_5$H$_7$O$_2$) in which Zr-O is at 702-818cm^{-1}. Mass spectra determine m/z ratio and percentage of each element is confirmed by elemental analysis.

**Keywords:** Zirconium (IV) derivatives, Acetylacetonate, Axial positions.

## INTRODUCTION

The involvement of porphyrins in many biological processes and the possibility to tailor their physical and chemical properties at the molecular level including very large dipole moments, polarizability, non-linear optical response, absorption spectrum, energy transfer and catalytic properties which make porphyrins and metalloporphyrins extremely versatile synthetic base materials for research projects in many disciplines of chemistry and physics, like electronic, opto-electronic, electrochemistry, catalysis and photophysics.Incorporation of porphyrins into zeolites has been explored as means to biomimetic oxidation catalysts [1]. Another area of recent interest is to find application of porphyrin materials in the field of conducting polymers and ferroelectric materials [2]. Furthermore, porphyrins and their structural analogues are used in broad technological applications such as electrophotographic photoreceptors, air deodorant, pigment preparations and photodynamic therapy [3] and in development of molecular electronic devices used in memory or logic applications [4]. Over the past few years, the d[0] transition-metal porphyrins

containing Sc(III), Ti(IV), Zr(IV), Hf(IV), Nb(V), and Ta(V) have been synthesized and characterized [5-9]. This has been mainly due to the use of these compounds in catalysis, photodynamic therapy of cancer cell [10], as materials with novel electrical properties [11] and as biomimetic model systems of primary processes of natural photosynthesis [12] and also due to their strong affinities for DNA and potential nuclease activity [13]. The reactivity [14] and the previously reported synthetic methods for zirconium(IV) porphyrinates are generally carried out in refluxing solvents (benzonitrile, dimethoxyethane, or toluene) using the $HfCl_4$ starting complex 80-95% yields of the $M(Por)Cl_2$ complex. The metal ions in these complexes are oxophilic; thus, the preference for carboxylate or other oxygen-bearing anionic ligands. Zr(IV) has an electron configuration of $[Kr]4f^{14}$, is closed shell metal ion and Because of the lack of functional groups on the porphyrin moieties, there is a paucity of supramolecular materials with designed, hierarchical structures [15-30] containing Zr(Por). The key entry to the organometallic zirconium porphyrin complexes would be Zr-(Porphyrin)$Cl_2$, analogous to $ZrCp_2Cl_2$. The dichloride complex may be converted to organometallic σ-complexes such as dialkyl complexes by the reactions with alkyllithium or Grignard reagents. It may also form organometallic π-complexes by replacing the two chlorides with a cyclooctatetraenyl dianion or a dicarbollide dianion. Arnold and coworkers published[31] the synthesis and characterization of Zr(OEP)$Cl_2$ and several organometallic complexes derived from it, including Zr(OEP)$(CH_2SiMe_3)_2$ [31a] and Zr(OEP)$(\eta^5$-$C_2B_9H_{11})$ (31b). Also an extensive series of out of plane cis (OEP)Zr$R_2$ dialkyls have been investigated due to their reactivity[32-36]. These complexes undergo rapid Zr-C protonolysis, yielding new (OEP)Zr$X_2$ ($X^-$=TfO$^-$,R'CO$_2^-$Cl$^-$) and (OEP)Zr(R)$^+$ derivatives, and also cleanly insert $CO_2$ and acetone, yielding carboxylate and alkoxide complexes. Hydrogenolysis of (OEP)Zr$(CH_2SiMe_3)_2$ yields hydride species which can be trapped by olefins yielding (OEP)Zr$(CH_2SiMe_3)(CH_2CH_2R)$ and (OEP)Zr$(CH_2CH_2R)_2$ (R=H,Me). This system catalytically hydrogenates ethylene, presumably via an insertion/Zr-C hydrogenolysis process. Recently, Inoue reported that (TPP)Zr$X_2$ complexes ($X^-$=RCO$_2$Cl$^-$)$_2$ catalyze the carboalumination of terminal alkynes [37].

In this study, we report the synthesis of p-methoxy-meso-tetraphenylporphyrinatozirconium(IV)acetylacetonate with various phenols as axial ligands and spectroscopic parameters of these complexes.

## MATERIALS AND METHODS

The Optical absorption spectra of the compounds were recorded on a Hitachi U-3400, lambda 35 UV- Vis. Spectrophotometer and Elico spectral treats UV-Vis. spectrophotometer using a pair of matched quartz cells of 10mm path length at an ambient temperature. The oscillator strength ($f$) of the transitions in absorption spectra were calculated from the expression [38].

$$f = 4.33 \times 10^{-9} \times \varepsilon \times \Delta\nu_{1/2}$$

Where ε is the molar absorption coefficient in $dm^3$ mol$^{-1}$ cm$^{-1}$ and $\Delta\nu_{1/2}$ is the full width at half maximum in cm$^{-1}$.The $^1$H NMR spectra were recorded on an av 500 NMR Spectrometer in CDCl$_3$ using tetramethylsilane (TMS) as internal standard.Porphyrin solutions (0.5 ml) of 10$^{-2}$ to 10$^{-3}$ M in CDCl$_3$ were used for $^1$H NMR studies. The δ values reported are in ppm with number of protons involved followed by the position of protons.Infrared Spectra(IR-Spectra) were recorded on a PERKIN ELMER spectrometer at room temperature in KBr pellets. In Infrared spectroscopy, the detection of metal-nitrogen (M-N), metal-axial ligand (M-L) vibrations[39-42] and metalloporphyrins with different pure metal isotopes were studied over a large frequency range. The far-infrared region, which apparently provides valuable information on M-N vibrations, has been investigated. The elemental analysis of the precursor p-methoxy-meso-tetraphenylporphyrin and its Axially Ligated Zirconium(IV)acetylacetonate, with different phenolates as an axial ligand were performed on Elemental Analyser CHNS-932, LECO, USA at a temperature of about 1000ºC using helium as carrier gas and oxygen for combustion.The MALDI Mass spectra were recorded on Bruker Daltonics Spectrophotometer. MALDI Data System in positive linear high power of detection at an accelerating voltage of 20 KV and laser power tuned depending on the sample and the spectra were recorded at room temperature and methanol as solvent.

Pyrrole (Fluka, Switzerland) was distilled over potassium hydroxide pellets under reduced pressure before use. Anisaldehyde(p-methoxybenzaldehyde) is procured from Aldrich, USA and used without further purification and Propionic acid used in the synthesis of tetraphenylporphyrin was obtained from Qualigens (India) and used as such. Silica gel (60-120 mesh) and silica gel (TLC grade, particle size = 75 μ procured from Merck, Germany) were used for column and thin layer chromatography respectively.Aluminium oxide (basic) purchased from Fluka, Switzerland and DDQ (2,3-dichloro-5,6-dicyano-p-benzoquinone) purchased from Merck, Germany were used as such.Zirconium(IV) acetylacetonate is purchased from Aldrich, USA and used without further purification.Anhydrous sodium sulphate ($Na_2SO_4$), potassium carbonate ($K_2CO_3$), sodium hydrogen carbonate ($NaHCO_3$), sodium hydroxide (NaOH) and calcium chloride ($CaCl_2$) procured from Ranbaxy Labs. Ltd. (India). The various phenols used were of AR grade (SISCO Research Laboratories Pvt. Ltd.) and used with further purification. The synthesis of the complexes of Zr(IV) was carried over a salt bath containing a mixture of $NaNO_3$(53%), $NaNO_2$(44%) and $KNO_3$(7%).The salt melts at 142°C temperature. The temperature of the mixture was maintained between 230-240°C. The $NaNO_3$, $NaNO_2$ and $KNO_3$ used for the preparation of salt bath were procured from Qualigens (India) and used as such.

**p-methoxy-meso-tetraphenylporphyrin (p-$OCH_3H_2$TPP)**

The preparation of p-$OCH_3H_2$TPP was carried out by condensation of pyrrole with anisaldehyde in refluxing propionic acid,p-$OCH_3H_2$TPP prepared was purified by column chromatography using $CHCL_3$ as eluent. UV-vis($CHCL_3$): λmax(nm) : 424, 518.2, 557, 596, 650.9. $^1$HNMR ($CDCL_3$) (δ,ppm): -2.10(s,2H,NH), 8.70(s,8H,β-pyrrole), 7.82(d,8H,$H_o$), 7.44(d,8H,$H_m$), 3.92(s,12H,$H_{ome}$). Anal.Calcd. for $C_{48}H_{38}O_4N_4$: C, 78.45; H, 5.21; N, 7.62. Found: C, 78.22; H, 5.22; N, 7.56.

**p-methoxy-mesotetraphenylporphinato-zirconium(IV)acetylacetonatophenoxide [Zr(p-$OCH_3$TPP)(acac)(Y)(X)]**

$Zr(acac)_4$(1.87x10$^{-3}$moles),p-methoxy-

mesotetraphenylporphyrin(3.74x10$^{-4}$moles) and respective phenol(1.06x10$^{-2}$ moles) were taken in a boiling tube covered with a funnel over the salt bath at about 200-220°C with constant stirring up to 25 minutes. After 25 minutes, the temperature was slightly raised and the given mixture was recharged with 1/3rd of initial amount of $Zr(acac)_4$ and then again refluxed for 25 minutes. After cooling the reaction mixture, it was extracted with 2*N* boiling NaOH solution. The compound recovered after extraction was passed through $Na_2SO_4$. The solvent was recovered under reduced pressure and the reaction mixture was chromatographed through basic alumina using chloroform as an eluent, recrysatallised and characterized by UV-vis and $^1$HNMR spectra (Scheme-1).

## RESULTS AND DISCUSSION

### $^1$HNMR Spectroscopy

$^1$H NMR was widely used as an analytical tool and the new structural insights that resulted were a major reason for the revival of interest in porphyrins chemistry. The $^1$H NMR spectra of the p-methoxy-meso-tetraphenylporphyrin and their Zr(IV) derivatives containing different phenolates as an axial ligand are highly characteristic and establish the structural integrity of these compounds in solution and data accumulated in (Table 1). The $^1$H NMR spectra of free-base porphyrins give three characteristic proton resonances (a) β-pyrrole protons (b) imino protons and (c) meso-aryl protons. The presence of subtiuent in β-positions and peripheral phenyl groups alters these proton resonances. The integrated intensity of the resonances agrees well with the number of protons. The presence of electron-donating methoxy group at the para-position of the meso-phenyl ring causes a slight shielding effect of the β-pyrrole protons resulting in a slight upfield shift of meso-substituted porphyrins relative to simple meso-tetraphenyl-porphyrin ($H_2$TPP).This shielding/deshielding is most likely a consequence of meso –C–C– dihedral angle much greater than 0°, thereby placing the β-pyrrole protons in a more shielded/deshielded environment produced by the anistropic effect of substituent ring current.

The inner imino protons of the $H_2$TPP resonate at -2.79 ppm, while those of p-$OCH_3H_2$TPP

appear at -2.10 ppm. The meso-aryl protons of $H_2TPP$ resonate as a singlet at 8.19 ppm of ortho and 7.59 ppm of meta and para protons respectively and are shifted marginally depending upon the nature of the substituents attached as in case of p-$OCH_3H_2TPP$ which has electron-donating methoxy groups, the resonance occurs at 7.82 ppm of ortho and 7.44 ppm of meta protons i.e, resonance is shifted upfield relative to $H_2TPP$ and meso-methoxy protons in p-$OCH_3H_2TPP$ resonate as a singlet at 3.92 ppm respectively. Generally, the presence of axially ligated Zr(IV) metal in the porphyrin ring shifts the resonances to down-field accompanied by marginal changes in the pattern. One of the important feature of axially ligated Zr(IV) derivatives of porphyrins is that the metal is almost certainly out of the plane of the porphyrin ring which have earlier been reviewed in literature, responsible for the production of asymmetric environment above and below the plane of the macrocycle which ultimately account for the pronounced non-equivalence of the ortho protons of the phenyl rings. In axially ligated zirconium compounds of p-$OCH_3TPP$, a slight

shielding (upfield) of protons is observed with respect to $H_2TPP$ (Table 2). The ^{1}H NMR of Zr(p-$OCH_3TPP$)(acac) (p-$NO_2PhO$), indicates that the β-pyrrole protons resonate as singlet at 9.18 ppm, the meso-aryl ortho protons resonate as duplet at 8.33 ppm and 8.07 ppm, the meso-aryl meta protons resonate as duplet at 7.81 ppm, the meso-methoxy protons resonate as singlet 4.24 ppm, the acac protons resonate as two singlets at 1.76 ppm and 4.51 ppm, the ortho protons of para nitro phenolate resonate as duplet at 7.13 ppm and the meta-protons of para nitro phenolate resonate as duplet at 7.32 ppm respectively which is downfield with respect to Zr(p-$OCH_3TPP$) (acac)(Oph) (Fig. 1). In case of Zr(p-$OCH_3TPP$) (acac)(p-$NH_2phO$, the β-pyrrole protons resonate as singlet at 8.32 ppm, the meso-aryl ortho protons resonate as duplet at 7.32 ppm and 7.19 ppm the meso-aryl meta protons resonate as multiplet at 7.02-7.10 ppm, the meso-methoxy protons resonate as singlet 4.01 ppm, the acac protons resonate as two singlets at 1.47 ppm and 3.71 ppm, the amino protons of para amino phenolate resonate as singlet at 4.65 ppm, the ortho
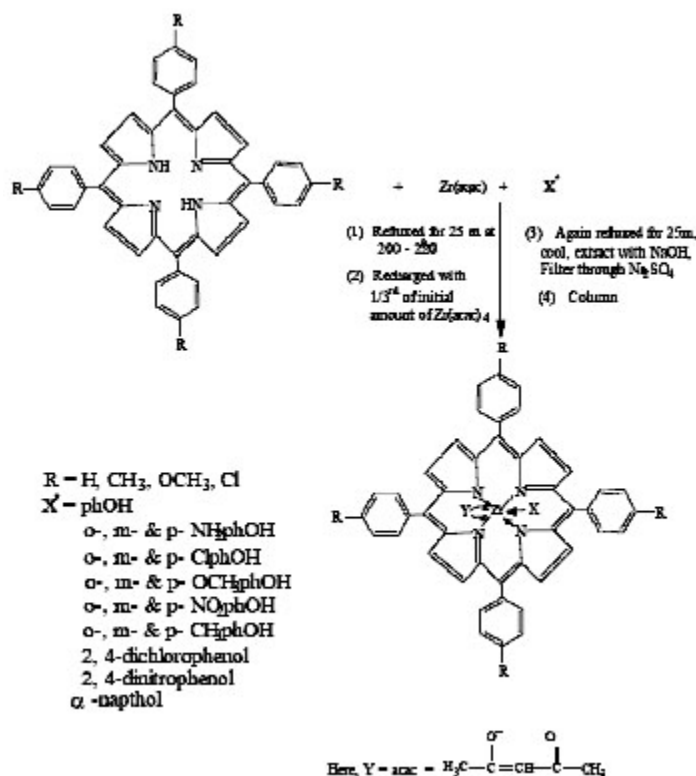


**Scheme 1: General Scheme for preparation of axialy ligated Zirconium (IV) porphyrins with different phenolates as an axial ligand**

**Table 1 : ¹H NMR data of free-base porphyrin (p-OCH₃H₂TPP) and Zr(p-OCH₃TPP)(Y)(X) (Y = acac and X = different phenolates as an axial ligand) in CDCl₃ at 298 K.**

| Porphyrins | β-Pyrrole Protons | Imino Protons | Meso-aryl Protons | Other Protons | |
| --- | --- | --- | --- | --- | --- |
| | | | | Acac protons | Phenolate protons |
| p-OCH₃ H₂TPP (C₄₈H₃₈O₄N₄) | 8.70(s) | -2.10(s) | 7.82(d,8H,Hₒ) 7.44(d,8H,Hₘ) 3.92(s,12H,HOMe) | - | - |
| Zr(p-OCH₃TPP)(acac)(Oph) [Zr(C₄₈H₃₆O₄N₄)(C₅H₇O₂)(C₆H₅O)] | 8.83(s) | - | 8.02(d,4H,Hₒ) 7.77(d,4H,Hₒ) 7.57(d,8H,Hₘ) 4.13(s,12H,HOMe) | 1.69(s,6H,H_Me) 4.44(s,H,H_CH) | 6.98(d,2H,Hₒ) 7.05-7.19(m,3H,Hm,p) |
| Zr(p-OCH₃TPP)(acac)(p-ClphO) [Zr(C₄₈H₃₆O₄N₄)(C₅H₇O₂)(C₆H₄OCl)] | 9.15(s) | - | 8.27(d,4H,Hₒ) 8.02(d,4H,Hₒ) 7.76(d,8H,Hₘ) 4.19(s,12H,HOMe) | 1.72(s,6H,H_Me) 4.47(s,H,H_CH) | 7.04(d,2H,Hₒ) 7.21(d,2H,Hₘ) |
| Zr(p-OCH₃TPP)(acac)(p-NO₂phO) [Zr(C₄₈H₃₆O₄N₄)(C₅H₇O₂)(C₆H₄O₃N)] | 9.18(s) | - | 8.33(d,4H,Hₒ) 8.07(d,4H,Hₒ) 7.81(d,8H,Hₘ) 4.24(s,12H,HOMe) | 1.76(s,6H,H_Me) 4.51(s,H,H_CH) | 7.13(d,2H,Hₒ) 7.32(d,2H,Hₘ) |
| Zr(p-OCH₃TPP)(acac)(p-NH₂phO) [Zr(C₄₈H₃₆O₄N₄)(C₅H₇O₂)(C₆H₆ON)] | 8.32(s) | - | 7.32(d,4H,Hₒ) 7.19(d,4H,Hₒ) 7.02-7.10(d,8H,Hₘ) 4.01(s,12H,HOMe) | 1.47(s,6H,H_Me) 3.71(s,H,H_CH) | 6.74(d,2H,Hₒ) 6.58(d,2H,Hₘ) 4.65(s,2H, H_NH2) |
| Zr(p-OCH₃TPP)(acac)(p-OCH₃phO) [Zr(C₄₈H₃₆O₄N₄)(C₅H₇O₂)(C₇H₇O₂)] | 8.36(s) | - | 7.42(d,4H,Hₒ) 7.37(d,4HH₀) 7.08-7.19(d,8H,H_M) 4.06(s,12H, H_OME) | 1.51(s,6H,H_Me) 3.76(s,H,H_CH) | 6.89(d, 4H, H₀,ₘ) 6.82(d,2H,Hₘ) 3.37(s,3H,H_OME) |

**Table 2 : Optical Absorption data of Zr(p-OCH$_3$TPP)(Y)(X), (Y = acac and X = different phenolates as an axial ligand in CHCl3 showing λmax together with log ε and ν$_{1/2}$.**

| Compounds | B-bands λmax(nm), (log ε) (M$^{-1}$ cm$^{-1}$) ν$_{1/2}$(cm$^{-1}$) | Q-bands λmax(nm), (log ε) (M$^{-1}$ cm$^{-1}$) ν$_{1/2}$(cm$^{-1}$) |
|---|---|---|
| Zr(p-OCH$_3$TPP)(acac)(Oph) [Zr(C$_{48}$H$_{36}$O$_4$N$_4$)(C$_5$H$_7$O$_2$)(C$_6$H$_5$O)] | 414.4, (5.098), 1320.5 | 501.3, (4.027) 537.3, (4.826) 581.6, (5.040), 1075.3 |
| Zr(p-OCH$_3$TPP)(acac)(p-OCH$_3$phO) [Zr(C$_{48}$H$_{36}$O$_4$N$_4$)(C$_5$H$_7$O$_2$)(C$_7$H$_7$O$_2$)] | 415.6, (5.129), 1349.2 | 502.4, (4.219) 538.8, (4.839) 583.3, (5.067), 1094.4 |
| Zr(p-OCH$_3$TPP)(acac)(o-OCH$_3$phO) [Zr(C$_{48}$H$_{36}$O$_4$N$_4$)(C$_5$H$_7$O$_2$)(C$_7$H$_7$O$_2$)] | 415.5, (5.121), 1350.4 | 502.2, (4.216) 538.5, (4.836) 583.1, (5.060), 1096.6 |
| Zr(p-OCH$_3$TPP)(acac)(m-OCH$_3$phO) [Zr(C$_{48}$H$_{36}$O$_4$N$_4$)(C$_5$H$_7$O$_2$)(C$_7$H$_7$O$_2$)] | 415.1, (5.116), 1336.6 | 501.9, (4.211) 538.1, (4.835) 582.6, (5.054), 1089.4 |
| Zr(p-OCH$_3$TPP)(acac)(p-CH$_3$phO) [Zr(C$_{48}$H$_{36}$O$_4$N$_4$)(C$_5$H$_7$O$_2$)(C$_7$H$_7$O)] | 415.9, (5.134), 1347.6 | 502.6, (4.223) 539.2, (4.844) 583.8, (5.069), 1091.9 |
| Zr(p-OCH$_3$TPP)(acac)(o-CH$_3$phO) [Zr(C$_{48}$H$_{36}$O$_4$N$_4$)(C$_5$H$_7$O$_2$)(C$_7$H$_7$O)] | 415.7, (5.127), 1349.8 | 502.7, (4.221) 538.8, (4.837) 583.7, (5.064), 1096.3 |
| Zr(p-OCH$_3$TPP)(acac)(p-NO$_2$phO) [Zr(C$_{48}$H$_{36}$O$_4$N$_4$)(C$_5$H$_7$O$_2$)(C$_6$H$_4$O$_3$N)] | 413.4, (5.080), 1285.2 | 500.2, (4.197) 536.2, (4.817) 580.7, (5.024), 1045.3 |
| Zr(p-OCH$_3$TPP)(acac)(o-NO$_2$phO) [Zr(C$_{48}$H$_{36}$O$_4$N$_4$)(C$_5$H$_7$O$_2$)(C$_6$H$_4$O$_3$N)] | 413.2, (5.077), 1282.8 | 500.1, (4.195) 536.1, (4.816) 580.5, (5.023), 1043.1 |
| Zr(p-OCH$_3$TPP)(acac)(m-NO$_2$phO) [Zr(C$_{48}$H$_{36}$O$_4$N$_4$)(C$_5$H$_7$O$_2$)(C$_6$H$_4$O$_3$N)] | 413.7, (5.085), 1291.4 | 500.6, (4.199) 536.8, (4.819) 580.9, (5.029), 1049.5 |
| Zr(p-OCH$_3$TPP)(acac)(p-ClphO) [Zr(C$_{48}$H$_{36}$O$_4$N$_4$)(C$_5$H$_7$O$_2$)(C$_6$H$_4$OCl)] | 414.6, (5.095), 1303.2 | 501.5, (4.205) 537.6, (4.825) 582.1, (5.037), 1060.3 |
| Zr(p-OCH$_3$TPP)(acac)(o-ClphO) [Zr(C$_{48}$H$_{36}$O$_4$N$_4$)(C$_5$H$_7$O$_2$)(C$_6$H$_4$OCl)] | 414.2, (5.093), 1299.8 | 501.1, (4.203) 537.2, (4.823) 581.9, (5.035), 1058.1 |
| Zr(p-OCH$_3$TPP)(acac)( p-NH$_2$phO) [Zr(C$_{48}$H$_{36}$O$_4$N$_4$)(C$_5$H$_7$O$_2$)(C$_6$H$_6$ON)] | 416.8, (5.149), 1368.9 | 503.4, (4.234) 540.5, (4.857) 584.9, (5.086), 1102.1 |
| Zr(p-OCH$_3$TPP)(acac)( o-NH$_2$phO) [Zr(C$_{48}$H$_{36}$O$_4$N$_4$)(C$_5$H$_7$O$_2$)(C$_6$H$_6$ON)] | 416.6, (5.143), 1364.5 | 503.1, (4.229) 539.9, (4.855) 584.5, (5.079), 1099.5 |
| Zr(p-OCH$_3$TPP)(acac)( m-NH$_2$phO) [Zr(C$_{48}$H$_{36}$O$_4$N$_4$)(C$_5$H$_7$O$_2$)(C$_6$H$_6$ON)] | 416.1, (5.139), 1361.7 | 502.7, (4.227) 539.6, (4.849) 584.3, (5.077), 1095.9 |
| Zr(p-OCH$_3$TPP)(acac)( 2,4-dichlorophO) [Zr(C$_{48}$H$_{36}$O$_4$N$_4$)(C$_5$H$_7$O$_2$)(C$_6$H$_3$OCl$_2$)] | 413.6, (5.088), 1268.7 | 499.8, (4.206) 535.8, (4.821) 580.3, (5.030), 1035.7 |
| Zr(p-OCH$_3$TPP)(acac)( a-naptholate) [Zr(C$_{48}$H$_{36}$O$_4$N$_4$)(C$_5$H$_7$O$_2$)(C$_{10}$H$_7$O)] | 414.1, (5.096), 1306.8 | 501.0, (4.204) 537.1, (4.822) 581.3, (5.038), 1061.2 |

protons of para amino phenolate resonate as duplet at 6.74 ppm and the meta-protons of para amino phenolate resonate as duplet at 6.58 ppm respectively which is upfield. Thus, for Zr(p-OCH$_3$TPP)(acac)(p-NO$_2$phO),the resonance of protons occur slightly downfield with respect to Zr(p-OCH$_3$TPP)(acac)(Oph) because of presence of "NO$_2$ at para-position of phenolate which are electron withdrawing groups and responsible for deshielding and for Zr(p-OCH$_3$TPP)(acac)(p-NH$_2$phO), the resonance of protons occur slightly upfield with respect to Zr(p-OCH$_3$TPP)(acac)(phO) because of presence of –NH$_2$ at para-position of phenolate which are electron releasing groups and are responsible for shielding.

**Absorption Spectroscopy**

The optical absorption spectrum is an important spectral phenomenon to distinguish between the free base porphyrins and their metalloderivatives based on profound theoretical analysis of the experimental and quantum-chemical data of the previously mentioned monograph[43]. According to this interpretation the absorption spectra of porphyrins do not exhibit bands of n→π* transitions because of the symmetry of the n orbitals and antisymmetry of the n orbitals with respect to the plane of the porphyrin molecule. All bands are of $\pi \rightarrow \pi*$ origin. The Soret band is due to an electronic $^1A_{1g} \rightarrow 1E2_u$ transition to the highest energy vacant π* orbital. In substituted porphyrins E2$_u$ is split into two states B2$_{2u}$ and B2$_{3u}$ which are close in energy, as a result of the reduced symmetry

of the π-electron cloud. The electronic transitions to state E2$_u$ (or B2$_{2u}$ and B2$_{3u}$) are allowed, therefore the intensity of the Soret band is always very high ($\varepsilon \approx 10^5$). Bands I and III of the visible region belong to quasi-forbidden electronic transitions. The reasons for transitions $^1A_{1g} \rightarrow B2_{3u}$ and $^1A_{1g} \rightarrow B2_{2u}$ being allowed, which is responsible for the appearance of band I and III. Bands II and IV are of vibrational origin, that is they are vibrational satellites of bands II and III, respectively. A factor that must be considered in the interpretation of the spectra in the visible and ultraviolet region is that the phenyl and substituted phenyl rings cannot be coplanar with the porphine nucleus. Examination of molecular models indicates that the four benzene rings have partial rotations that cannot bring them
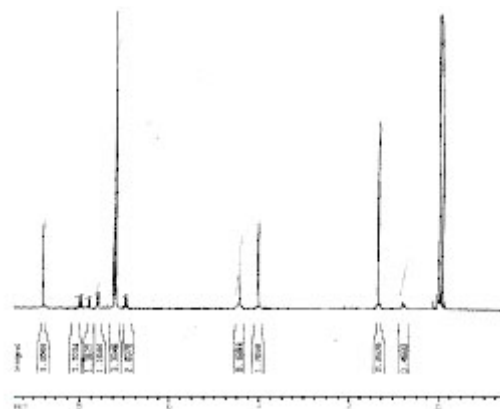


**Fig. 1 : $^1$H NMR spectra of Zr(p-OCH$_3$TPP)(acac)(Oph) in CDCl$_3$**
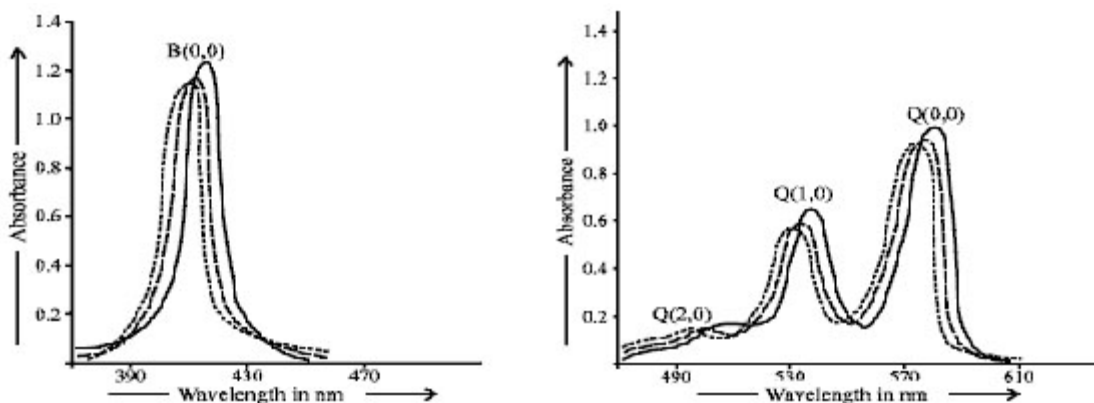


**Fig. 2 : Optical absorption spectra of Zr(p-OCH$_3$TPP)(acac)(Oph) in different solvents (——— CHCl$_3$, ————- Acetone, ———CH$_2$Cl$_2$).**

with in 60° of being coplanar with the resonating porphine system.Since the average angle of the attached rings is probably considerable greater than this. It is apparent that resonance interactions between two aromatic systems must be greatly reduced from what would be expected if they were coplanar. Hence, the bathochromic shifts and spectral intensifications observed are considerably less than what would be expected in simpler aromatic systems with greater freedom of rotation.

Generally, the absorption spectra of group IV B porphyrins are quite "normal" in that they exhibit the expected N, B and Q bands[44]. The N bands are less intense and appear at or below 350 nm. The optical absorption spectral data of Zr(IV) metal derivatives containing acetylacetonate (acac) and different phenolates as an axial ligand in chloroform is shown in the (Table 2). It is observed from the tables that the Zr(IV) metal derivatives of (p-$OCH_3$TPP) with phenolates as an axial ligand show hypso-chromic shift (blue-shift) and variation in intensities of absorption bands when compared to their respective free base porphyrins ($H_2$TPP), due to incorporation of the metal ion alongwith phenolate in the porphyrin rings. When a comparative study of optical absorption spectral data of Zr(p-$OCH_3$TPP)(Y)(X), (Y = acac and X = different phenolates as an axial ligand) in chloroform is done with respect to Zr($H_2$TPP)(Y)(X), a slight bathochromic shift (Red shift) i.e., to longer wavelength is observed because of the presence –$OCH_3$group at the para position of the meso-phenyl rings of porphyrin moiety. The optical absorption spectra of Zr(IV) metal derivatives of different porphyrins with different phenolates as an axial ligand show one soret band i.e. B(0, 0), two Q bands i.e., Q(0, 0), Q(1, 0) and one shoulder Q(2, 0). The order of absorbance of B and Q bands of axially ligated Zr(IV) metal derivatives of different porphyrins is B(0, 0) > Q(0, 0) > Q(1, 0) > Q(2, 0). When a comparative study is done among the axially ligated Zr(IV) porphyrins, with different phenolates attached to Zr(IV) metal atom , those having electron donating groups in phenolates have slightly red shifted B and Q bands while those having electron withdrawing groups in phenolates have blue shifted B and Q bands. When the optical absorption spectra of the compounds of Zr(p-$OCH_3$TPP)(Y)(Y) is recorded in different solvents (Table 3) and spectra

of Zr(p-$OCH_3$TPP)(acac)(Oph) is displayed in (Fig. 2), which shows only a marginal change in $\lambda_{max}$ values, absorption coefficient ($\varepsilon$) and oscillator strength ($f$) values is observed. The data also reveal that a change in polarity of the solvent result in slight change in the position of transitions but there is a significant increase in "Fwhm" ($v_{1/2}$) and '$f$' values of transitions by increasing the polarity of the solvent. The magnitude of change of the '$f$' value in axially ligated Zr(IV) metal derivatives of different porphyrins reveal the relative strength of $\pi \rightarrow \pi*$ interactions. It is found that with the increase in polarity of the solvents, B and Q-bands in axially ligated Zr(IV) metal derivatives with different porphyrins show a red shift with progressive broadening of bands indicating that the magnitude of red shift of B and Q bands depends on the nature of the solvent used.

**Infra Red Spectroscopy**

The IR spectra of free base porphyrins($H_2$TPP) and its axially ligated Zr(IV) metal derivatives containing -$OCH_3$ group have strong absorption bands of $v$(C-H), $v$(C-O-C)$_{sym}$ and $v$(C-O-C)$_{asym}$ at (2810 – 2955cm$^{-1}$), (1000 – 1050cm$^{-1}$) and (1200–1300cm$^{-1}$) In p-$OCH_3H_2$TPPP, $v$(N-H) vibrates at 3446.5cm$^{-1}$, aromatic $v$(C-H) at 2963.3cm$^{-1}$, $v$(C-H) at 1350.2 cm$^{-1}$, $v$(C=C) at 1567.8 cm$^{-1}$ and additional vibrations due to presence -$OCH_3$ group at p-position of meso-phenyl ring also occurs in which $v$(C-H) vibrates at 2906.8cm$^{-1}$, $v$(C-O-C)$_{sym}$ at 1019.4cm$^{-1}$ and í(C-O-C)$_{asym}$ at 1259.6cm$^{-1}$ respectively. The IR absorption spectra of p-$OCH_3$TPPand their corresponding axially ligated Zr(IV) acetylacetonate (acac) and different phenolates as an axial ligand is shown in the (Table. 4). The metallation of porphyrin is confirmed by the appearance of Zr–N band (45) in the range of 457–502cm$^{-1.}$ The incorporation of various phenolates in Zr(p-$OCH_3H_2$TPP)(Y)(X), (Y = acetylacetonate ($C_5H_7O_2$) and X = different phenolates as an axial ligand) is confirmed by the appearance of Zr–O vibrational frequencies in the range of 649–680cm$^{-1}$ and acetylacetonate(acac) is confirmed by the appearance of C=O vibrational frequencies in the range of 1617–1641cm$^{-1}$ and Zr–O in the range of 702–818.5cm$^{-1}$ respectively. In case of IR spectra Zr(p-$OCH_3H_2$TPP)(acac)(Oph) (Fig. 3), aromatic $v$(C-H) vibrates at 2952.5cm$^{-1}$,$v$(C-N) at 350.3cm$^{-1}$, $v$(C=C) at 1589.3cm$^{-1}$, $v$(Zr-N) at

**Table 3 : Optical Absorption data of Zr(p-OCH$_3$TPP) (Y)(X), (Y = acac and X = different phenolates as an axial ligand) in different solvents.**

| Compounds | Solvent | λmax(nm), (log ε) (M$^{-1}$cm$^{-1}$) | | | | ν$_{1/2}$(cm$^{-1}$) | | Q(0, 0)f |
|---|---|---|---|---|---|---|---|---|
| | | B(0,0) | Q(2,0) | Q(1,0) | Q(0,0) | B(0,0) | Q(0,0) | |
| Zr(p-OCH$_3$TPP)(acac)(Oph) | CHCl$_3$ | 414.4 | 501.8 | 537.3 | 581.6 | 1320.5 | 1075.3 | 0.255263 |
| [Zr(C48H36O4N4)(C5H7O2)(C6H5O)] | | 5.098 | 4.206 | 4.826 | 5.040 | | | |
| | CH$_2$Cl$_2$ | 409.7 | 496.4 | 531.7 | 575.9 | 1262.6 | 1038.6 | 0.217724 |
| | | 5.066 | 4.177 | 4.773 | 4.986 | | | |
| | Acetone | 411.8 | 500.2 | 535.5 | 578.8 | 1296.3 | 1057.3 | 0.225246 |
| | | 5.077 | 4.200 | 4.786 | 4.993 | | | |
| Zr(p-OCH$_3$TPP)(acac)(o-NH2phO) | CHCl$_3$ | 416.6 | 503.1 | 539.9 | 584.5 | 1364.5 | 1099.5 | 0.285531 |
| [Zr(C48H36O4N4)(C5H7O2)(C6H6ON)] | | 5.143 | 4.228 | 4.855 | 5.079 | | | |
| | CH$_2$Cl$_2$ | 414.2 | 500.3 | 536.4 | 580.7 | 1319.5 | 1060.3 | 0.239821 |
| | | 5.102 | 4.190 | 4.803 | 5.019 | | | |
| | Acetone | 415.4 | 501.5 | 537.9 | 582.4 | 1344.8 | 1081.6 | 0.249761 |
| | | 5.114 | 4.209 | 4.820 | 5.028 | | | |
| Zr(p-OCH$_3$TPP)(acac)(m-NO2phO) | CHCl$_3$ | 413.2 | 500.1 | 536.1 | 580.5 | 1291.4 | 1049.5 | 0.242907 |
| [Zr(C48H36O4N4)(C5H7O2)(C6H4O3N)] | | 5.085 | 4.199 | 4.819 | 5.029 | | | |
| | CH$_2$Cl$_2$ | 408.1 | 494.9 | 531.2 | 574.8 | 1232.1 | 1007.2 | 0.200250 |
| | | 5.039 | 4.162 | 4.765 | 4.963 | | | |
| | Acetone | 409.8 | 498.2 | 533.4 | 577.6 | 1270.3 | 1030.4 | 0.215508 |
| | | 5.056 | 4.181 | 4.780 | 4.985 | | | |

**Fig. 3: IR Spectra of Zr(p-OCH₃TPP)(acac)(Oph)**
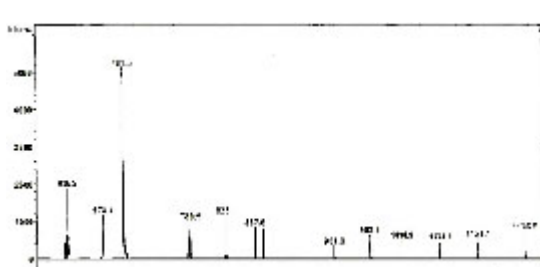


**Fig. 4(a): Mass Spectra of Zr(p-OCH₃TPP)(acac)(p-NH₂phO)**
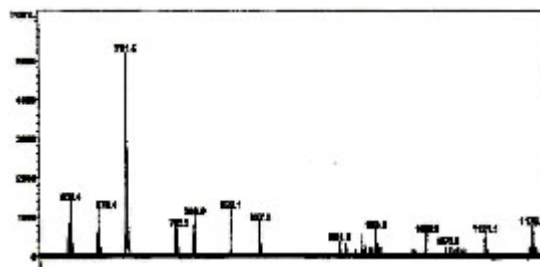


**Fig. 4(b): Mass Spectra of Zr(p-OCH₃TPP)(acac)(p-ClphO)**

495.1cm$^{-1}$, $\nu$(Zr-O) of phenolate at 664.2cm$^{-1}$,í(Zr-O) of acac at 702.0cm$^{-1}$ and 802.4 cm$^{-1}$,$\nu$(C=O) of acac at 1630.5cm$^{-1}$ and methoxy group vibration appear for $\nu$(C-H), at 2825.1cm$^{-1}$ for $\nu$(C-H), at 2825.1cm$^{-1}$,$\nu$(C-O-C)$_{sym}$ at 1023.1cm$^{-1}$ and $\nu$(C-O-C)$_{asym}$ at 1261.5cm$^{-1}$.

**Elemental Analysis**

The purity of Zr(IV) metal derivative of p-methoxy-meso-tetraphenylporphyrin containing different phenolates as axial ligand  are also

characterized by their elemental anylasis and data is accumulated in (Table 5).

**Mass Spectroscopy**

Mass spectroscopy is the most accurate method employed for determining the molecular mass of the axially ligated Zr(IV) metal derivative containing acetylacetonate and different phenolates as an axial ligand and their data is accumulated in (Table 6) and spectra of some representative compound are displayed in the (Fig. 4(a) and 4(b)).

**Table 4: Main Vibrational frequencies corresponding to the various groups in Zr(p-OCH₃TPP)(Y)(X), (Y = acac and X = different phenolates as an axial ligand).**

| Porphyrin | ν(N-H) (cm⁻¹) | ν(C-H) (cm⁻¹) | ν(C-N) (cm⁻¹) | ν(C=C) (cm⁻¹) | ν(Zr-N) (cm⁻¹) | ν(Zr-O) of phenolate (cm⁻¹) | ν(Zr-O) of acac (cm⁻¹) | ν(CH₃) (cm⁻¹) | ν(OCH₃) (cm⁻¹) | ν(NH₂) (cm⁻¹) | ν(NO₂) (cm⁻¹) | ν(C-Cl) (cm⁻¹) | ν(C=O) of acac (cm⁻¹) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $p$-OCH₃H₂TPP [C₄₈H₃₈O₄N₄] | 3446.5 | 2963.3 | 1350.2 | 1567.8 | - | - | - | - | ν(C–H)=2906.8<br>ν(C-O-C)$_{sym}$=1019.4<br>ν(C-O-C)$_{asym}$=1259.6 | - | - | - | - |
| Zr(p-OCH₃TPP)(acac)(Oph) [Zr(C₄₈H₃₆O₄N₄)(C₅H₇O₂)(C₆H₅O)] | - | 2952.5 | 1350.3 | 1589.3 | 495.1 | 664.2 | 702.0<br>802.4 | - | ν(C–H)=2825.7<br>ν(C-O-C)$_{sym}$=1023.1<br>ν(C-O-C)$_{asym}$=1261.5 | - | - | - | 1630.5 |
| Zr(p-OCH₃TPP)(acac)(p-OCH₃phO) [Zr(C₄₈H₃₆O₄N₄)(C₅H₇O₂)(C₇H₇O₂)] | - | 2949.1 | 1349.8 | 1579.3 | 462.2 | 651.4 | 702.5<br>802.6 | - | ν(C–H)=2842.3<br>ν(C-O-C)$_{sym}$=1022.6<br>ν(C-O-C)$_{asym}$=1260.9 | - | - | - | 1630.9 |
| Zr(p-OCH₃TPP)(acac)(a-naptholate) [Zr(C₄₈H₃₆O₄N₄)(C₅H₇O₂)(C₁₀H₇O)] | - | 2949.3 | 1350.0 | 1587.4 | 471.6 | 665.1 | 702.3<br>802.7 | - | ν(C–H)=2824.2<br>ν(C-O-C)$_{sym}$=1023.0<br>ν(C-O-C)$_{asym}$=1261.4 | - | - | - | 1630.7 |
| Zr(p-OCH₃TPP)(acac)(p-ClphO) [Zr(C₄₈H₃₆O₄N₄)(C₅H₇O₂)(C₆H₄OCl)] | - | 2958.3 | 1350.7 | 1590.4 | 470.6 | 663.2 | 703.2<br>802.9 | - | ν(C–H)=2953.6<br>ν(C-O-C)$_{sym}$=1023.4<br>ν(C-O-C)$_{asym}$=1261.8 | - | - | 780.9 | 1633.1 |
| Zr(p-OCH₃TPP)(acac)(p-CH₃phO) [Zr(C₄₈H₃₆O₄N₄)(C₅H₇O₂)(C₇H₇O)] | - | 2942.8 | 1348.4 | 1573.2 | 466.3 | 649.1 | 702.3<br>802.5 | 2890.2 | ν(C–H)=2841.2<br>ν(C-O-C)$_{sym}$=1021.8<br>ν(C-O-C)$_{asym}$=1260.3 | - | - | - | 1629.8 |
| Zr(p-OCH₃TPP)(acac)(2,4-dichlorophO) [Zr(C₄₈H₃₆O₄N₄)(C₅H₇O₂)(C₆H₃OCl₂)] | - | 2961.6 | 1351.9 | 1590.9 | 476.3 | 665.9 | 703.9<br>804.1 | - | n(C–H)=2954.2<br>ν(C-O-C)$_{sym}$=1023.6<br>ν(C-O-C)$_{asym}$=1262.1 | - | - | 785.1 | 1635.4 |
| Zr(p-OCH₃TPP)(acac)(p-NH₂phO) [Zr(C₄₈H₃₆O₄N₄)(C₅H₇O₂)(C₆H-ON)] | - | 2963.7 | 1350.4 | 1592.2 | 457.4 | 654.1 | 702.9<br>802.8 | - | ν(C–H)=2849.4<br>ν(C-O-C)$_{sym}$=1023.0<br>ν(C-O-C)$_{asym}$=1261.5 | n(NH₂)$_{sym}$ = 3289.3<br>n(NH₂)$_{asym}$ = 3367.1 | - | - | 1631.6 |
| Zr(p-OCH₃TPP)(acac)(p-NO₂phO) [Zr(C₄₈H₃₆O₄N₄)(C₅H₇O₂)(C₆H₄O₃N)] | - | 2960.4 | 1351.5 | 1590.8 | 479.4 | 665.6 | 704.3<br>804.5 | - | ν(C–H)=2955.3<br>ν(C-O-C)$_{sym}$=1023.8<br>ν(C-O-C)$_{asym}$=1262.7 | - | n(NO₂)$_{sym}$ = 1341.3<br>n(NO₂)$_{asym}$ = 1540.9 | - | 1635.2 |

**Table 5 : Elemental Analytical data of Zr(p-OCH$_3$TPP)(acac)(Y)(X) (Y = acac and X = different phenolates as an axial ligand) along with their calculated values.**

| Compounds | Calculated Percentage | | | Found Percentage | | |
|---|---|---|---|---|---|---|
| | C | H | N | C | H | N |
| Zr(p-OCH$_3$TPP)(acac)(Oph) [Zr(C$_{48}$H$_{36}$O$_4$N$_4$)(C$_5$H$_7$O$_2$)(C$_6$H$_5$O)] | 69.72 | 4.76 | 5.51 | 69.59 | 4.74 | 5.46 |
| Zr(p-OCH$_3$TPP)(acac)( p-NH$_2$phO) [Zr(C$_{48}$H$_{36}$O$_4$N$_4$)(C$_5$H$_7$O$_2$)(C$_6$H$_6$ON)] | 64.05 | 4.79 | 6.79 | 63.94 | 4.76 | 6.72 |
| Zr(p-OCH$_3$TPP)(acac)(o-ClphO) [Zr(C$_{48}$H$_{36}$O$_4$N$_4$)(C$_5$H$_7$O$_2$)(C$_6$H$_4$OCl)] | 62.87 | 4.51 | 5.33 | 62.78 | 4.52 | 5.29 |
| Zr(p-OCH$_3$TPP)(acac)(p-OCH$_3$phO) [Zr(C$_{48}$H$_{36}$O$_4$N$_4$)(C$_5$H$_7$O$_2$)(C$_7$H$_7$O$_2$)] | 68.88 | 4.82 | 5.36 | 68.73 | 4.80 | 5.31 |
| Zr(p-OCH$_3$TPP)(acac)(a-naptholate) [Zr(C$_{48}$H$_{36}$O$_4$N$_4$)(C$_5$H$_7$O$_2$)(C$_{10}$H$_7$O)] | 70.96 | 4.73 | 5.25 | 70.84 | 4.67 | 5.21 |
| Zr(p-OCH$_3$TPP)(acac)(p-NO$_2$phO) [Zr(C$_{48}$H$_{36}$O$_4$N$_4$)(C$_5$H$_7$O$_2$)(C$_6$H$_4$O$_3$N)] | 66.77 | 4.46 | 6.60 | 66.64 | 4.45 | 6.55 |
| Zr(p-OCH$_3$TPP)(acac)(2,4-dichlorophO) [Zr(C$_{48}$H$_{36}$O$_4$N$_4$)(C$_5$H$_7$O$_2$)(C$_6$H$_3$OCl$_2$)] | 65.30 | 4.27 | 5.16 | 65.19 | 4.19 | 5.12 |
| Zr(p-OCH$_3$TPP)(acac)(p-CH$_3$phO) [Zr(C$_{48}$H$_{36}$O$_4$N$_4$)(C$_5$H$_7$O$_2$)(C$_7$H$_7$O)] | 69.95 | 4.89 | 5.44 | 69.72 | 4.63 | 5.38 |

**Table 6 : Mass Data for Zr(p-OCH$_3$TPP)(Y)(X), (Y = acac and X = different phenolates] as an axial ligand).**

| Compounds | m/z ratio | |
|---|---|---|
| | Observed | Calculated |
| Zr(p-OCH$_3$TPP)(acac)(Oph) [Zr(C$_{48}$H$_{36}$O$_4$N$_4$)(C$_5$H$_7$O$_2$)(C$_6$H$_5$O)] | 1015.7 | 1016.28 |
| Zr(p-OCH$_3$TPP)(acac)(p-NH$_2$phO) [Zr(C$_{48}$H$_{36}$O$_4$N$_4$)(C$_5$H$_7$O$_2$)(C$_6$H$_6$ON)] | 1030.9 | 1031.29 |
| Zr(p-OCH$_3$TPP)(acac)(p-ClphO) [Zr(C$_{48}$H$_{36}$O$_4$N$_4$)(C$_5$H$_7$O$_2$)(C$_6$H$_4$OCl)] | 1051.2 | 1050.72 |
| Zr(p-OCH$_3$TPP)(acac)(p-OCH$_3$phO) [Zr(C$_{48}$H$_{36}$O$_4$N$_4$)(C$_5$H$_7$O$_2$)(C$_7$H$_7$O$_2$)] | 1046.5 | 1046.30 |
| Zr(p-OCH$_3$TPP)(acac)(a-naptholate) [Zr(C$_{48}$H$_{36}$O$_4$N$_4$)(C$_5$H$_7$O$_2$)(C$_{10}$H$_7$O)] | 1065.4 | 1066.34 |
| Zr(p-OCH$_3$TPP)(acac)(p-NO$_2$phO) [Zr(C$_{48}$H$_{36}$O$_4$N$_4$)(C$_5$H$_7$O$_2$)(C$_6$H$_4$O$_3$N)] | 1060.6 | 1061.27 |
| Zr(p-OCH$_3$TPP)(acac)(2,4-dichlorophO) [Zr(C$_{48}$H$_{36}$O$_4$N$_4$)(C$_5$H$_7$O$_2$)(C$_6$H$_3$OCl$_2$)] | 1085.8 | 1085.17 |
| Zr(p-OCH$_3$TPP)(acac)(p-CH$_3$phO) [Zr(C$_{48}$H$_{36}$O$_4$N$_4$)(C$_5$H$_7$O$_2$)(C$_7$H$_7$O)] | 1029.2 | 1030.31 |

## CONCLUSION

On the basis of above studies,it is found that the environment around Zr(IV) metal in their axially ligated porphyrins could be depicted as shown in the scheme.2.
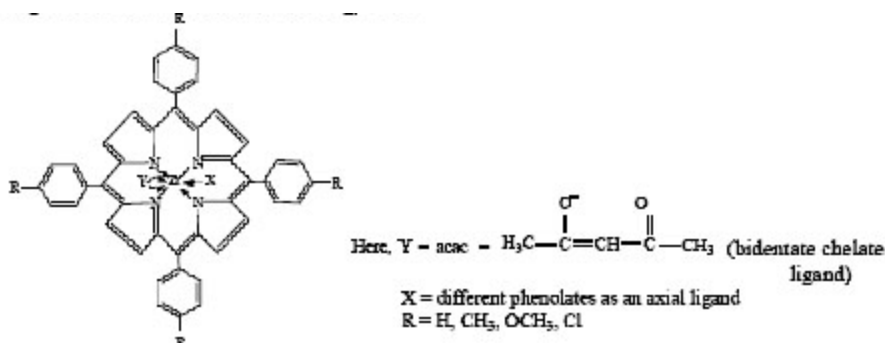


**Scheme 2: Axially Ligated Zr(IV) Porphyrins**

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