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Synthesis and Characterization of Zirconium (IV) Derivatives of Meso-tetra(p-methylphenyl)porphyrin with Acetylacetonate and Different Phenolates at Axial Positions

GAURI D. BAJJU*, SUNIL KUMAR ANAND,
SUJATA KUNDAN, DEEPMALA, ASHU and GITA

Department of Chemistry, University of Jammu, New Campus,
Baba Sahib Ambedkar Road, Jammu-180 006, Jammu & Kashmir, India.
*Email:-gauribajju@gmail.

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ABSTRACT

In continuation with the previous research work carried out with axially ligated Zirconium(IV)p-methoxy-meso-tetraphenylporphyrin[Zr(p-OCH_3TPP)(Y)(X) [Y = acac and X = different phenolates] here we have undertaken to synthesize meso-tetra(p-methylphenyl) porphinatozirconium (IV) acetylacetonatophenolates containing different phenols as axial ligands i. e. [Zr(p-CH_3TPP)(Y)(X)] [Y=acac and X=different phenolates] by the reaction of meso-tetra(p-methylphenyl)porphyrin (p-CH_3H_2TPP) with Zirconium(IV)acetylacetonate ($Zr(acac)_4$) and different phenols at 200-220°C. The separation and isolation of these compounds were achieved through chromatographic methods and their characterization were done by Electronic absorption spectra, IR spectra, ^{1}H NMR, elemental analysis and mass spectroscopy. The incorporation of metal ion in the porphyrin ring was confirmed by IR spectra by appearance of Zr-N band at 457-502cm^{-1}, Zr-O band at 649-680cm^{-1} and also the incorporation of (acac)($C_5H_7O_2$) in which Zr-O band appeared at 702-818cm^{-1}.The absorption spectra of these compounds showed one soret band i.e., B(0,0), two normal Q bands i.e., Q(0,0), Q(1,0) and one shoulder Q(2,0). The ^{1}H NMR spectra showed upfield (shielded) as compared to meso-tetra(p-methylphenyl)porphyrin (p-CH_3H_2TPP). The Mass spectra determined m/z ratio's which agreed well with calculated m/z values and percentage of various elements in these compounds were confirmed by elemental analysis.

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

INTRODUCTION

Porphyrins and metalloporphyrins are unique class of compounds which have received considerable attention from many investigators in various fields in order 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. 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[1-5]. Synthesis and functionalization of porphyrins and metalloporphyrins of Group IV B elements like Ti, Zr, Hf have received much attention, mainly due to the use of these compounds in catalysis, photodynamic therapy of cancer cell[6], as materials with novel electrical properties[7] and as biomimetic model systems of primary processes of natural photosynthesis[8]. Cationic water soluble porphyrins and their metal complexes have been a subject of interest due to their strong affinities for DNA and potential nuclease activity[9]. The Group IV B transition metals such as Ti, Zr & Hf show +4 oxidation state on metallation with porphyrins and have d^0 configuration. These metals undergo metallation with the parent porphines such as OEP $[(OEP)H_2]$ or a, b, g, d-tetraphenylporphine $[(TPP)H_2]$ and result in the formation of metal porphines such as (OEP)TiO, $(OEP)Zr(OAc)_2$, $(OEP)Hf(OAc)_2$, Zr(TPP) and Zr(OEP). (OEP)TiO was analogous in structure to the vanadyl porphyrins[10], whereas the metals in $(OEP)Zr(OAc)_2$ and $(OEP)Hf(OAc)_2$ were eight coordinate with both acetates bidentate on the same side of the porphyrin ring[11]. These porphyrins exhibit moderate fluorescence and phosphorescence.

The Chemistry of early transition metal porphyrin complexes, especially, that of the second- and third-row metal complexes has been developed much due in part to their high oxophilicity[12]. The zirconium and hafnium porphyrin complexes showed a rich organometallic chemistry as zirconocene derivatives did[13]. The key entry to the organometallic zirconium porphyrin complexes would be $Zr\text{-}(Porphyrin)Cl_2$, analogous to $ZrCp_2Cl_2$. Recently, Inoue reported that $(TPP)ZrX_2$ complexes ($X^- = RCO_2^-$, Cl^-)[2] catalyze the carboalumination of terminal alkynes[14]. Arnold and coworkers published[15] the synthesis and characterization of $Zr(OEP)Cl_2$ and several organometallic complexes derived from it, including $Zr(OEP)(CH_2SiMe_3)_2$[15a] and $Zr(OEP)(h^5\text{-}C_2B_9H_{11})$[15b] The dichloride complex may be converted to organometallic s-complexes such as dialkyl complexes by the reactions with alkyllithium or Grignard reagents. It may also form organometallic p-complexes by replacing the two chlorides with a cyclooctatetraenyl dianion or a dicarbollide dianion. Arnold has also prepared an extensive series of out of plane cis $(OEP)ZrR_2$ dialkyls and investigated their reactivity.[16-20] These complexes undergo rapid Zr-C protonolysis, yielding new $(OEP)ZrX_2$ ($X^- = TfO^-$, $R'CO_2^-$, 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. Brand and Arnold[15a] recently reported the synthesis of the OEP complex using $ZrCl_4(THT)_2$ (THT = tetrahydrothiophene).For zirconium, few derivatives were also known apart from oxoligated derivatives originally developed by Buchler and co-workers[21-22]. The vast majority of known metalloporphyrin chemistry is based on derivatives involving late transition metals, where an in-plane geometry directs ligands to mutually trans positions[23]. Due to the lack of readily accessible cis coordination sites, mechanisms involving free radicals dominate reactivities of the latter group of compounds[24].

In the present work, Mesotetra(p-methylphenyl) porphinatozirconium (IV) acetylacetonatophenolate containing different phenolates as axial ligand $[Zr(p\text{-}CH_3TPP)(Y)(X)]$ [Y=acac and X=different phenolates] were synthesised and characterized by means of various spectroscopic techniques. Studies revealed that in these complexes, Zr(IV) metal ion has been bonded to acetylacetonate and different phenolates at their axial position.

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[25]

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

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 ^1H 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 ^1H NMR studies. The ä 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[26-29] 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 meso-tetra(p-methylphenyl)porphyrin 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 1000°C 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. p-tolualdehyde (p-methybenzaldehyde) was procured from Aldrich, USA and used without further purification and Propionic acid used in the synthesis of meso-tetra(p-methylphenyl)porphyrin (p-CH_3H_2TPP) 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 was used as such. Zirconium(IV) acetylacetonate was purchased from Aldrich, USA and used without further purification. Anhydrous sodium sulphate (Na_2SO_4), 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 without 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.

Meso-tetra(p-methylphenyl)porphyrin (p-CH_3H_2TPP)

The synthesis of meso-tetra(p-methylphenyl)porphyrin was prepared by refluxing equimolar concentration (0.1 mole) of freshly distilled pyrrole and p-tolualdehyde in 500 ml of propionic acid for 12 hours. After refluxing, the reaction mixture was then vacuum filtered, washed with cold water, dried in a vacuum oven at 80^0C for 48 hours and was chromatographed through a column of basic alumina using chloroform as eluent.

UV-Vis ($CHCl_3$) : λ_{max}(nm) : 419.6, 517, 552.4, 592, 649.4.

^{1}HNMR ($CDCL_3$) (δ,ppm): -2.77(s,2H,NH), 8.73(s,8H,β-pyrrole), 7.85(d,8H,H_o), 7.42(d,8H,H_m), 2.64(s,12H,H_{me}).

Anal.Calcd. for $C_{48}H_{38}N_4$: Calcd. (Found): C, 85.94 (85.68); H, 5.71 (5.62); N, 8.35 (8.28).

Mesotetra(p-methylphenyl) porphinato-zirconium(IV) acetyl-acetonato-phenolate [Zr(p-CH_3TPP)(acac)(Y)(X)]

The general scheme for the synthesis of axially ligated Zr(IV) metal derivatives of meso-tetra(p-methylphenyl)porphyrin (p-CH_3H_2TPP) containing acetylacetonate and different phenolates as axial ligand is shown in Scheme I. $Zr(acac)_4$ (1.87 x 10^{-3} moles), meso-tetra(p-methylphenyl)porphyrin (3.74 x 10^{-4} moles) and respective phenol (1.06 x 10^{-2} moles) were taken in a boiling tube covered with a funnel in a salt bath having temperature between 200-220 °C, kept over magnetic stirrer for constant stirring. The reaction mixture was refluxed for about 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, recrystallized and characterized by UV-vis and ^{1}HNMR spectra

RESULTS AND DISCUSSION

^{1}HNMR Spectroscopy

^{1}H NMR spectra was widely used as an analytical tool for establishing the structural integrity of the compounds synthesized. The ^{1}H NMR spectra of the meso-tetra(p-methylphenyl)porphyrin and their Zr(IV) derivatives containing different phenolates as an axial ligand were highly characteristic and establish the structural integrity of these compounds in solution and it is listed in Table 1. The ^{1}H NMR spectra of free-base porphyrins gave three characteristic proton resonances (a) β-pyrrole protons (b) imino protons and (c) meso-aryl protons. The presence of subtituent in â-positions and peripheral phenyl groups altered these proton resonances. The integrated intensity of the resonances agreed well with the number of protons. The presence of electron-donating methyl group at the para-position of the meso-phenyl ring caused a slight shielding effect of the â-pyrrole protons resulting in a slight upfield shift of meso-substituted porphyrins relative to simple meso-tetraphenylporphyrin(H_2TPP). This shielding/ deshielding was most likely a consequence of meso "C"C" dihedral angle much greater than 0°, thereby placing the b-pyrrole protons in a more shielded/ deshielded environment produced by the anisotropic effect of substituent ring current. The inner imino protons of the H_2TPP resonated at -2.79 ppm, while those of p-CH_3H_2TPP appear at -2.77 ppm. The meso-aryl protons of H_2TPP resonated as a singlet at 8.19 ppm of ortho and 7.59 ppm of meta and para protons respectively and were shifted marginally depending upon the nature of the substituents attached as in case of p-CH_3H_2TPP which has electron-donating methyl groups, the resonance occurred at 7.85 ppm of ortho and 7.42 ppm of meta protons i.e, resonance was shifted upfield relative to H_2TPP and meso-methyl protons in p-CH_3H_2TPP resonated as a singlet at 2.64 ppm respectively. Generally, the presence of axially ligated Zr(IV) metal in the porphyrin ring shifted 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 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. The ^{1}H NMR spectra of Zr(p-CH_3TPP)(acac)(p-CH_3PhO) shown in Figure 1 which indicated that the b"pyrrole protons resonated as singlet at 8.80 ppm, the meso-aryl ortho protons resonated as duplet at 8.11 ppm and 7.99 ppm, the meso-aryl meta protons resonated as duplet at 7.56 ppm, the meso-methyl protons resonated as singlet at 2.57 ppm, acac protons resonated as two singlets at 1.51 ppm and 4.15 ppm, the methyl protons of para-methyl phenolate resonated as singlet at 3.42 ppm, the ortho and meta protons para-methyl phenolate resonate as duplet at 7.26 ppm respectively which is upfield as compare to Zr(p-CH_3TPP)(acac)(OPh).The ^{1}H NMR data of various axially ligated Zr(IV) compounds of p-CH_3H_2TPP revealed that the presence of electron withdrawing groups like -NO_2, -Cl at para position of phenolate caused slight downfield shift (deshielding) and the presence of electron releasing group like -CH_3, -NH_2 at para position of phenolate caused upfield shift (shielding) of protons with respect to Zr(p-CH_3TPP)(acac)(Oph) which have simple phenolate as an axial ligand.

Absorption Spectroscopy

The electronic absorption spectra of porphyrins is one of the most important fascinating and characteristics feature which reliably characterizes the structure of porphyrins, metalloporphyrins and adequately represent the state of their intramolecular energies. The optical absorption spectra is an important spectral phenomenon to distinguish between the free base porphyrins and their metalloderivatives. Metalloporphyrins have more symmetrical macrocycles than free-base porphyrins, so that their Q band spectra generally consist of only two bands. This dramatic effect is due to enhancement of the D_{2h} symmetry of the free base porphyrins to D_{4h} on metallation. In the free-base porphyrins, the Q_x(0, 0) and Q_y(0, 0) bands are no longer degenerate because of presence of two imino protons that lower

Table 1. ^{1}H NMR data of free-base porphyrin (p-CH_3H_2TPP) and Zr(p-CH_3H_2TPP)(Y)(X) (Y = acac and X = different phenolates as an axial ligand) in $CDCl_3$ at 298 K.

Porphyrins	β-Pyrrole Protons	Imino Protons	Meso-aryl Protons	Other Protons	
				Acac Protons	Phenolate Protons
p-CH_3H_2TPP ($C_{48}H_{38}N_4$)	8.73(s)	-2.77(s)	7.85(d,8H,H_o) 7.42(d,8H,H_m) 2.64(s,12H,H_{Me})	-	-
Zr(p-CH_3TPP)(acac)(Oph) [Zr($C_{48}H_{36}N_4$)($C_5H_7O_2$)(C_6H_5O)]	8.88(s)	-	8.07(d,4H,H_o) 7.81(d,4H,H_o) 7.58(d,8H,H_m) 2.81(s,12H,H_{Me})	1.72(s,6H,H_{Me}) 4.49(s,H,H_{CH})	6.99(d,2H,H_o) 7.08-7.23(m,3H,$H_{m,p}$)
Zr(p-CH_3TPP)(acac)(p-ClphO) [Zr($C_{48}H_{36}N_4$)($C_5H_7O_2$)(C_6H_4OCl)]	9.16(s)	-	8.31(d,4H,H_o) 8.08(d,4H,H_o) 7.79(d,8H,H_m) 2.93(s,12H,H_{Me})	1.75(s,6H,H_{Me}) 4.48(s,H,H_{CH})	7.09(d,2H,H_o) 7.27(d,2H,H_m)
Zr(p-CH_3TPP)(acac)(p-NO_2phO) [Zr($C_{48}H_{36}N_4$)($C_5H_7O_2$)($C_6H_4O_3N$)]	9.21(s)	-	8.38(d,4H,H_o) 8.08(d,4H,H_o) 2.97(s,12H,H_{Me})	1.78(s,6H,H_{Me}) 4.55(s,H,H_{CH})	7.16(d,2H,H_o) 7.36(d,2H,H_m) 7.85(d,8H,H_m)
Zr(p-CH_3TPP)(acac)(2,4-dichlorophO) [Zr($C_{48}H_{36}N_4$)($C_5H_7O_2$)($C_6H_3OCl_2$)]	9.18(s)	-	8.34(d,4H,H_o) 8.04(d,4H,H_o) 7.81(d,8H,H_m) 2.95(s,12H,H_{Me})	1.76(s,6H,H_{Me}) 4.51(s,H,H_{CH})	7.14(d, H, H_o) 7.31(d,2H,H_m)
Zr(p-CH_3TPP)(acac)(p-CH_3phO) [Zr($C_{48}H_{36}N_4$)($C_5H_7O_2$)(C_7H_7O)]	8.80(s)	-	8.11(d,4H,H_o) 7.99(d,4H,H_o) 7.56 (d,8H,H_m) 2.57(s,12H,H_{Me})	1.51(s,6H,H_{Me}) 4.15(s,H,H_{CH})	7.26(d,4H,$H_{o,m}$) 3.42(s,3H,H_{Me})

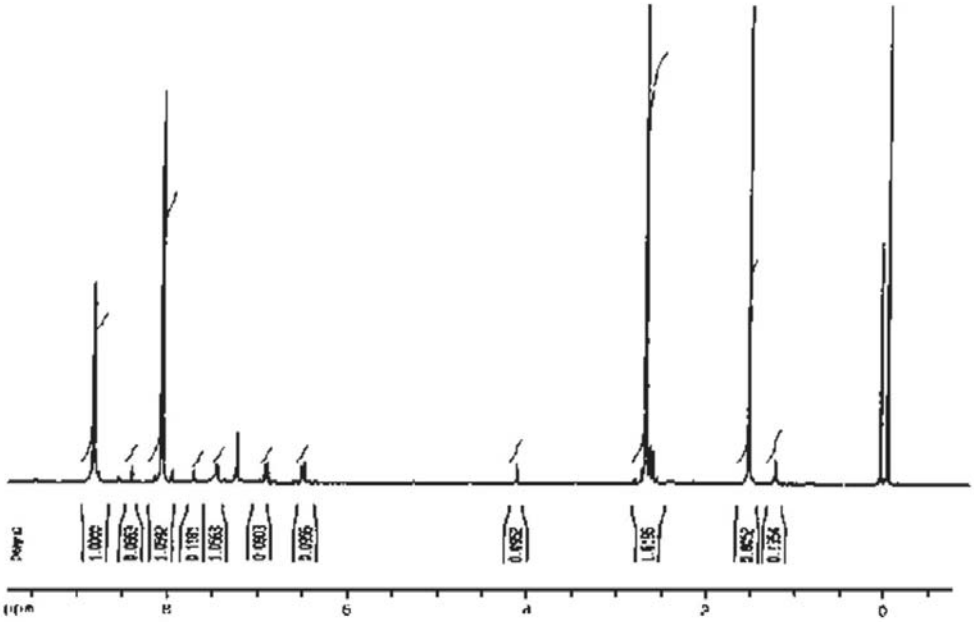


Fig 1. ^{1}H NMR spectra of Zr(p-CH$_3$TPP)(acac)(p-CH$_3$phO) in CDCl$_3$

the symmetry. Gouterman[30] has introduced a broad classification of metalloporphyrins as either regular or irregular and in terms of their absorption, into three main classes i.e., normal, hypso and hyper type. Generally, the absorption spectra of group IV B porphyrins are quite "normal" in that they exhibit the expected N, B and Q bands[31]. The N bands are less intense and appear at or below 350 nm. The optical absorption spectral data of Zr(IV) metal derivatives of meso-tetra(p-methylphenyl)porphyrin (p-CH$_3$H$_2$TPP) containing acetylacetonate (acac) and different phenolates as an axial ligand in chloroform is listed in Table 2.

Data revealed that the axially ligated Zr(IV) metal derivatives of porphyrin with different 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, 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-CH$_3$TPP)(Y)(X), (Y = acac and X = different phenolates as an axial ligand) in chloroform was done with respect to Zr(TPP)(Y)(X), a slight bathochromic shift (Red shift) i.e., to longer wavelength is observed because of the presence of -CH$_3$ at the para position of the meso-phenyl rings of porphyrin moiety. The optical absorption spectra of some representative compounds of Zr(p-CH$_3$TPP)(Y)(X), in chloroform is displayed in Figure 2 and 3 respectively.

The optical absorption spectra of Zr(IV) metal derivatives of meso-tetra(p-methylphenyl)porphyrin (p-CH$_3$H$_2$TPP) with different phenolates as an axial ligand showed 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 porphyrin was B(0, 0) > Q(0, 0) > Q(1, 0) > Q(2, 0). When a comparative study was 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-CH$_3$TPP)(Y)(X), (Y = acac and X = Phenolates as an axial ligand) were recorded in different solvents as listed in Table 3 , only a marginal change in λ_{max} values, absorption

Table 2: Optical Absorption data of Zr(p-CH_3TPP)(Y)(X), (Y = acac and X = different phenolates as an axial ligand, p-CH_3TPP = dianion of meso-tetra(p-methylphenyl)porphyrin) in $CHCl_3$ showing λ_{max} together with log ε and $\nu_{1/2}$.

Compounds	B-bands λ_{max}(nm), log ε) (M^{-1} cm^{-1}) $\nu_{1/2}$(cm^{-1})	Q-bands λ_{max}(nm), log ε) (M^{-1} cm^{-1}) $\nu_{1/2}$(cm^{-1})
Zr(p-CH_3TPP)(acac)(Oph) [$Zr(C_{48}H_{36}N_4)(C_5H_7O_2)(C_6H_5O)$]	413.1, (5.074), 1309.3	500.5, (4.183) 535.7, (4.796) 579.9, (5.009), 1067.2
Zr(p-CH_3TPP)(acac)(p-OCH_3phO) [$Zr(C_{48}H_{36}N_4)(C_5H_7O_2)(C_7H_7O_2)$]	414.2, (5.101), 1340.2	501.5, (4.197) 536.8, (4.812) 580.9, (5.031), 1085.9
Zr(p-CH_3TPP)(acac)(o-OCH_3phO) [$Zr(C_{48}H_{36}N_4)(C_5H_7O_2)(C_7H_7O_2)$]	413.8, (5.094), 1341.6	501.3, (4.193) 536.5, (4.809) 580.4, (5.024), 1086.1
Zr(p-CH_3TPP)(acac)(m-OCH_3phO) [$Zr(C_{48}H_{36}N_4)(C_5H_7O_2)(C_7H_7O_2)$]	413.6, (5.090), 1329.8	501.1, (4.191) 536.6, (4.805) 580.3, (5.021), 1078.6
Zr(p-CH_3TPP)(acac)(p-CH_3phO) [$Zr(C_{48}H_{36}N_4)(C_5H_7O_2)(C_7H_7O)$]	413.9, (5.104), 1338.7	501.7, (4.200) 537.4, (4.814) 581.4, (5.033), 1083.2
Zr(p-CH_3TPP)(acac)(o-CH_3phO) [$Zr(C_{48}H_{36}N_4)(C_5H_7O_2)(C_7H_7O)$]	414.7, (5.097), 1344.8	501.9, (4.196) 537.3, (4.813) 581.1, (5.028), 1089.5
Zr(p-CH_3TPP)(acac)(p-NO_2phO) [$Zr(C_{48}H_{36}N_4)(C_5H_7O_2)(C_6H_4O_3N)$]	412.9, (5.056), 1270.3	501.4, (4.168) 535.1, (4.788) 580.8, (4.990), 1035.2
Zr(p-CH_3TPP)(acac)(o-NO_2phO) [$Zr(C_{48}H_{36}N_4)(C_5H_7O_2)(C_6H_4O_3N)$]	412.2, (5.055), 1267.4	499.7, (4.167) 534.5, (4.787) 579.1, (4.989), 1031.9
Zr(p-CH_3TPP)(acac)(m-NO_2phO) [$Zr(C_{48}H_{36}N_4)(C_5H_7O_2)(C_6H_4O_3N)$]	413.0, (5.057), 1277.6	500.4, (4.171) 535.5, (4.792) 580.8, (4.994), 1040.8
Zr(p-CH_3TPP)(acac)(p-ClphO) [$Zr(C_{48}H_{36}N_4)(C_5H_7O_2)(C_6H_4OCl)$]	413.3, (5.068), 1290.7	500.8, (4.177) 536.1, (4.795) 580.2, (5.005), 1049.6
Zr(p-CH_3TPP)(acac)(o-ClphO) [$Zr(C_{48}H_{36}N_4)(C_5H_7O_2)(C_6H_4OCl)$]	413.2, (5.065), 1288.6	500.5, (4.172) 536.0, (4.794) 580.1, (5.003), 1047.4
Zr(p-CH_3TPP)(acac)(p-NH_2phO) [$Zr(C_{48}H_{36}N_4)(C_5H_7O_2)(C_6H_6ON)$]	415.1, (5.119), 1354.9	502.9, (4.214) 538.9, (4.828) 583.5, (5.049), 1090.6
Zr(p-CH_3TPP)(acac)(o-NH_2phO) [$Zr(C_{48}H_{36}N_4)(C_5H_7O_2)(C_6H_6ON)$]	414.9, (5.114), 1351.4	502.7, (4.208) 538.5, (4.823) 582.8, (5.042), 1089.1
Zr(p-CH_3TPP)(acac)(m-NH_2phO) [$Zr(C_{48}H_{36}N_4)(C_5H_7O_2)(C_6H_6ON)$]	414.5, (5.110), 1347.2	502.2, (4.205) 538.2, (4.819) 582.1, (5.039), 1087.5
Zr(p-CH_3TPP)(acac)(2,4-dichlorophO) [$Zr(C_{48}H_{36}N_4)(C_5H_7O_2)(C_6H_3OCl_2)$]	411.8, (5.061), 1251.6	499.2, (4.172) 534.3, (4.793) 578.8, (4.997), 1026.8
Zr(p-CH_3TPP)(acac)(2,4-dinitrophO) [$Zr(C_{48}H_{36}N_4)(C_5H_7O_2)(C_6H_3O_5N_2)$]	410.9, (5.049), 1237.9	498.5, (4.159) 532.9, (4.781) 578.3, (4.472), 1015.6
Zr(p-CH_3TPP)(acac)(a-naptholate) [$Zr(C_{48}H_{36}N_4)(C_5H_7O_2)(C_{10}H_7O)$]	412.8, (5.068), 1297.2	500.3, (4.178) 535.4, (4.795) 579.7, (5.007), 1051.2

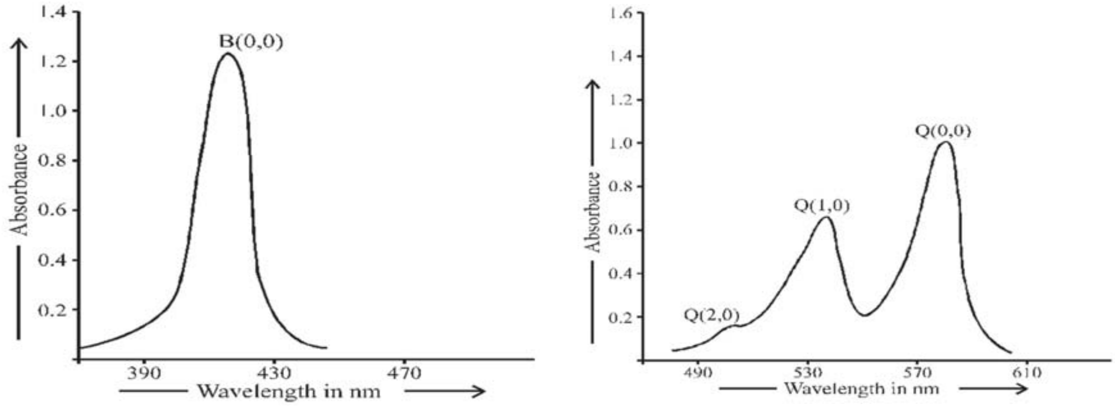


Fig.2 :Optical absorption spectra of Zr(p-CH_3TPP)(acac)(p-OCH_3phO) in $CHCl_3$.

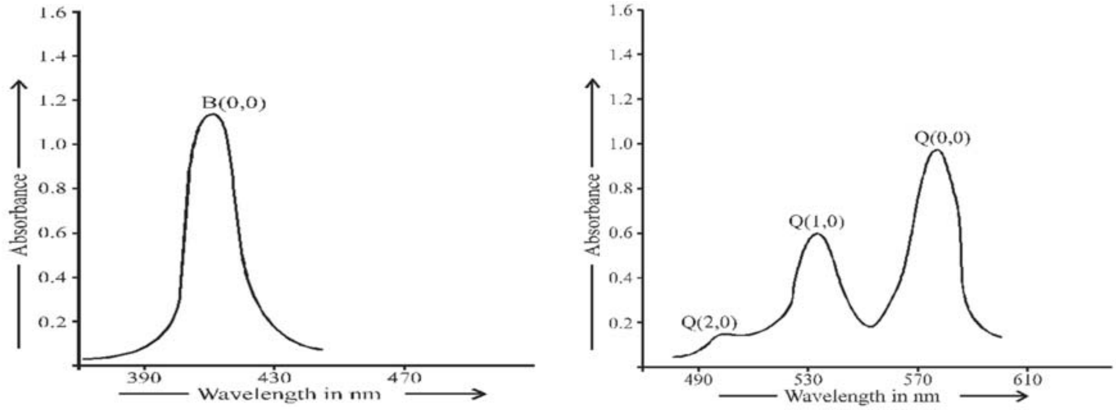


Fig. 3: Optical absorption spectra of Zr(p-CH_3TPP)(acac)(o-NO_2phO) in $CHCl_3$.

coefficient (ε) and oscillator strength (f) values was observed. The optical absorption spectra for Zr(p-CH_3TPP)(acac)(p-OCH_3phO) is displayed in Figure 4. Data revealed that, a change in polarity of the solvent result in slight change in the position of transitions but there was a significant increase in 'Fwhm' ($\nu_{1/2}$) and 'f' values of transitions by increasing the polarity of the solvent. The magnitude of change in 'f' value in axially ligated Zr(IV) metal derivatives of porphyrin revealed the relative strength of π - π^* interactions. It was also found that with the increase in polarity of the solvents, B and Q-bands in axially ligated Zr(IV) metal derivatives showed 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 spectroscopy is most powerful and widely used analytical tools for the determination of various functional groups and elucidation of the structure of unknown compounds including porphyrins and metalloporphyrins[32]. The Zr(IV) metal derivatives of different porphyrins synthesized contain acetylacetonate (acac) and different phenolates as an axial ligand. All the free base porphyrins showed characteristics vibrational frequency of imino-protons. The metallation of porphyrin was confirmed by the absence of vibrational frequencies occurring due to imino groups of the porphyrin ring and appearance of Zr–N band[33] in the range of 457–502 cm^{-1}. The incorporation of various phenolates in Zr(IV) metal derivatives of porphyrin i.e., Zr(p-CH_3TPP)(Y)(X),

Table 3: Optical Absorption data of Zr(p-CH_3TPP)(Y)(X), (Y = acac and X = different phenolates as an axial ligand) in different solvents

Compounds	**Solvent**	**λ_{max}(nm), (log ε) ($M^{-1}cm^{-1}$)**				**$\nu_{1/2}$(cm^{-1})**		**Q(0, 0)**
		B(0,0)	**Q(2,0)**	**Q(1,0)**	**Q(0,0)**	**B(0,0)**	**Q(0,0)**	**f**
Zr(p-CH_3TPP)	$CHCl_3$	413.1	500.5	535.7	579.9	1309.3	1067.2	0.235887
(acac)(Oph)		5.074	4.183	4.796	5.009			
[Zr($C_{48}H_{36}N_4$)	CH_2Cl_2	409.4	496.3	532.2	575.8	1241.6	1020.7	0.197404
($C_5H_7O_2$)		5.030	4.126	4.721	4.951			
(C_6H_5O)]	Acetone	411.3	498.5	533.4	577.5	1278.1	1041.1	0.207468
		5.042	4.139	4.735	4.964			
Zr(p-CH_3TPP)	$CHCl_3$	414.2	501.5	536.8	580.9	1340.2	1085.9	0.2524
(acac)(p-OCH_3phO)		5.101	4.197	4.812	5.031			
[Zr($C_{48}H_{36}N_4$)	CH_2Cl_2	409.8	496.4	530.6	574.9	1279.9	1039.3	0.2075
($C_5H_7O_2$)($C_7H_7O_2$)]		5.057	4.172	4.749	4.965			
	Acetone	411.9	498.3	534.2	578.5	1312.6	1062.4	0.2136
		5.063	4.178	4.765	4.968			
Zr(p-CH_3TPP)	$CHCl_3$	412.9	501.4	535.1	580.8	1270.3	1035.2	0.219019
(acac)(p-NO_2phO)		5.056	4.168	4.788	4.990			
[Zr($C_{48}H_{36}N_4$)	CH_2Cl_2	409.7	496.3	532.3	576.4	1218.3	992.6	0.183752
($C_5H_7O_2$)($C_6H_4O_3N$)]		5.002	4.131	4.718	4.932			
	Acetone	411.2	499.1	533.8	577.9	1236.8	1007.9	0.194033
		5.012	4.147	4.729	4.949			

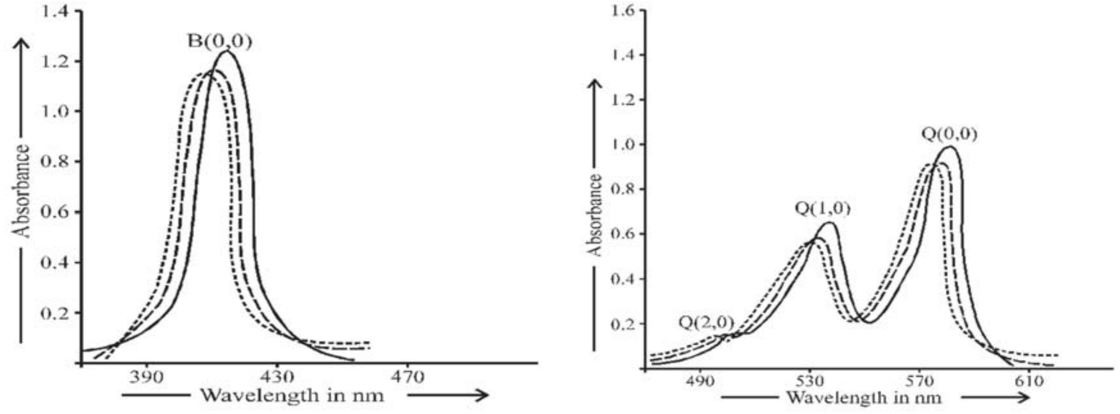


Fig.4: Optical absorption spectra of Zr(p-CH_3TPP)(acac)(p-OCH_3phO) in different solvents ($CHCl_3$, - - - -Acetone, ————CH_2Cl_2).

Table.4: Main Vibrational frequencies corresponding to the various groups in Zr(p-CH_3TPP)(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(CH_3) (cm^{-1})**	**ν(OCH_3) (cm^{-1})**	**ν(NH_2) (cm^{-1})**	**ν(NO_2) (cm^{-1})**	**ν(C-Cl) (cm^{-1})**	**ν(C=O) of acac (cm^{-1})**
p-CH_3H_2TPP [$C_{48}H_{38}N_4$]	3446.9	2964.6	1350.2	1568.1	-	-	-	2852.8	-	-	-	-	-
Zr(p-CH_3TPP)(acac)(Oph) [Zr($C_{48}H_{36}N_4$)($C_5H_7O_2$)(C_6H_5O)]	-	2954.3	1351.1	1590.9	473.2	664.9	703.1 803.3	2907.6	-	-	-	-	1632.3
Zr(p-CH_3TPP)(acac)(p-NH_2phO) [Zr($C_{48}H_{36}N_4$)($C_5H_7O_2$)(C_6H_6ON)]	-	2964.2	1351.5	1592.4	460.3	655.6	703.6 804.1	2891.3	-	$\nu(NH_2)_{sym}$ = 3292.1 $\nu(NH_2)_{asym}$ = 3366.3	-	-	1633.4
Zr (p-CH_3TPP)(acac)(a-naptholate) [Zr($C_{48}H_{36}N_4$)($C_5H_7O_2$)($C_{10}H_7O$)]	-	2952.4	1350.8	1589.3	472.9	659.7	702.4 802.9	2898.4	-	-	-	-	1631.9
Zr(p-CH_3TPP)(acac)(p-ClphO) [Zr($C_{48}H_{36}N_4$)($C_5H_7O_2$)(C_6H_4OCl)]	-	2959.2	1350.9	1590.6	474.7	665.7	703.8 803.1	2906.5	-	-	-	783.1	1634.2
Zr(p-CH_3TPP)(acac)(p-OCH_3phO) [Zr($C_{48}H_{36}N_4$)($C_5H_7O_2$)($C_7H_7O_2$)]	-	2964.1	1350.4	1590.3	481.5	653.3	702.2 802.8	2893.7	ν(C– H) = 2816.6 $\nu(C–O–C)_{sym}$ = 1024.6 $\nu(C–O–C)_{asym}$ = 1261.5	-	-	-	1631.4
Zr(p-CH_3TPP)(acac)(2,4-dichlorophO) [Zr($C_{48}H_{36}N_4$)($C_5H_7O_2$)($C_6H_3OCl_2$)]	-	2963.8	1351.7	1592.9	478.9	670.8	704.6 804.5	2908.3	-	-	-	787.8	1636.7
Zr(p-CH_3TPP)(acac)(p-CH_3phO) [Zr($C_{48}H_{36}N_4$)($C_5H_7O_2$)(C_7H_7O)]	-	2950.2	1349.8	1584.6	468.1	650.7	702.1 802.6	2895.2	-	-	-	-	1630.5
Zr(p-CH_3TPP)(acac)(p-NO_2phO) [Zr($C_{48}H_{36}N_4$)($C_5H_7O_2$)($C_6H_4O_3N$)]	-	2963.6	1351.8	1592.7	483.9	667.3	704.7 804.9	2909.5	-	-	$\nu(NO_2)_{sym}$ = 1342.3 $\nu(NO_2)_{asym}$ = 1543.1	-	1636.4

(Y = acetylacetonate ($C_5H_7O_2$) and X = different phenolates) was confirmed by the appearance of Zr–O vibrational frequencies in the range of 649 – 680 cm^{-1}. The incorporation of acetylacetonate (acac) in axially ligated Zr(IV) derivatives was confirmed by the appearance of C=O vibrational frequencies in the range of 1617 – 1641 cm^{-1} and Zr–O in the range of 702 – 818.5 cm^{-1} respectively.

The IR absorption spectra of p-CH_3TPP and their corresponding axially ligated Zr(IV)acetylacetonate (acac) containing different phenolates as an axial ligand is listed in Table 4.The IR spectra of Zr(p-CH_3TPP)(acac)(p-OCH_3phO) is shown in Figure 5. In Zr(p-CH_3TPP)(acac)(p-OCH_3phO), aromatic n(C-H) band stretch appeared at 2964.1 cm^{-1}, n(C-N) at1350.4 cm^{-1}, n(C = C) at 1590.3 cm^{-1}, n(Zr-N) at 481.5 cm^{-1}, n(Zr-O) of phenolate at 653.3 cm^{-1}, n(Zr-O) of acac at 702.2 $cm^{-1}$and 802.8 cm^{-1}, n(C=O) of acac at 1631.4 cm^{-1} and n(CH_3) at 2893.7 cm^{-1}. The presence of -OCH_3 group at p-position of the phenolate ligand in this compound vibrated at 2816.6 cm^{-1} for n(C-H), 1024.6 cm^{-1} for n(C-O-C)$_{sym}$ and 1261.5 cm^{-1} for n(C-O-C)$_{asym}$ respectively.

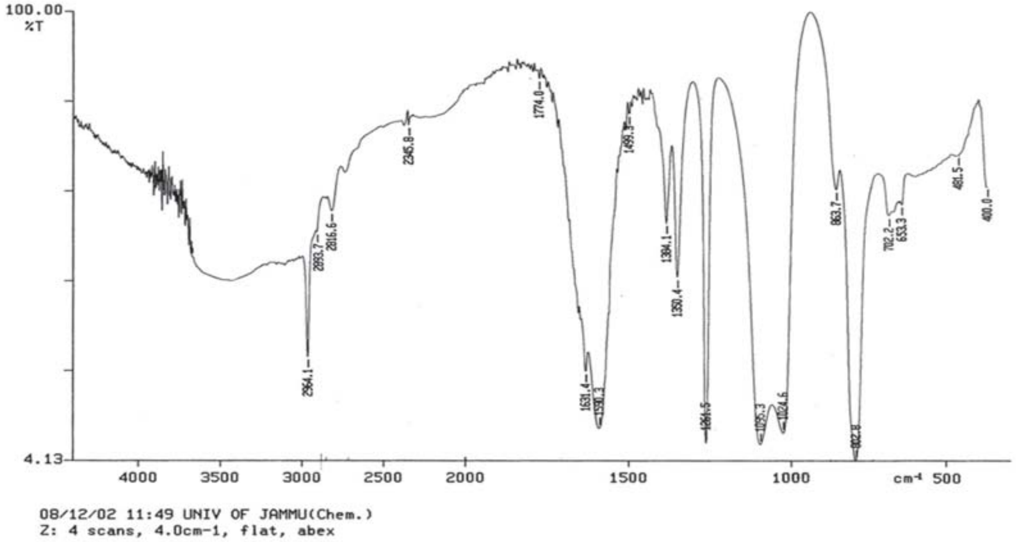


Fig. 5: IR Spectra of Zr(p-CH_3H_2TPP)(acac)(p-OCH_3phO)

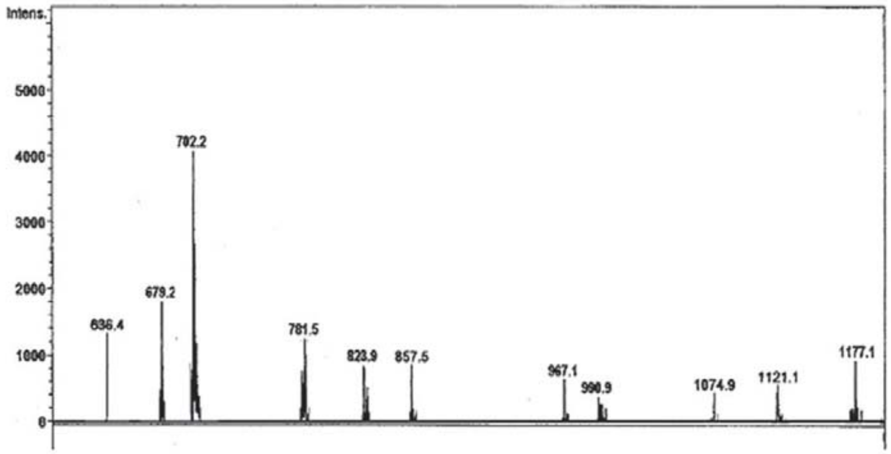


Fig 5(a): Mass Spectra of Zr(CH_3TPP)(acac)(p-NH_2phO)

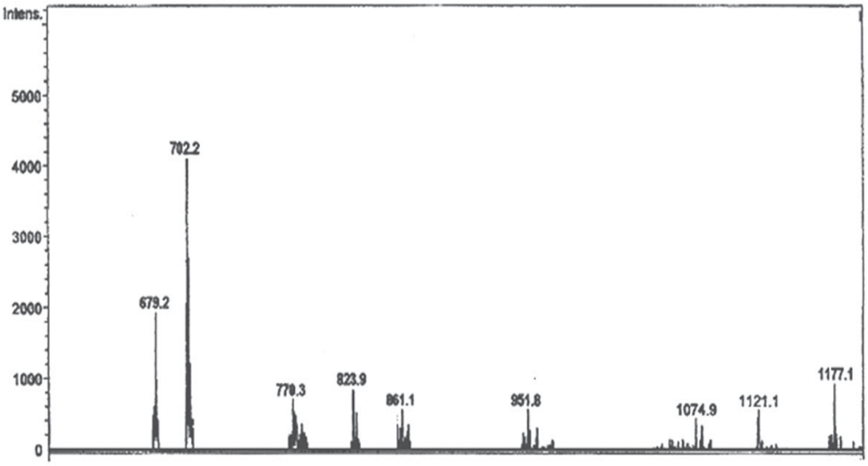
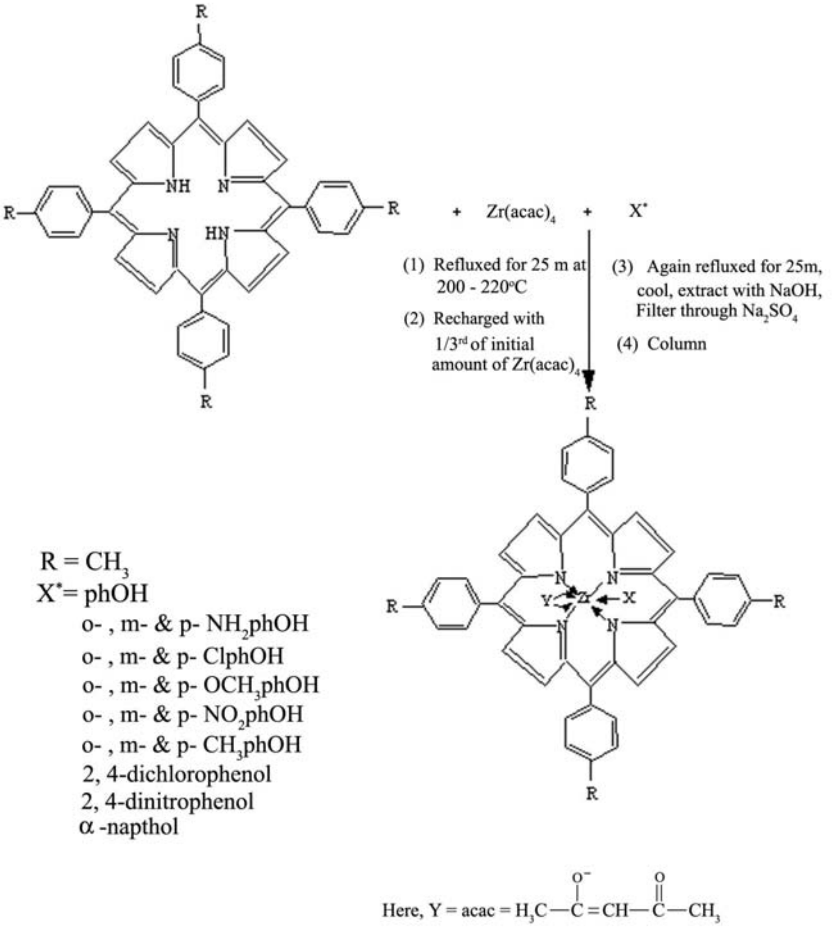


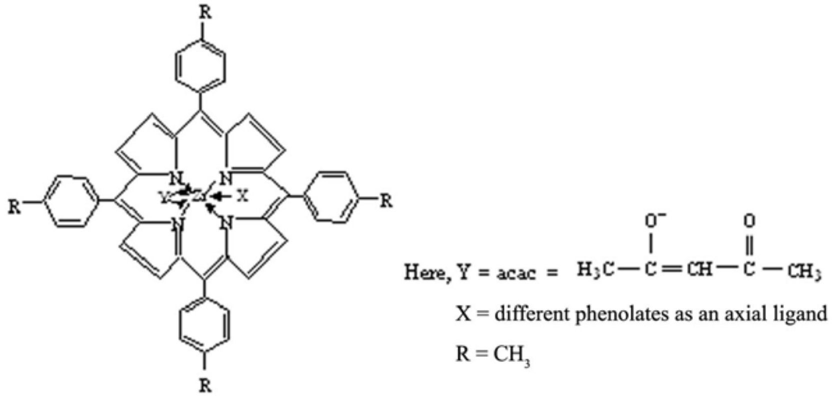
Fig. 5(b): Mass Spectra of Zr(CH$_3$TPP)(acac)(phO).

Table 5 :Elemental Analytical data of Zr(p-CH$_3$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-CH$_3$TPP)(acac)(Oph) $[Zr(C_{48}H_{36}N_4)(C_5H_7O_2)(C_6H_5O)]$	74.42	5.08	5.88	74.26	5.05	5.83
Zr(p-CH$_3$TPP)(acac)(p-NH$_2$phO) $[Zr(C_{48}H_{36}N_4)(C_5H_7O_2)(C_6H_6ON)]$	73.26	5.11	7.24	73.12	5.02	7.22
Zr(p-CH$_3$TPP)(acac)(o-ClphO) $[Zr(C_{48}H_{36}N_4)(C_5H_7O_2)(C_6H_4OCl)]$	71.81	4.80	5.68	71.66	4.81	5.64
Zr(p-CH$_3$TPP)(acac)(p-OCH$_3$phO) $[Zr(C_{48}H_{36}N_4)(C_5H_7O_2)(C_7H_7O_2)]$	73.36	5.13	5.70	73.23	5.06	5.62
Zr(p-CH$_3$TPP)(acac)(a-naptholate) $[Zr(C_{48}H_{36}N_4)(C_5H_7O_2)(C_{10}H_7O)]$	75.49	5.03	5.59	75.33	5.01	5.55
Zr(p-CH$_3$TPP)(acac)(p-NO$_2$phO) $[Zr(C_{48}H_{36}N_4)(C_5H_7O_2)(C_6H_4O_3N)]$	71.06	4.75	7.02	70.95	4.12	6.96
Zr(p-CH$_3$TPP)(acac)(2,4-dichlorophO) $[Zr(C_{48}H_{36}N_4)(C_5H_7O_2)(C_6H_3OCl_2)]$	69.04	4.54	5.49	69.31	4.52	5.43
Zr(p-CH$_3$TPP)(acac)(p-CH$_3$phO) $[Zr(C_{48}H_{36}N_4)(C_5H_7O_2)(C_7H_7O)]$	74.58	5.22	5.80	73.65	4.88	5.42
Zr(p-CH$_3$TPP)(acac)(2,4-dinitrophO) $[Zr(C_{48}H_{36}N_4)(C_5H_7O_2)(C_6H_3O_5N_2)]$	67.99	4.45	8.06	67.87	4.36	8.01



Scheme I : General Scheme for the preparation of Mesotetra(p methylphenyl)porphinatozirconium(IV)acetylacetonatophenolate containing differant phenolates as axial ligand.



Scheme 2. Depicted Structure for mesotetra(p-methylphenyl)porphinatozirconium(IV)acetylacetonatophenolate.

Table 6: Mass Data for Zr(p-CH_3TPP)(Y)(X), (Y = acac and X = different phenolates as an axial ligand).

Compounds	m/z ratio	
	Observed	Calculated
Zr(p-CH_3TPP)(acac)(Oph) [Zr($C_{48}H_{36}N_4$)($C_5H_7O_2$)(C_6H_5O)]	951.8	952.28
Zr(p-CH_3TPP)(acac)(p-NH_2phO) [Zr($C_{48}H_{36}N_4$)($C_5H_7O_2$)(C_6H_6ON)]	967.1	967.30
Zr(p-CH_3TPP)(acac)(o-ClphO) [Zr($C_{48}H_{36}N_4$)($C_5H_7O_2$)(C_6H_4OCl)]	985.7	986.30
Zr(p-CH_3TPP)(acac)(p-OCH_3phO) [Zr($C_{48}H_{36}N_4$)($C_5H_7O_2$)($C_7H_7O_2$)]	982.8	982.31
Zr(p-CH_3TPP)(acac)(a-naptholate) [Zr($C_{48}H_{36}N_4$)($C_5H_7O_2$)($C_{10}H_7O$)]	1001.6	1002.34
Zr(p-CH_3TPP)(acac)(p-NO_2phO) [Zr($C_{48}H_{36}N_4$)($C_5H_7O_2$)($C_6H_4O_3N$)]	996.6	997.28
Zr(p-CH_3TPP)(acac)(2,4-dichlorophO) [Zr($C_{48}H_{36}N_4$)($C_5H_7O_2$)($C_6H_3OCl_2$)]	1021.5	1021.17
Zr(p-CH_3TPP)(acac)(p-CH_3phO) [Zr($C_{48}H_{36}N_4$)($C_5H_7O_2$)(C_7H_7O)]	965.2	966.31
Zr(p-CH_3TPP)(acac)(2,4-dinitrophO) [Zr($C_{48}H_{36}N_4$)($C_5H_7O_2$)($C_6H_3O_5N_2$)]	1042.6	1042.28

Elemental Analysis

Elemental analysis determined the purity and the percentage of carbon, hydrogen and nitrogen present in axially ligated Zr(IV) metal derivatives of meso-tetra(p-methylphenyl)porphyrin (p-CH_3H_2TPP) containing acetylacetonate (acac) and different phenolates as an axial ligand which agreed well with their calculated percentages as listed 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 of meso-tetra(p-methylphenyl)porphyrin (p-CH_3H_2TPP) containing acetylacetonate and different phenolates as an axial ligand and their data is listed in Table 6. The mass spectra of some representative compound were shown in Figure.5(a) and 5(b).

CONCLUSION

Spectroscopic data revealed the ligation of acetylacetonate and different phenolates at axial position on Zr(IV) metal atom in mesotetra(p-methylphenyl)porphinatozirconium 1(IV)acetylacetonatophenolate [Zr(p-CH_3TPP)(acac)(Y)(X)] and helped in depicting the environment around Zr(IV) metal in these axially ligated porphyrins as shown in Scheme 2.

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