Research Article

Synthesis, Comparative Study on the Characterization and Biological Activity of Axially ligratedoxovanadium(IV) and chlorochromium(III) porphyrins with oxygen and N-donors

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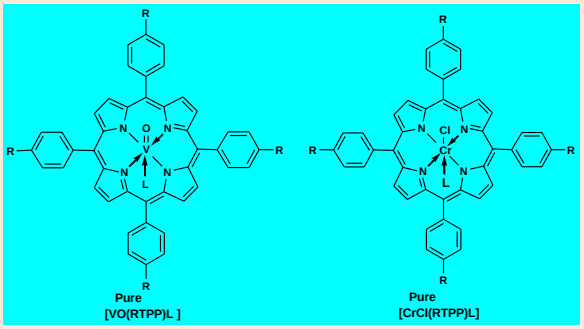
Abstract

A series of six co-ordinatedoxovanadium(IV) and chlorochromium(III) porphyrin complexes of general formula [Vo{RTPP}(L)] and [CrCl{RTPP}(L)] where R = H, -CH3, -OCH3 and Cl groups and L = 2-aminophoH, 2,5-dimephoH and 4-ethylpyridine were prepared by reacting the ligands with various VO(RTPP) and CrCl(RTPP). These complexes were characterized by elemental analysis, I.R, uv-visible, 1H NMR spectral studies. The complexes of oxovanadium(IV) porphyrins show V=0 stretching vibrations between 932 cm-1 and 1050 cm-1. The presence of three d-d transitions occurring between 400-625nm confirm the d1 electronic configuration for vanadium complexes whereas in case of chlorochroniumporphyrins the vibrational frequency due to Cr-N appears at 430-495 cm-1 and bands appearing in range of 370-430 cm-1 are attributed due to □(Cr-Cl) vibrations and those in the range of 830-890 cm-1 are attributed due □(Cr-O) vibrations. The presence of two bands occurring between 300-610 nm gives the presence of Cr(III), porphyrin with 3d3 configuration. The spectroscopic and magnetic studies provide the information for the octahedral geometry to these complexes. Biologically the oxovanadiumporphyrin complexes exhibit +ive antibacterial andantitioxidant but negative antifungal action where aschlorochromiumporphyrin complexes shows only +ive antifungal behaviourbut negative antibacterial and antioxidant activity.

Keywords: Comparative octahedral oxovanadium and chlorochromiumporphyrins with axial oxygen and nitrogen donors biologically active complexes.



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Introduction

Porphyrins and metalloporphyrins have been the subject of intense interest since the early 19th century; have attracted scientists from many years due to their immense biological importance and their fascinating physical, chemical and spectroscopic properties [1, 2]. Due to their wide applications, the synthesis of porphyrins and their assemblies has become a very attractive research area [3]. In recent years, a few porphyrins assemblies are constructed for their potential applications in molecular scale electronic/photonic devices [4]. Mesotetraphenylporphyrins offers the best molecular motif for the construction of such assemblies in view of its case of synthesis and wide choice of modulation of electronic structure that is possible arising from the substitution of various groups of different perpherial positions. The choice of porphyrin units is important in the design and synthesis of multicomponent molecular assemblies for the display of desired properties. A number of recent studies of model compounds have demonstrated the importance of substituents effects inporphyrins [5]. Because of conjugated nature of the porphyrins ring system, the electrons

donating or electron withdrawing substituents on the periphery of the molecule have shown to effect the basicity of the iminonitrogens [6] of porphyrins, the rate of N-H tautomerism in free base porphyrins, the chemical shifts of pyrrole and N-H protons in tetraphenylporphyrins [7]. The peripheral substitution also affects the rates of phenyl ring rotation [8], visible absorption spectra, spin states, EPR parameters [9]. Porphyrins derivatives containing electronegative substituents like –Cl, -NO_2 at β-pyrrole position of porphyrin have been synthesized and effects on optical and redox properties have been investigated [10].

Metalloporphyrins have attracted considerable attention because of their interesting biological functions as the active sites of hemoprotiens and photosynthetic centres where a considerable mechanistic understanding and chemical modeling of their function have been central interests. Porphyrins and related tetrapyrrolic compounds occur widely in nature and play important roles in various biological processes. For example, the hemeprotoporphyrin complex is the prosthetic group in Hb and Mb which are responsible for oxygen transportation in red blood cells and oxygen storage in living cells. Five co-ordinate vandaylporphyrins display d-d transitions which are heavily affected by co-ordination of ligand (L) in the sixth position trans to the oxygen atom. All these transitions lie in the doublet manifold due to conservation of spin in the system. In addition to the π-π* and d-d transitions, a low lying charge-transfer (CT) state was also calculated. The CT state results in generation of a porphyrinπ-anion radical. Compounds in which L is derived from phenols can be used to initiate the polymerization of propylene oxide, β-propiolactone and β-butyrolactone giving oligoethers and oligoesters having narrow molecular weight distribution. Due to the interesting behavior of vandayl and chromium porphyrinswe have aimed at the synthesis, spectroscopic characterization of axially ligated vandayl and chromium porphyrin in order to understand the steric and electronic effects of the exial ligands on the properties of porphyrins and their biological activity. Axial ligands chosen for investigation are phenols 2-aminophenol, 2,3-dimephenol and4-ethylpyridine. A systematic comparative study of the effects of various substituents incorporated in optical absorption/emission spectra other spectroscopic properties and biochemical studies have been carried out.

Experimental

Materials and Instruments

All the chemicals were of analytical grade. Pyrrole was distilled over KOH pellets under vacuum before one. All the organic solvents that were used for synthesis and chromatographic use were dried and repeatedly distilled. Elemental analyses C, H and N were obtained on vario EI-III and CHNS-932Leco-elemental analyser. U.V/visible spectra were recorded on T.90 U.V/visible spectrophotometer in range of 350-800 nm. I.R spectra were recorded on a Perkin Elmer spectrum 400 FTIR spectrophotometer using KBr pellets in the range of 4000-400 cm^{-1} and ^1H NMR spectra were recorded on a Bruker Advance II 500(500 MHz) using TMS as standard and DMSO + $CDCl_3$ as solvents in the department of chemistry university of Jammu.

Biological Analysis Studies

Antibacterial studies: Qualitative analysis for screening of anti-bacterial activity was carried out by Agar well diffusion method. The samples were tested for antibacterial activity against ix bacterial strains viz. Micrococcus litues, Enterococcus facalis, Bacillus cereus, Bacillus subtilis, Alcaligenesdentirificans and pseudomonas alcaligenes 20 ml of sterilized nutrient agar was inoculated with 100 ml of bacterial suspension (108 CFU/ml) and then, poured to sterilized petriplate. The agar plate was left to solidify at room temperature. A well of 6 nm was aseptically bored into the agar plate. Then, 20mL of the complexes (diluted with DMSO 1:1) was added to each well. Chloromphenicol (10μg) was used as a positive reference to determine the sensitivity of bacteria. The plates were kept at 40°C for 24 hrs to allow the dispersal and then uncubated at 37 °C for 24 hrs.

Antioxidant studies: 1,1-Diphenyl-2-picrylhydrazyl (DPPH) radical scavenging assay. In this assay, free radical scavenging activity was determined by measuring the bleaching of purple-colored methanol solution of DPPH radical. The radical scavenging activity was determined according to method of Blois et al with modification [12]. Total of 1

ml from a 0.5M methanol solution of the DPPD radical was mixed to 2 ml of sample and to this 2 ml of 0.1M sod.acetate buffer (P^H5.5) was added. The mixtures were well shaken and kept at room temperature in dark for 30 minutes. The absorbance was measured at 517 nm using double beam U.V-vis spectrophotometer. The radical scavenging activity (RSA) was calculated as a percentage of DPPH radical discoloration using the equation % RSA = $[(A_o-A_s)/A_o] \times 100$

Where A_o is the absorbance of the control and A_s is the absorbance of the test compound. These studieswere done at SKUAST Jammu

Antifungal studies: The in vitro biological screening effects of the investigated complexes were tested against the pathogen "Sclerotiumrolfsi" by poisoned food method using Potato Dextorse/Agar (PDA) nutrient as the medium [13]. The linear growth of fungus in control and treatment were recorded at different concentration of the complexes. These studies were also carried out in SKUAST Jammu.

Synthesis of Oxovanadium(IV) and Chloro chromium(III) porphyrins

$RTPPH_2$, Vo(RTPP) and CrCl(RTPP) were synthesized according to literature methods [14-17].

Synthesis of axially ligated VO(IV) and CrCl(III) porphyrins with substituted phenols and ethyl pyridine: Phenols such 2-amino, 2,3-dimephoH, 4-ethylpyridine and VO(RTPP) and CrCl(RTPP) were mixed in 1:1 molar ratio in 20 ml of dry $CHCl_3$. The reaction mixture was stirred on magnetic stirrer for 48 hrs without heating. The completion of reaction was indicated by TLC and UV spectra. The complexes of phenol were extracted with 2NNaOH solution and pyridine complexes were extracted with 1NHCl and the extract was evaporated by vacuum pump and dry material was dissolved in $CHCl_3$. It is filtered though anhydrous sod. sulphate and evaporated through vacuum pump. The final product was purified by column chromatography using basic alumina and $CHCl_3$ as elutent. The dry product was crystallized with $CHCl_3$ and recystallised with pet.ether. The yield of oxovanadium complexes was 30-35% whereas that of chloro chromium complexes the yield was 15-20%.

The general synthetic routes to synthesize the above saidRTPP, their metallated and axially ligated oxovanadium(IV) and chlorochromium(III) porphyrinsis given below in the **Scheme I** and **II**.

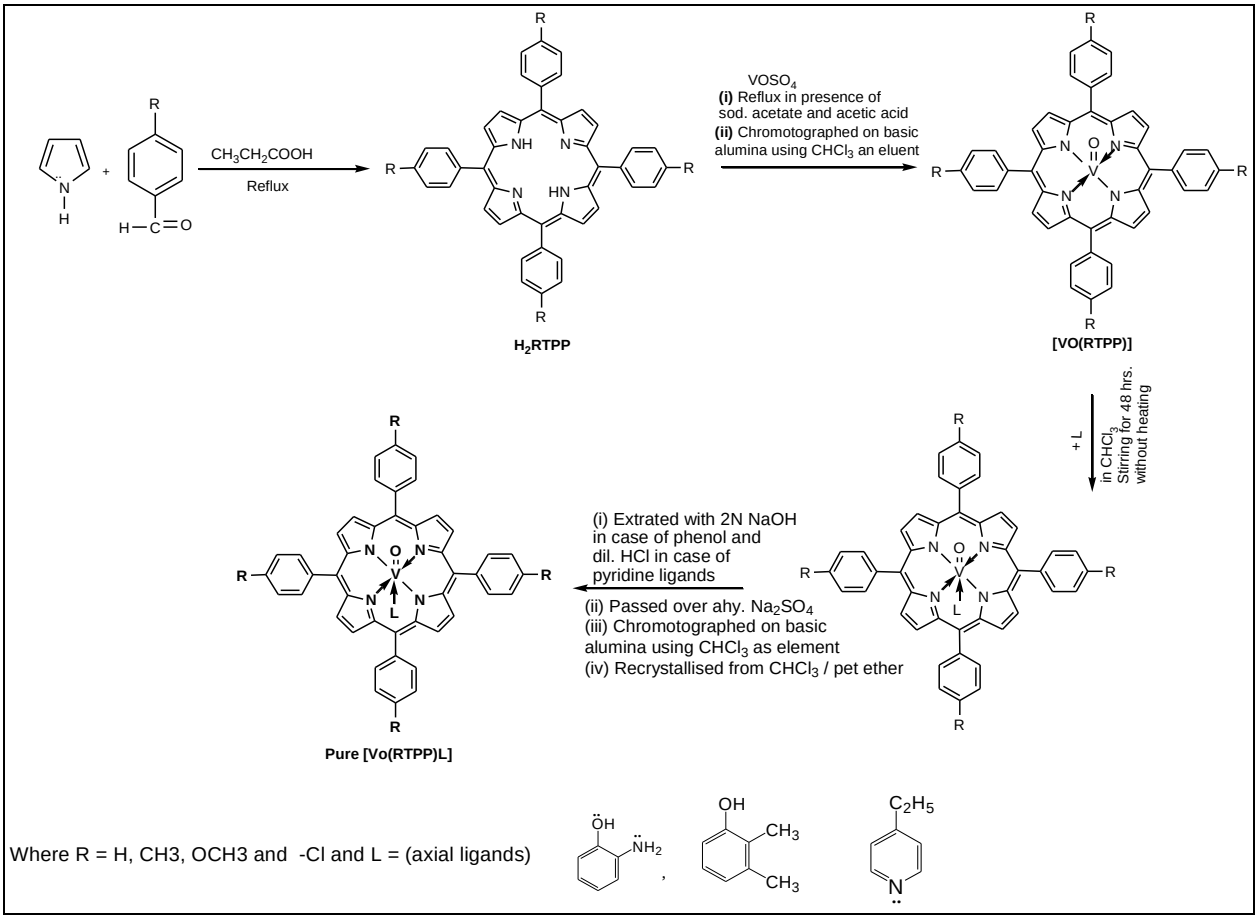
All the new oxovanadium(IV) and chrochromium(III)porphyrins complexes prepared were characterized by spectroscopic methods such as uv/visible, IR, ^{1}H-NMR, mass spectra and elemental analysis. The characterizations of the new compounds were consistent with assigned formula. The complexes of both vanadium and chromium were stable at room temperature, coloured and soluble in $CHCl_3$, DMSO, DMF, CH_3OH and CH_3CN but insoluble in water acetone and ether.

Results and discussion

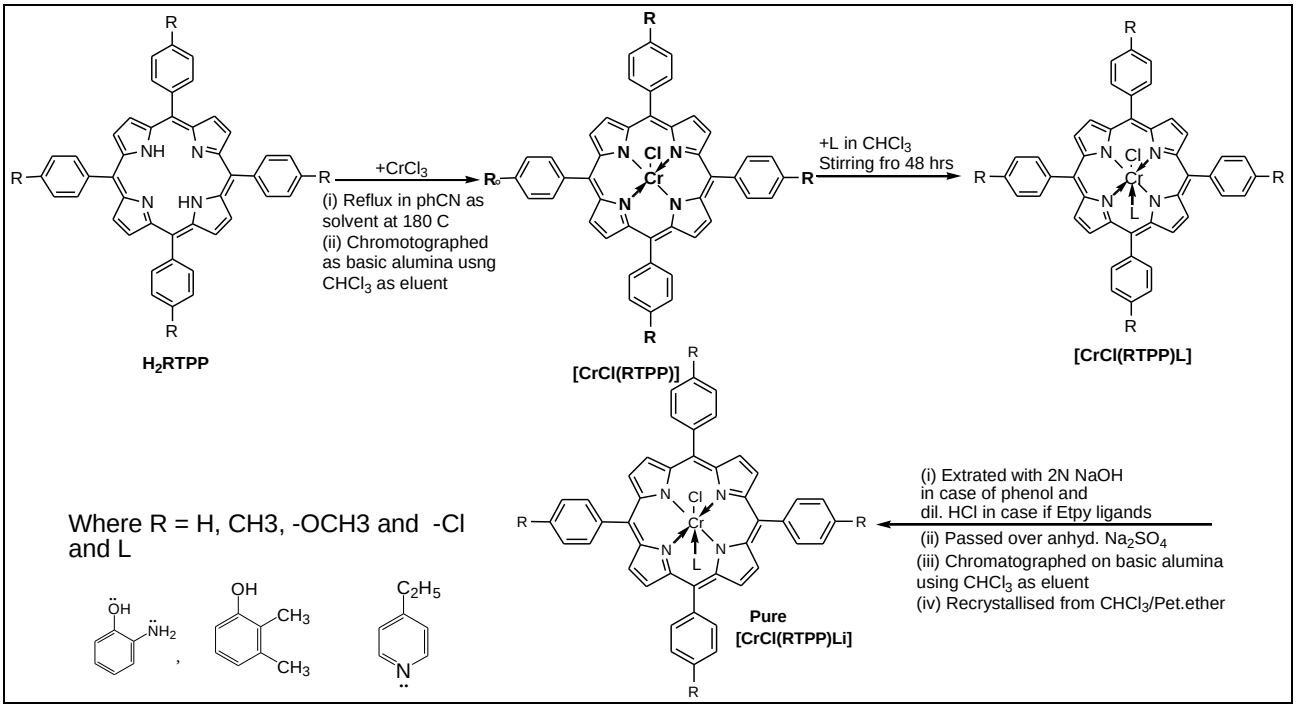
Conductance and magnetic measurements

The molar conductivity of complexes in DMSO at 10^{-3}M concentration were recorded to show the values in the range of$^{10-15}\Omega^{-1}cm^2mol^{-1}$ for oxovanadium complexes and for chromium chloro complexes the conductivityvalues ration in DMSO of 10^{-3}M concentration were found to be in the range of15-20 $\Omega^{-1}cm^2mol^{-1}$ shaving that both oxovanadium complexes are well as chromium chloro complexes are non-electrolytes or they neutral in nature.

The vanadium complexes have magnetic moments in the range of 1.73-1.79 B.M with one unpaired electron of $3d^1$ configuration. Whereas chlorochromium complexes the magnetic moment in the range of 3.66-3.80 B.M showing that chromium complexes have $3d^3$ configuration. These results shown that both vanadium and chromium complexes are monomeric octahedral complexes [15, 19-20].



Scheme I



Scheme II

Table 1 Elemental analytical data of [VO(RTPP)L] where R = H, CH_3, OCH_3 and Cl L = phenolic and 4-ethylpyridine

Compound	Mol. formula	Calculated percentage			Found percentage		
		C	H	N	C	H	N
[(2-aminoPhoH)VO(TPP)]	$C_{50}H_{35}N_5VO_2$	67.0	4.44	8.88	66.69	4.30	8.79
[(2,3-dimePhoH)VO(TPP)]	$C_{52}H_{38}N_4VO_2$	77.90	4.74	6.99	77.83	4.70	6.90
[(4-Etpy)Vo(TPP)]	$C_{51}H_{37}N_5VO$	77.86	4.70	8.90	77.81	4.67	8.83
[(2-aminoPhoH)VO(p-MeTPP)]	$C_{54}H_{43}N_5VO_2$	76.77	5.09	8.29	76.73	5.01	8.20
[(2,3-dimePhoH)VO(p-MeTPP)]	$C_{56}H_{47}N_4VO_2$	78.41	5.48	6.53	78.40	5.47	6.50
[(4-EtPy)VO(P-MeTPP)]	$C_{55}H_{45}N_5VO$	78.38	5.34	8.31	78.30	5.28	7.96
[(2-aminoPhoH)VO[p-MeoTPP]]	$C_{54}H_{43}N_5VO_6$	71.52	4.74	7.72	71.39	4.69	7.74
[(2,3-dimePhoH)VO(p-MeoTPP)]	$C_{56}H_{47}N_4VO_6$	72.96	5.10	6.08	72.91	5.16	6.09
[(4-Etpy)VO(p-MeoTPP)]	$C_{55}H_{45}N_5VO_5$	72.84	4.96	7.72	72.77	4.91	7.68
[(2-aminoPhoH)VO(ClTPP)]	$C_{50}H_{31}N_5Cl_4VO_2$	64.79	3.34	7.55	64.72	3.30	7.51
[(2,3-dimePhoH)VO(ClTPP)]	$C_{52}H_{34}N_4Cl_4VO_2$	66.45	3.62	5.96	66.18	3.60	5.90
[(4-Etpy)VO(ClTPP)]	$C_{51}H_{33}N_5Cl_4VO$	66.23	3.57	7.57	66.14	3.53	7.49

Table 2 Elemental analytical data of [CrCl(RTPP)L] where R = H, -CH_3, OCH_3 and L = phenolic and4-etpy ligands

Compound	Mol. formula	Calculated percentage			Found percentage		
		C	H	N	C	H	N
[(2-aminoPhoH)CrCl(TPP)]	$C_{50}H_{35}N_5OCrCl$	74.25	4.32	8.65	74.19	4.30	8.59
[(2,3-dimePhoH)CrCl(TPP)]	$C_{52}H_{38}N_4OCrCl$	75.95	4.62	6.81	75.90	4.58	6.78
[(4-Etpy)CrCl(TPP)]	$C_{51}H_{37}N_5CrCl$	75.88	4.58	8.67	75.83	4.54	6.63
[(2-aminoPhoH)CrCl(p-MeTPP)]	$C_{54}H_{43}N_5OCrCl$	74.95	4.97	8.09	74.86	4.93	8.01
[(2,3-dimePhoH)CrCl(p-MeTPP)]	$C_{56}H_{46}N_4OCrCl$	76.58	5.24	6.38	76.52	5.18	6.29
[(4-EtPy)CrCl(p-MeTPP)]	$C_{55}H_{45}N_5CrCl$	76.52	5.21	8.11	76.40	5.18	8.04
[(2-aminoPhoH)CrCl[(p-MeoTPP)]	$C_{54}H_{43}N_5O_5CrCl$	73.93	4.90	7.98	73.86	4.88	7.93
[(2,3-dimePhoH)CrCl(p-MeoTPP)]	$C_{56}H_{47}N_4O_5CrCl$	85.11	5.95	7.09	85.10	5.86	7.0
[(4-Etpy)CrCl(p-MeoTPP)]	$C_{55}H_{45}N_5O_4CrCl$	85.12	5.18	9.03	85.03	5.76	8.9
[(2-aminoPhoH)CrCl(p-ClTPP)]	$C_{50}H_{31}N_5Cl_5CrO$	63.39	3.27	7.39	63.28	3.25	7.3
[(2,3-dimePhoH)CrCl(p-ClTPP)]	$C_{52}H_{34}N_4Cl_5CrO$	65.03	3.54	5.83	64.93	3.51	5.80
[(4-Etpy)CrCl(p-ClTPP)]	$C_{51}H_{33}N_5Cl_5Cr$	64.79	3.49	7.41	64.66	3.43	7.38

Table 3 Molar conductivity and magnetic moments of isolated oxovanadium complexes

Compound	Molar conductive in $\Omega^{-1}cm^2mol^{-1}$	Magnetic moment in B.M
[(2-aminoPhoH)VO(TPP)]	11	1.73
[(2,3-dimePhoH)VO(TPP)]	14	1.75
[(4-Etpy)VO(TPP)]	15	1.74
[(2-aminoPhoH)VO(p-MeTPP)]	12	1.76
[(2,3-dimePhoH)VO(p-MeTPP)]	10	1.79
[(4-EtPy)VO(p-MeTPP)]	11	1.76
[(2-aminoPhoH)VO[p-MeoTPP]]	13	1.77
[(2,3-dimePhoH)VO(p-MeoTPP)]	14	1.76
[(4-Etpy)Vo(p-MeOTPP)]	15	1.73
[(2-aminoPhoH)VO(p-ClTPP)]	10	1.75
[(2,3-dimePhoH)VO(p-ClTPP)]	10	1.78
[(4-Etpy)VO(p-ClTPP)]	12	1.78

Table 4 Molar conductivity and magnetic moments of isolated chlorochromium complexes

Compound	Molar conductance in $\Omega^{-1}cm^2mol^{-1}$	Magnetic moment in B.M
[(2-aminophoH)CrCl(TPP)]	16	3.78
[(2,3-dimephoH)CrCl(TPP)]	18	3.66
[(4-Etpy)CrCl(TPP)]	19	3.85
[(2-aminophoH)CrCl(p-MeTPP)]	20	3.83
[(2,3-dimephoH)CrCl(p-MeTPP)]	15	3.84
[(4-EtPy)CrCl(p-MeTPP)]	18	3.86
[(2-aminoPhoH)CrCl[(p-MeOTPP)]	17	3.87
[(2,3-dimePhoH)CrCl(p-MeOTPP)]	17	3.88
[(4-Etpy)CrCl(p-MeOTPP)]	16	3.67
[(2-aminoPhoH)CrCl(p-ClTPP)]	15	3.69
[(2,3-dimePhoH)CrCl(p-ClTPP)]	20	3.75
[(4-Etpy)CrCl(p-ClTPP)]	19	3.87

Electronic spectra

Free-baseporphyrins display four visible bands and metallophorphyrins exhibit two clear visible bands. The UV and visible spectra of tetraporphyrous have been divided into two groups, the first in the region of 800 nm to about 400 nm, and the 2nd from 450-350 nm. The absorption bands in 800-450 nm region can be regarded as vibrational term of common electronic transition while the intense band in the near U.V region, the so called "Soret" band can corresponds to a different electronic transition [20-21].

Oxovanadium(IV) tetraporphyrins shows normal spectra with one Soret or B-band and one Q-band. The representative absorption spectral data of RTPP (free base porphyrin) and VO(TPP) (metalloporphyrins) in solvent $CHCl_3$ and CH_2Cl_2 is accumulated in **Table 5**. It is observed that many of absorption bands of oxovanadium(IV) porphyrins exhibit smaller shift to longer wavelength (bathchronicshift) as compared to free base porphyrin due to incorporation of metal ion in the porphyrin ring. The optical absorption spectra of RTPP and Vo(TPP) in $CHCl_3$ is shown in **Table 6**.

Table 5 Optical absorption spectral data of free baseporphyrins and VO(VI) derivatives in $CHCl_3$ and CH_2Cl_2 solvents shaving λ_{max} together with optical density

Porphyrins	Solvent	Soret Band (B-Band) λ_{max} (in nm)abs.	Q-bands λ_{max} (in nm) abs.			
Meso-TPP	$CHCl_3$	418(0.802)	515(0.559)	548(0.230)	590(0.162)	646(0.140)
	CH_2Cl_2	422(0.850)	510(0.383)	540(0.210)	587(0.148)	641(0.120)
H_2-P-MeTPP	$CHCl_3$	420(0.767)	518(0.568)	540(0.23)	590(0.162)	640(0.141)
	CH_2Cl_2	418(0.856)	520(0.566)	546(0.228)	593(0.163)	644(–)
H_2-P-MeOTP	$CHCl_3$	4.21(0.864)	516(0.558)	540(0.235)	590(0.158)	660(0.443)
	CH_2Cl_2	423(0.864)	518(0.583)	545(0.235)	587(0.160)	646(0.414)
H_2-P-ClTPP	$CHCl_3$	425(0.082)	515(0.563)	548(0.230)	570(0.161)	645(0.143)
	CH_2Cl_2					
TPP-VO(IV)	$CHCl_3$	420(0.846)	550(0.125)			
	CH_2Cl_2	423(0.840)	547(0.228)			
(p-MeTPP)VO(IV)	$CHCl_3$	421(0.841)	555(0.216)			
	CH_2Cl_2	425(0.843)	550(0.218)			
(p-MeTPP)VO(IV)	CH_2Cl_2	423(0.854)	560(0.218)			
	CH_2Cl_2	430(0.844)	550(0.216)			
(p-ClTPP)VO(IV)	CH_3Cl_3	425(0.864)	540(0.223)			
	CH_2Cl_2	420(0.816)	548(0.216)			

Table 6 Optical Absorption spectral data of oxovanadiumporphyrins showing λ_{max} together with log ε in $CHCl_3$

Compound	B-bands λ_{max}(nm) (log ε $m^{-1}cm^{-1}$ ν½ cm^{-1})	Q. bands λ_{max}(nm) (log ε m^{-1} cm^{-1} ν½ (cm^{-1})
[(2-aminophoH)VO(TPP)]	414.7 (4.713), 925	536.6 (4.415), 867
[(2,3-dimephoH)VO(TPP)]	415.5(4.715), 972	537.3 (4.265), 845
[(3-Etpy)VO(TPP)]	425.8 (4.842), 995	558.1 (4.293), 825
[(2-aminophoH)VO(p-MeTPP)]	415.8 (4.716), 925	536.6 (4.415), 869
[(2,3-dimephoH)VO(P-MeTPP)]	415.8 (4.732), 975	538.3 (4.269), 852
[(4-Etpy)VO(p-MeTPP)]	425.5 (4.825), 989	557.8 (4.284), 852
[(2-aminophoH)VO(p-MeOTPP)]	414.7 (4.713), 925	336.6 (4.416), 824
[(2,3-dimephoH)VO(p-MeOTPP)]	416.2 (4.711), 926	538.5 (4.325), 835
[(4-Etpy)VO(p-MeOTPP)]	425.5 (48.25), 989	557.8 (4.284), 852
[(2-aminophoH)VO(p-ClTPP)]	414.7 (4.713), 925	536.6 (4.415), 824
[(2,3-dimephoH)VO(p-ClTPP)]	415.8 (4.732), 975	538.3 (4.269), 869
[(4-Etpy)VO(p-ClTPP)]	427.6 (4.742), 990	559.7 (4.284), 872

The axially ligated metalloporphyrins undergo changes in both the wavelength and relative intensities of the absorption bands as compared to their free base porphyrins. The optical absorption spectraare shown in the Table 5 and VI in $CHCl_3$. It is observed from data that the Q-band and B-band of six co-ordinatedoxovanadium (IV) porphyrins with phenols as axial ligands are blue shifted relative to their five co-ordinatedoxovanadium(IV) porphyrins because of presence of various phenolic ligands attached with VO(IV) which alters the orbital emerges relative to oxovanadium(IV) porphyrins and red-shifted with Etpy as axial ligand due to basic nature of pyridine. The non-bonding electrons present on N hetro atom of the pyridine can be easily donated and hence it requires less energy for transition therefore shows bathochronic shift.On other hand phenols are acidic in nature and phenyl ring present in phenols being electronic with drawing attracts the lone pair of electrons an oxygen towards itself. With the result its tendency to denote the electrons decreases and therefore requires higher energy for transition and hence shows hypsochronic shift. There is also formation of new band around 610 nm.

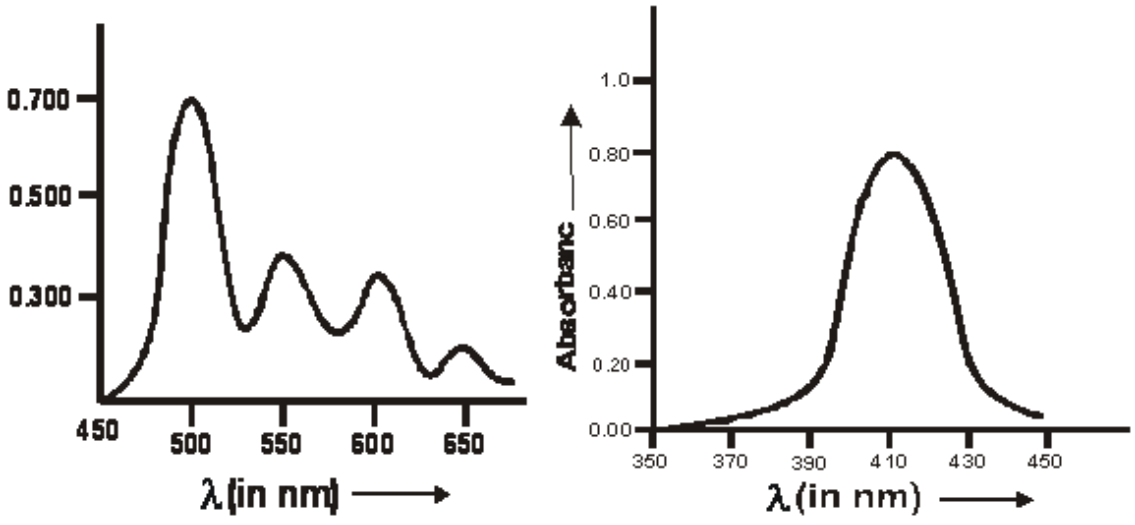


Figure 1 Optical absorption spectra of H_2RTPP in $CHCl_3$

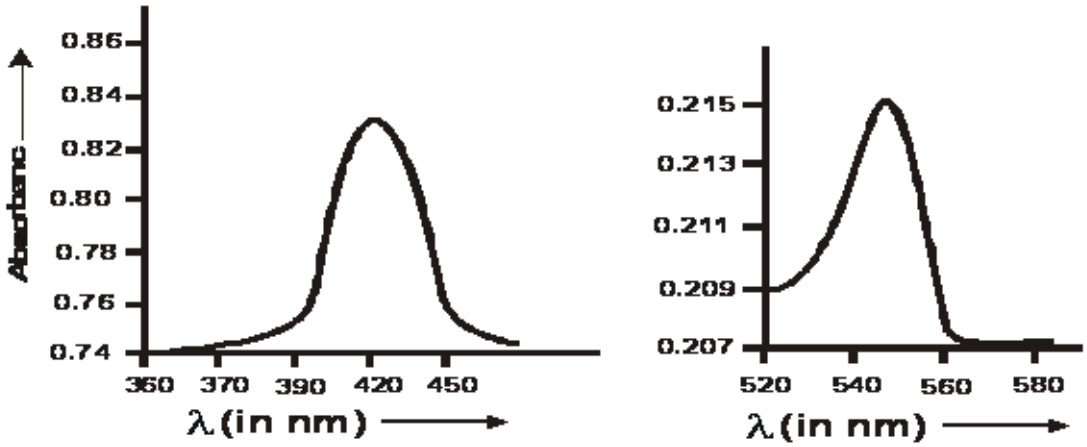


Figure 2 Optical absorption spectra ofVO(RTPP) in $CHCl_3$

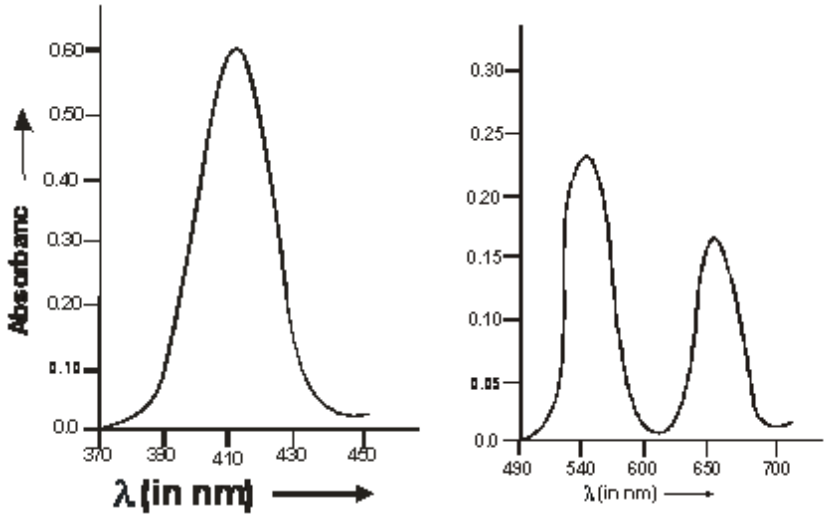


Figure 3 Optical absorption spectra of [VO(RTPP)L] where L = 2-aminophoH and 2,3-dimephoH in $CHCl_3$

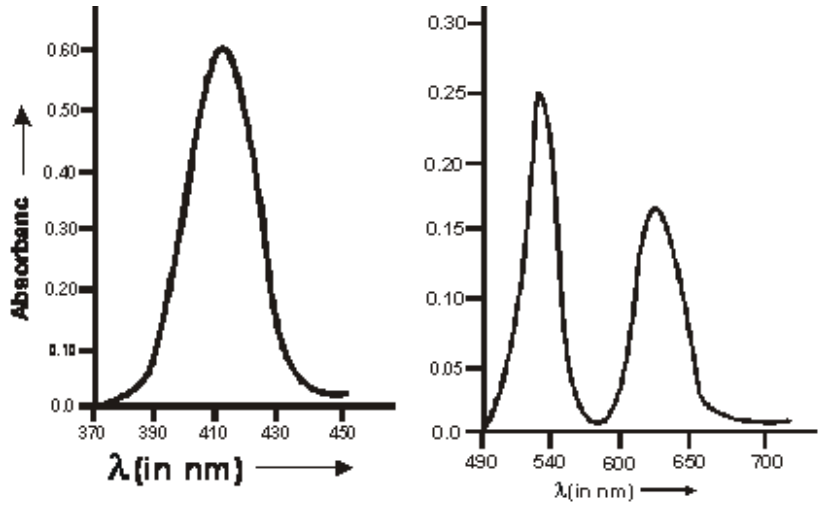


Figure 4 Optical absorption spectra of [VO(RTPP)L] where L = 4-Etpy

The optical absorption spectral data of chlorochromium(III) porphyrin in different solvent is given in **Table 7**. It is observed from the table that chloroderivatives of Cr(III) porphyrin show bathochromic shift when compared to their respective free-baseporphyrins due to incorporation of metal ion in the porphyrin rings. It is also found that Cr(p-CH_3TPP), Cr(p-OCH_3TPP) and Cr(p-ClTPP) exhibits light shift to longer wavelength as compared to CrTPPbecause of the presence of -CH_3, -OCH_3 and –Cl groups respectively at the p-position of mesophenyl rings of porphyrin moiety. The most pronounced bathochromic shift occurs in chlorochromium(ClTPP). The chlorochromium(MeTPP) and chlorochromium (-OCH_3TPP) onthe other hand have minor shifts.

The six co-ordinatedCr(III) porphyrins also show variations in wavelengths and intensities of the absorption bands as compared to their five co-ordinated chromium(III) porphyrins. The optical absorption data of six co-ordinatedchromim(III) porphyrins with 2-aminophenol and 2,3-dimethylphenols and 4-Etpy as the sixth ligand in $CHCl_3$ are shown in Table 7. It is observed from data that in the complexes the soret band and visible bands of all six co-ordinated chromium(III)porphyrins with phenolic ligands are blue shifted relative to their five co-ordinatedchlorochromium(III)porphyrins because of presenceof phenolic ligands attached to Cr(III) which alters the orbital energies relative to chlorochromium(III) porphyrins. It is interesting to note that among the different phenolic ligands attached to Cr(III) both –NH_2 group and -CH_3 group have electron donating ability and these have soretand visible bands slightly red shifted. The 4-ethylpyridine as ligand with chlorochromium(III)porphyrins also shows slight red shift.

Table 7 Optical absorption data of [Cr(RTPP)L] where L = 2-aminophenol, 2,3-dimephOH and 4-Etpy in $CHCl_3$ showing λmax together with log ε and ν½.

Compound	**B-bands** λ_{max}**(nm) (log ε** $m^{-1}cm^{-1}$**ν½** cm^{-1}**)**	**Q. bands** λ_{max}**(nm) (log ε** $m^{-1}cm^{-1}$ **ν½** cm^{-1}**)**
[(2-aminophoH)CrCl(TPP)]	396.3 (3.991) 448.7 (4.874), 1162.1	563.6 (4.389), 996.2 601.8 (4.137)
[(2,3-dimephoH)CrCl(TPP)]	394 (3.982) 445.3 (4.835), 1031.1	562 (4.35), 669.8 600.1 (4.089)
[(4-Etpy)CrCl(TPP)]	395.9 (3.968) 447.8 (4.827) 1160.8	563.3 (4.362) 9954 601.4 (4.143)
[(2-aminophoH)CrCl(p-MeTPP)]	396.1 (4.037) 451 (4.893) 1162.1	563.8 (4.301) 998.2 602.9 (4.212)
[(2,3-dimephoH)CrCl(p-MeTPP)]	395.9 (3.982) 450.8 (4.893) 1159.2	564 (4.338) 997.2
[(4-EtPy)CrCl(P-MeTPP)]	394.5 (4.009) 450.3 (4.849) 1139.2	601.2 (4.135) 503.2 (–)
[(2-aminoPhoH)CrCl[(p-MeoTPP)]	394.3 (4.017) 450 (4.864) 119.2	562.2 (4.309) 998.3 601.4 (4.20)
[(2,3-dimePhoH)CrCl(p-MeoTPP)]	396.2 (3.987) 451.4 (4.889)1184.2	564.1 (4.307) 100.1 603 (4.107)
[(4-Etpy)CrCl(p-MeoTPP)]	3949 (4.053) 449.2 (4.899) 1082.1	563 (4.441) 957.6 601.1 (4.086)
[(2-aminoPhoH)CrCl(p-ClTPP)]	394.1 (4.0001) 447.1 (4.922) 1062.3	562.2 (4.418) 972.6 601 (4.079)
[(2,3-dimePhoH)CrCl(p-ClTPP)]	394.2 (4.0003) 446.2 (4.972) 1046.2	562 (4.412) 967.3 601.3 (4.809)
[(4-Etpy)CrCl(p-ClTPP)]	395.7 (4.007) 450.6 (4.887) 1164	563.6 (4.305) 998.8 602.4 (4.199)

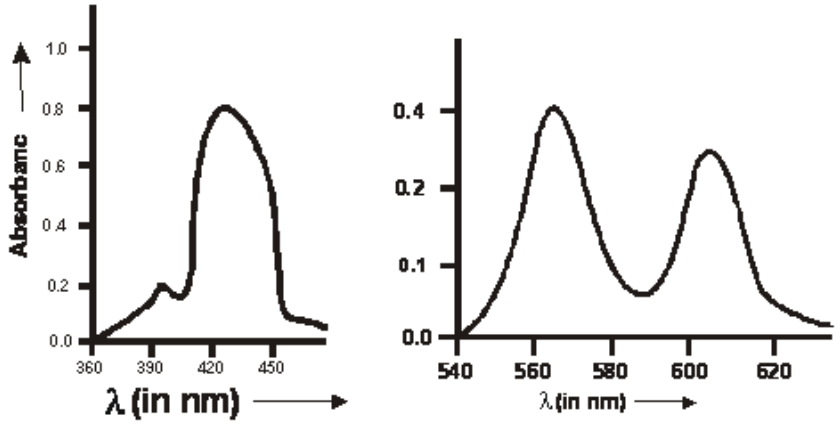


Figure 5 Optical absorption spectra of [CrCl(RTTP)L] where L = 2-aminophoH and 2,3-dimephoH

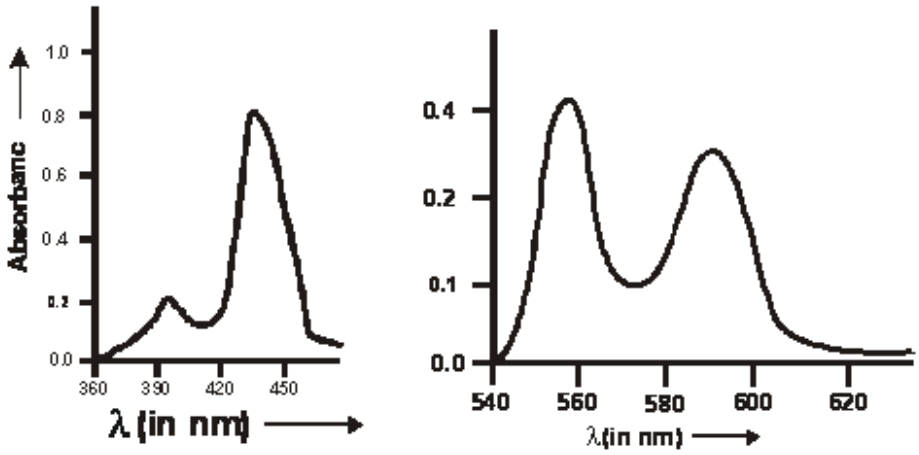


Figure 6 Optical absorption spectra of [CrCl(RTTP)L] where L = 4-Etpy

I.R- Spectral studies: I.R spectral data provides a great structural information regarding the attachment of porphyrin group with metal [20]. The I.R spectra of these porphyrin complexes were recorded in range of 4000-400 cm^{-1} in order to investigate the mode of co-ordination of phenols and 4-ethylpyridine ligands with central metal ion. The porphyrin ring containing phenyl group at meso position exhibit strong absorption bands. The vibration occurring in this porphyrin are ν(N-H) at 3450 cm^{-1}, aromatic ν(C-H) at 2963 cm^{-1}, ν(C-N) at 1095 cm^{-1}, ν(C= N) at 2360 cm^{-1} and ν(C= C) at 1637 cm^{-1}. The spectra of Vo(RTPP) shows shifts in the values of absorption peaks as compared to their corresponding free base porphyrins. This is due to incorporation of vanadium metal in meso-TPP and new frequencies occurs at 2961 cm^{-1} for aromatic ν(C-H) at 1088 cm^{-1} for ν(C-N) at 2358 cm^{-1} for ν(C=N) and 1634 cm^{-1} for (C=C) stretch. There is disappearance of N-H band stretch and appearance of additional V = O band stretch at 1015 cm^{-1} which confirm the presence of vanadium metal in porphyrin. The axial ligation of phenols and 4-Etpy in oxovanadium(IV) porphyrin causes a slight shift variation in the value of vibrational frequencies as shown in **Table 8** for some representative compounds. The vanadium metal in the centre of porphyrin ring co-ordinate with the oxygen at in case of phenolic ligands and with N-atom in case of 4-ethylpyridine attached axially to form six co-ordinate complexe of VO(IV) porphyrinoxovanadium(IV) porphyrin with phenols as axial ligands shows a typical V-O band stretch which usually occurs in the range of 420-480 cm^{-1}. For 2-aminophenol VO(IV) porphyrin there is additional stretching vibration due to presence of NH_2 group which lies at 3274 cm^{-1} for $\nu(NH_2)_{sym}$ and 3362 cm^{-1} for $\nu(NH_2)_{asym}$ in addition to vibration for aromatic ν(C-H) at 2957 cm^{-1}, ν(O-H) at 3463 cm^{-1}, ν(C=C) at 1655 cm^{-1}, ν(C-N) at1090 cm^{-1}, ν(C=N) at 2355cm^{-1}, ν(V=O) at 1008 cm^{-1} and ν(V-O) at 470 cm^{-1} respectively.Oxovanadium(IV) porphyrins with 4-Etpy as axial ligand also shows a shift in values of vibrational frequency as compared to VO(RTPP) where the

vibrational frequencies occur at 2953 cm^{-1} for aromatic ν(C-H) 1640 $cm^{-1}$for ν(C=C), 1095 cm^{-1} for ν(C-N) 2350 cm^{-1} for ν(C=N); 1009 cm^{-1} for ν(V=O), 2920 cm^{-1} for ν(C-H), of ethyl group attached to p-position of ethyl pyridine. After incorporation of phenols and pyridine ligands in VO(IV) porphyrins the V=O gets displaced to lower frequencies in comparison to VO(IV) porphyrins. On the other hand axially ligated chromium(III) derivatives with porphyrins shows a light variation in the frequencies of various groups compared to free-baseporphyrins due to incorporation of chromium(III) atom in the porphyrin ring. The metallation of porphyrins is confirmed by the absence of vibrational frequency occurring due to imino group of porphyrin ring.

Table 8 Mean I.R. absorption band frequencies corresponding to various groups in porphyrins in its axially ligated [VO(RTPP)L] when R = H, Me, OCH_3,Cl and L = 2-aminophoH, 2,3-dimephOH and 4-Ethylpyridine

Porphyrin	ν(N-H) cm^{-1}	ν(O-H) cm^{-1}	ν(C-H) cm^{-1}	ν(C-C) cm^{-1}	ν(C-N) cm^{-1}	ν(C=N) cm^{-1}	ν(V=O) cm^{-1}	ν(V-O) cm^{-1}	ν(CH_2-CH_3) cm^{-1}	ν(NH_2) cm^{-1}
RTPP	3450	–	2963	1637	1095	2360	–	–	–	–
VO(RTPP)	–	–	2961	1634	1088	2358	1015	–	–	–
(2-aminophoH) VO(RTPP)	–	3460	2959	1655	1090	2355	1008	470	–	4ν(NH_2)sym =3274 5ν(NH_2)asym =3362
(2,3-dimephOH) VO(RTPP)	–	3462	2962	1630	1093	2358	1010	472	–	–
(4-Etpy) VO(RTPP)	–	–	2953	1640	1095	2350	1009	–	ν(C-H)2930	–

Table 9 Main I.R. absorption band frequencies corresponding to various groupsporphyrins in its axially ligated CrCl(RTPP)L where L = 2-aminophOH, 2,3-dimephOH and 4-Etpy

Porphyrin	ν(O-H) cm^{-1}	ν(C-H) cm^{-1}	ν(C-N) cm^{-1}	ν(C=C) cm^{-1}	ν(C=N) cm^{-1}	ν(Cr-N) cm^{-1}	ν(Cr-O) cm^{-1}	ν(NH_2) cm^{-1}	ν(CrCl) cm^{-1}
CrCl(RTPP)	–	2948	1351	1592	2346	473.7	–	–	404.5
(2-aminophOH) CrCl(RTPP)	3482	2960	1356	1592	2353	471.9	864.6	ν(NH_2)sym 3290.5 ν(NH_2)asym 3372	402.4
(2,3-dimephOH) CrCl(RTPP)	3479	2958	1352	1590	2352	479.0	864.2	–	403.8
(4-etpy) CrCl(RTPP)	–	2953	1348	1592	2350	475.0	–	–	403.9

In case of chlorochromium(III)porphyrins, two additional bands for Cr-N and Cr-Cl are observed but with incorporption of 2-aminophenol, 2,3-dimephoH as sixth ligand of Cr(III) to CrCl(RTPP) the vibrational frequency due to Cr-O is also observed. The presence of Cr-N bands is shown by appearance of Cr-N stretching vibrations of 430-495 cm^{-1}. Bands appearing ring in the range of 370-430 cm^{-1} are attributed due to ν(Cr-Cl) vibrations and those in the range of 830-890 cm^{-1} are attributed to ν(Cr-O) vibrations[24]. The infrared data of chlorochromium(III) porphyrin complexes are depicted in **Table 9**. The vibrational bands observed are 2948-2960 cm^{-1} are for aromatic ν(C-H), 1348-1352 cm^{-1} for ν(C-N), 1590-1592 cm^{-1} and for ν(C=C), 2346-235 cm^{-1} respectively.

^{1}H NMR spectral data: The β-pyrrole protons of meso-tetraphenylporphyrinresonate as a singlet at 8.84 ppm while inner imino protons of the simple free base porphyrin resonate as a singlet at -2.79 ppm and in case of meso aryl protons the ortho protons resonate as a singlet at 8.17 ppm whereas meta and para protons resonate at 7.6 ppm and appear as a singlet in RTPP and these chemical shiftsvalues are shifted marginally depending upon the nature of the substituents attached at the meso-position. Due to steric hinderance the phenyl protons in RTPP are out of pane of

macrocycle, they do not rotate freely and mesomeric interaction between the four phenyl groups and the microcycle are efficiently reduced. The very similar chemical shifts for the m- and p-protons of the phenyl groups can be explained on the basis. Although the m-protons are closer to the macrocycle, they are out of its plane, and are thus positioned in a less deshilded region. In general, the presence of VO(IV) metal ion in the porphyrin ring results in the shift of the resonances towards low-field (at higher frequency) accompanied by the marginal changes in the ^{1}H NMR spectra. All the free base porphyrins reveal characteristic resonances of iminoprotons, while the metallated derivatives show the absence of inner iminoprotons signals. The β-pyrrole protons of VO(TPP) resonate is a singlet at 9.8 ppm which are downfield relative to RTPP and mesoaryl protons resonate as doublet at 8.4 ppm of ortho and 7.9 ppm of meta and para protons which are also deshilded as compared to RTPP due to the presence of electron releasing oxo group. The ^{1}H NMR spectra of 2-aminophoH VORTPP 2,3-dimethylphoH(RTPP) and 4-Etpy VO(RTPP) shows the there is a shielding of β-pyrrole and mesoaryl protons which shifts the spectrum to upfield (at lower frequency) due to presence of electron donating amino(-NH_2) –CH_3 and CH_2-CH_3 groups and p-protons of phenol and pyridine ring. There is a additional peak which resonates as a singlet at 5.3 ppm for OH proton and for CH_2-CH_3 group of 4-Etpyridine there is quartet for –CH_3- proton at 4.15 ppm and triplet for –CH_2 protons at 1.25 ppm. There is broad singlet for -NH_2 group of 2-aminophoH at 5.6 ppm and 4-Etpy at 3.4 ppm. All these values shows that axially ligated oxovanadium compounds shows marginal changes in chemical shift values relative to free-baseporphyrins. The data also shows that protons of phenolic ring and pyridine ring axially ligated to central metal ion are merged with protons of tetraphenyl ring of porphyrin. The ^{1}H NMR data of compounds are expressed in **Table 10**.

Table 10 ^{1}H NMR data showing chemical shift (δ in PPm) value of the free base and axially ligated VO(IV) porphyrins in $CDCl_3$

Porphyrin	β-pyrrole protons	Iminoprotons	Mesoaryl protons	Other protons
Mesotetraphenylphorphyrin (RTPP)	8.84(s, 8H)	-2.79 (s)	817 (s, 8H, H_o), 7.6(s, 12H, $H_{m,p}$)	–
Meso-TPPVO(IV)[VO(RTPP)]	9.8(s, 8H)	–	8.49(d, 8H, H_o) 7.98(m, 12H, $H_{m,p}$)	–
[(2-aminophoH)VO(RTPP)]	9.45(s, 8H)	–	8.23(d, 10H, H_o) 7.79(d, 14H, $H_{m,p}$)	5.6(s, 2H, HNH_2), 5.2(s, 1H, H_{OH})
[(2,3-dimephoH)VO(RTPP)]	9.5(s, 8H)	–	8.21(d, 19H, H_o) 7.77(d, 14H, $H_{m,p}$)	2.7(s, 3H, H_{me}) 5.5(s, 1H, H_{oH})
[(4-Etpy)VO(RTPP)]	9.3(s, 8H)	–	8.18(d, 10H, H_o) 9.95(d, 14H, $H_{m,p}$)	4.15(q, 2H, CH_2) 1.25(t, 3H, H_{me})

On other hand in comparison to oxovanadium compounds in axially ligated chromium compounds the resonance also occurs down field as compared to RTPP. The ^{1}H NMR spectra shows that β-pyrole protons resonate at 8.95 PPm and ortho and meta protons of mesoaryl rings resonate as doubletat 8.21 PPm and multiplet at 7.50 PPm respectively while methyl protons and proton protons resonate as singlet at 4.02 PPm and 5.35 PPm respectively. The amino proton of 2-aminophoH and ethylprotons of 4-ethyl pyridine are similarto that of oxovanadium compounds as shown in **Table 11**.

All these values show that axially legated chromium compounds shows downfield to free base porphyrin and porphyrins (RTPP) shows up field shifting as compared to simple RTPP (R = H) although the difference in values is very marginal. The data also shows that the protons of phenolic ring axially co-ordinated to the central metal ion are merged with protons of tetraphenyl ring of porphyrin.

Table 11 ^{1}H NMR data of axially ligated Cr(III) porphyrins in L

Porphyrin	β-pyrrole protons	Imino protons	Mesoaryl protons	Other protons
[(2-aminophoH) VO(RTPP)]	9.01(s)	–	8.25(d, 10H, Ho) 7.65(d,14H, H_{mp})	4.8(s, 2H, NHH_2) 5.4(s, 1H, HoH)
[(2,3-dimephoH) VO(RTPP)]	8.99(s)	–	8.26(d, 10H, Ho) 7.64(d, 1H, H_{mp})	3.94(s, 3H,HCH_3) 5.41(s,1H, HoH)
[(4-Etpy)VO(RTPP)]	9.4(s, 8H)	–	8.18(d, 10H, Ho) 9.95(d, 14H, H_{mp})	4.15(q, 2H, H) 1.25(t, 3H, H_{Me})

Mass spectral studies: Mass spectroscopy is the most accurate method for determining the mol. mass of the compounds like porphyrins and multiporphyrins by MALDI-Mass spectroscopy technique [25]. The mass of these complexes are in good agreement with the structure suggested by elemental analysis, spectral and magnetic properties. The mass of the molecular ion peak (m/z) for these compounds are**.**

Table 12 Mass spectra of oxovanadium(IV) compound

1	[(2-aminophoH)VO(TPP)]$^{+}$	787.89	(Calc. $C_{50}H_{35}N_5VO_2$:788)
2	[(2,3-dimephoH)]VO(TPP)]$^{+}$	800.06	(Calc.$C_{52}H_{38}N_4VO_2$: 801.00)
3	[(4-Etpy)VO(TPP)]$^{+}$	786.01	(Calc.$C_{51}H_{37}N_5VO$:786)
4	[(2-aminophoH)VO(p-MeTPP)]$^{+}$	843.86	(Calc. $C_{54}H_{43}N_5VO_2$:844)
5	[(2,3-dimephoH)VO(p-MeTPP)]$^{+}$	856.89	(Calc. $C_{48}H_{36}N_4VO$:842)
6	[(4-Epty)VO(p-MoTPP)]$^{+}$	841.93	(Calc. $C_{55}H_{45}N_4VO$:842)
7	[(2-aminophoH)VO(p-MeOTPP)]$^{+}$	905.91	(Calc. $C_{54}H_{43}N_5VO_6$: 906)
8	[(2,3-dimephoH)VO(p-MeOTPP)]$^{+}$	920.89	(Calc. $C_{56}H_{47}N_4VO_6$:921)
9	[(4-Etpy)VO(p-MeOTPP)]$^{+}$	905.93	(Calc. $C_{55}H_{45}N_5VO_5$:906)
10	[(2-aminophoH)VO(p-ClTPP)]$^{+}$	962.03	(Calc. $C_{50}H_{31}N_5Cl_4$:926)
11	[(2,3-dimephoH)VO(p-ClTPP)]$^{+}$	938.51	(Calc. $C_{52}H_{34}N_4Cl_4VO_2$:939)
12	[(4-Etpy)VO(p-ClTPP)]$^{+}$	923.80	(Calc. $C_{51}H_{33}N_5Cl_4VOs$:924)

Table 13 Mass spectra of chlorochromium series compounds

[(2-aminophoH)CrCl(TPP)] $^{+}$	808.46	(Calc. $C_{50}H_{35}N_5OCrCl$:808.5)
[(2,3-dimephoH)]CrCl(TPP)] $^{+}$	821.48	(Calc.$C_{52}H_{38}N_4OCrCl$: 821.5)
[(4-Etpy)CrCl(TPP)]$^{+}$	806.47	(Calc.$C_{51}H_{37}N_5CrCl$:806.5)
[(2-aminophoH)CrCl(p-MeTPP)]$^{+}$	864.46	(Calc. $C_{54}H_{43}N_5OCrCl$:864.5)
[(2,3-dimephoH)CrCl(p-MeTPP)]$^{+}$	877.47	(Calc. $C_{56}H_{46}N_4OCrCl$:877.5)
[(4-Epty)CrCl(p-MoTPP)] $^{+}$	862.45	(Calc. $C_{55}H_{45}N_5CrCl$:862.5)
[(2-aminophoH)CrCl(p-MeoTPP)]$^{+}$	876.43	(Calc. $C_{54}H_{43}N_5O_5CrCl$: 876.5)
[(2,3-dimephoH)CrCl(p-MeoTPP)]$^{+}$	789.39	(Calc. $C_{56}H_{47}N_4O_5CrCl$:789.5)
[(4-Etpy)CrCl(p-MeoTPP)]$^{+}$	774.39	(Calc. $C_{55}H_{45}N_5O_4CrCl$:774.5)
[(2-aminophoH)CrCl(p-ClTPP)]$^{+}$	946.47	(Calc. $C_{50}H_{31}N_5Cl_5OCr$:946.5)
[(2,3-dimephoH)CrCl(p-ClTPP)]$^{+}$	959.9	(Calc. $C_{52}H_{34}N_4Cl_5CrO$:959.5)
[(4-Etpy)CrCl(p-ClTPP)]$^{+}$	944.48	(Calc. $C_{51}H_{33}N_5C_5Cr$:944.5)

Antibacterial studies: Antibacterial activity of synthesized complexes was tested by Agar-well diffusion method (**Table14**). The samples were tested for antibacterial activityagainst six bacterial stains, viz., *Bacillus subtilis, Alcaligenes denitrificans and Pseudomonas alcaligenes., Micrococcus luteus, Enterococcus faecalis and Bacillus cereus.*

It was found that almost all vanadium porphyrin complexes shared good activity of inhibition against all the bacterial stains whereas chromium complexes have no antibacterial action.

Table 14 Antibacterial assay by agar well diffusion of oxovanadium and chlorochromium porphyrin complexes zone of inhibition (mm)

Compound	Zone inhibition (mm)					
	M. Latens	E. Fecalis	B. Cereus	B. Subtilis	A. denitroficans	P-alcaligenes
[(2-aminophoH)VO(TPP)]	13±0.13	–	–	16±0.06	18.2±0.07	14±0.23
[(2,3-dimephOH)]VO(TPP)	–	12±0.22	14±0.23	15±0.04	14±0.03	13±0.22
[(4-etpy)VO(TPP)]	12±0.02	13±001	16±0.24	13±0.02	8±0.07	–
[(2-aminophoH)VO(p-MeTPP)]	–	13±0.40	18±0.32	8±0.06	8.8±0.06	15±0.3
[(2,3-dimephoH)VO(p-MeTPP)]	14±0.12	12±0.23	13±0.13	7±0.08	10±0.32	12±0.26
[(2-aminophoH)CrCl(TPP)]	–	–	–	–	–	–
[(2-aminophoH)CrClTP)]	–	–	–	–	–	–
[(4-Etpy)CrCl(p-MeTPP)]	–	–	–	–	–	–
[(2-aminophoH)CrCl(p-MeTPP)]	–	–	–	–	–	–
[(2,3-dimephoH)CrCl(p-MeTPP)]	–	–	–	–	–	–
[(2-aminophphoH)CrCl(p-MeoTPP)]	–	–	–	–	–	–
[(4-Etpy)CrCl(p-MeoTPP)]	–	–	–	–	–	–
+ control	13±0.40	14±0.74	22±0.78	18±0.92	17±003	18±0.39

Antioxidant studies: DPPH is a stable free radical that is often used for detection of radical scavenging activity in chemical analysis. The reduction capability of DPPH radicals was determined by the decrease in its absorbance at 517 nm which can be induced by antioxidants. The results of antioxidant studies showed promising results with oxovanadium porphyrins with IC_{50} values of 36 μg/ml, 37 μg/ml, 45 μg/ml and 48 μg/mlrespectively. These complexes showed remarkable scavenging activity with radical scavenging activity with lowest IC_{50} values where as on other hand chromium complexes do not show such a behavior of antioxidant action.

Antifungal studies: The *in vitro* biological screening effects of the complexes reported were tested against the pathogen "*Sclerotium rolfsi*" by poisoned method using potato Dextrose Agar (PDA) nutrient as the medium [13]. The linear growth of fungus in control and treatment *were* recorded at different concentrations of the complexes. **Table 15** shows that on increasing the concentration of the complexes of chromium porphyrins, the colony diameter of the fungus decreases and hence percent inhibition also doubles showing linear relation between concentration and percent inhibition. The increase in antimicrobial activity is due to faster diffusion of chromium metal complexes as a whole through the cell membrane or due to combined activity of the metal and ligand. Such increased activity of metal complexes can be explained on the basis of overtone's concept [26] and Tweedy's chelation theory [27]. The lipid membrane that surrounds the cell favors passage of only lipid solublematerials due to liphophilicity being

important factor which controls antimicrobial activity. On other hand the oxovanadium porphyrin complexes shows such antifungal activity equal to negligible.

Table 15 *Invitro* evaluation of porphyrin complexes against *Sclerotium rolfsi*. Mean Colony diameter of control = 50mm

S. No	Complex	Concentration (PPm)	Colony diameter (mm)	% Inhibition I =[(C-T)/C] x 100
1	[(2-aminophOH)Vo(TPP)]	100	–	–
		200	–	–
		300	–	–
2	[(2,3-dimephOH)]Vo(TPP)	100	–	–
		200	–	–
		300	–	–
3	[(4-etpy)Vo(TPP)]	100	–	–
		200	–	–
		300	–	–
4	[(2-aminophOH)CrCl(TPP)]	100	38	24
		200	21	58
		300	14	72
5	[(2,3-dimephOH)CrCl(TPP)]	100	15	70
		200	8.6	83
		300	4.8	90
6	[(4-epty)CrCl(TPP)]	100	34	72
		200	14	54
		300	8.1	84
7	[(2-aminophOH)CrCl(P-MeTPP)]	100	47	28
		200	36	72
		300	14	82

Conclusion

On the basis of elemental analysis and spectrochemical studies both oxovanadium and chlorochromiumporphyrin complexes possess a monomericoctahedral structure. The biological studies show that oxovanadium complexes have antibacterial and antioxidant behavior whereas chlorochromium complexes are found to be active against fungal strains.

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