

Research Article

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

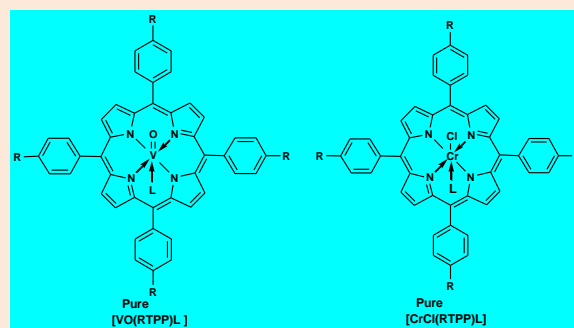
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Abstract

A series of six co-ordinated oxovanadium(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-aminophenol, 2,5-dimethylphenol 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=O 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 chlorochromiumporphyrins 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 $\nu(Cr-Cl)$ vibrations and those in the range of 830-890 cm⁻¹ are attributed due to $\nu(Cr-O)$ 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 and antioxidant but negative antifungal action where a chlorochromiumporphyrin complexes shows only +ive antifungal behaviour but 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 ease of synthesis and wide choice of modulation of electronic structure that is possible arising from the substitution of various groups of different peripheral 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 in porphyrins [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, -NO₂ 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 hemoproteins 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 heme protoporphyrin 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 vanadylporphyrins display d-d transitions which are heavily affected by coordination 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 porphyrin π -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 vanadyl and chromium porphyrins we have aimed at the synthesis, spectroscopic characterization of axially ligated vanadyl and chromium porphyrin in order to understand the steric and electronic effects of the axial ligands on the properties of porphyrins and their biological activity. Axial ligands chosen for investigation are phenols 2-aminophenol, 2,3-dimethoxyphenol and 4-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 use. 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-932 Leco-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 + CDCl₃ 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 six bacterial strains viz. Micrococcus luteus, Enterococcus faecalis, Bacillus cereus, Bacillus subtilis, Alcaligenes denitrificans 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 mm was aseptically bored into the agar plate. Then, 20 mL of the complexes (diluted with DMSO 1:1) was added to each well. Chloramphenicol (10 μ g) 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 incubated 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 ($\text{pH} 5.5$) 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 $\% \text{ RSA} = [(A_o - A_s)/A_o] \times 100$

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

Antifungal studies: The in vitro biological screening effects of the investigated complexes were tested against the pathogen "Sclerotium rolfsii" by poisoned food method using Potato Dextrose/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

RTPPH₂, 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-dimethoxy, 4-ethylpyridine and VO(RTPP) and CrCl(RTPP) were mixed in 1:1 molar ratio in 20 ml of dry CHCl₃. 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 2N NaOH solution and pyridine complexes were extracted with 1N HCl and the extract was evaporated by vacuum pump and dry material was dissolved in CHCl₃. It is filtered through anhydrous sod. sulphate and evaporated through vacuum pump. The final product was purified by column chromatography using basic alumina and CHCl₃ as eluent. The dry product was crystallized with CHCl₃ and recrystallised 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 said RTPP, their metallated and axially ligated oxovanadium(IV) and chlorochromium(III) porphyrins given below in the **Scheme I** and **II**.

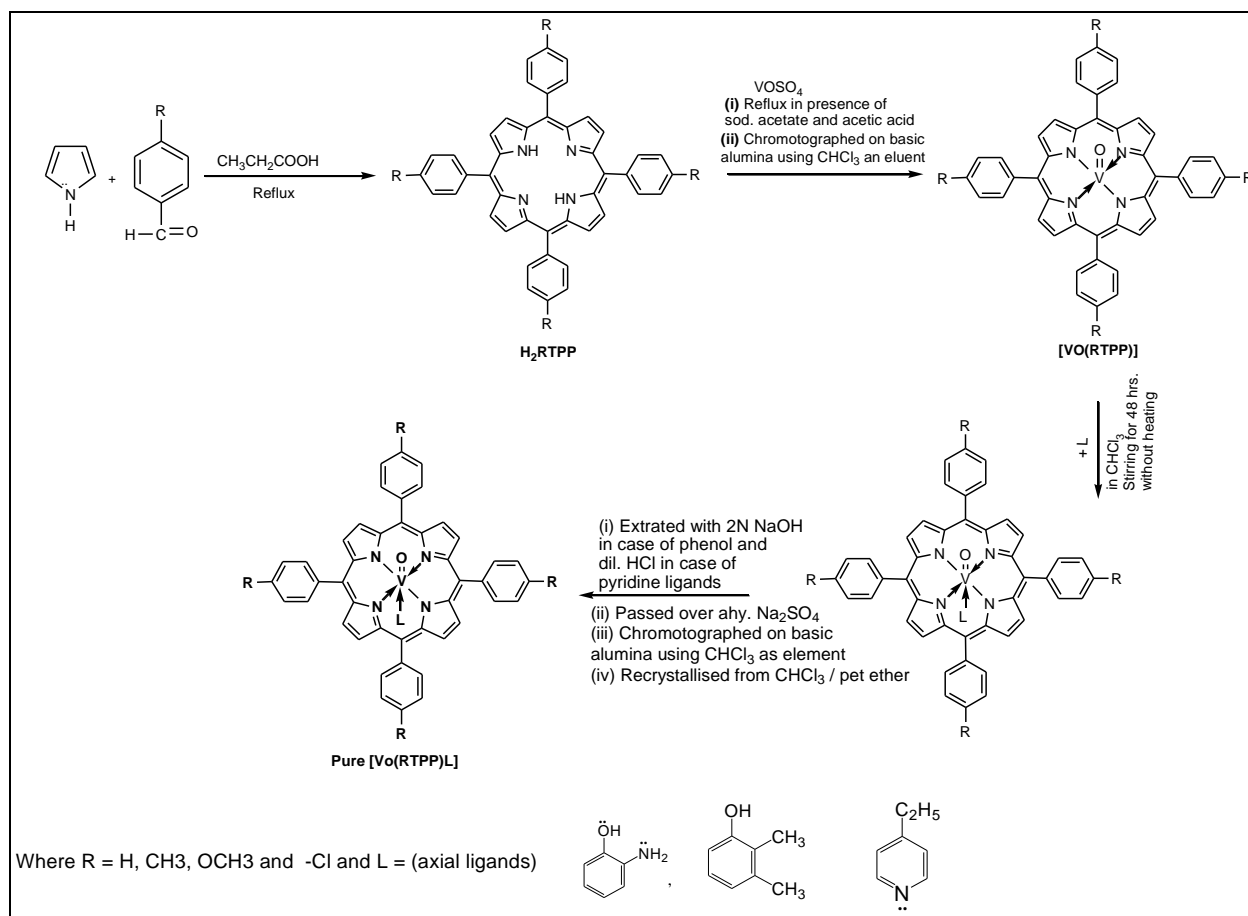
All the new oxovanadium(IV) and chlorochromium(III) porphyrins complexes prepared were characterized by spectroscopic methods such as uv/visible, IR, ¹H-NMR, mass spectra and elemental analysis. The characterizations of the new compounds were consistent with assigned formula. The complexes of both vanadium and chromium were stable at room temperature, coloured and soluble in CHCl₃, DMSO, DMF, CH₃OH and CH₃CN but insoluble in water acetone and ether.

Results and discussion

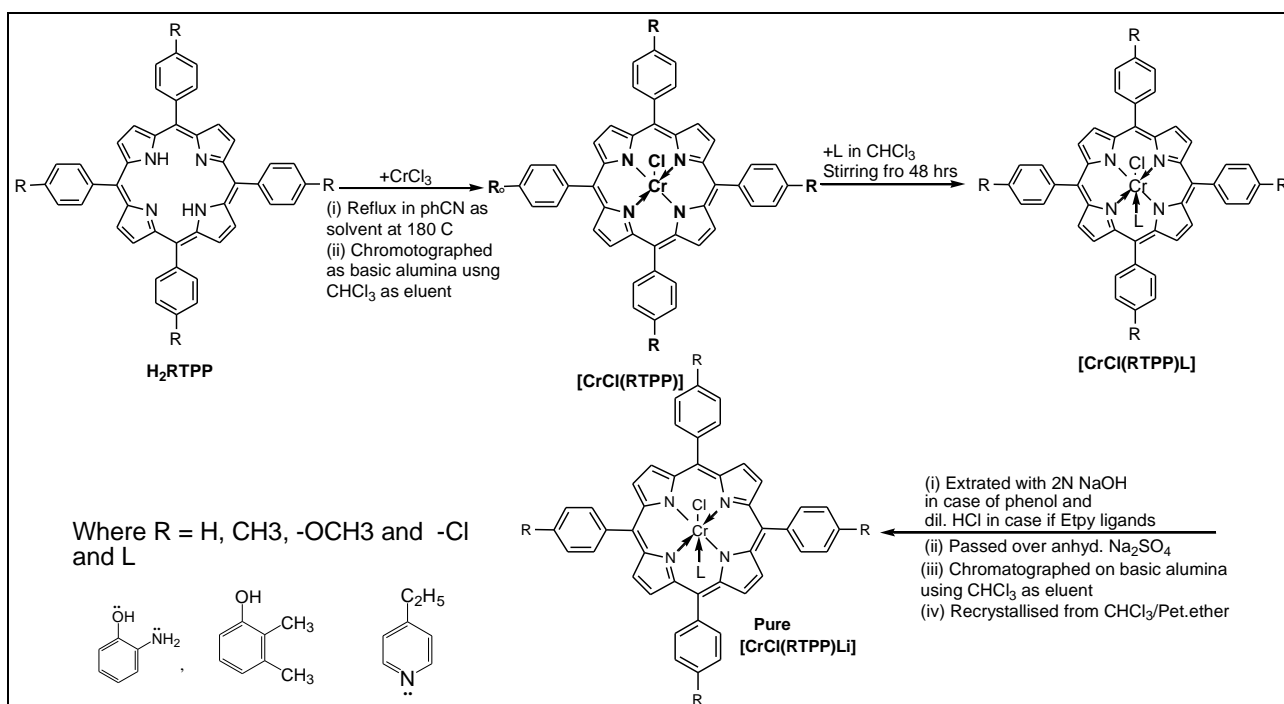
Conductance and magnetic measurements

The molar conductivity of complexes in DMSO at 10⁻³M concentration were recorded to show the values in the range of 10¹⁰⁻¹⁵ Ω⁻¹cm²mol⁻¹ for oxovanadium complexes and for chromium chloro complexes the conductivity values in DMSO of 10⁻³M concentration were found to be in the range of 15-20 Ω⁻¹cm²mol⁻¹ showing that both oxovanadium complexes as well as chromium chloro complexes are non-electrolytes or they are neutral in nature.

The vanadium complexes have magnetic moments in the range of 1.73-1.79 B.M with one unpaired electron of 3d¹ configuration. Whereas chlorochromium complexes the magnetic moment in the range of 3.66-3.80 B.M showing that chromium complexes have 3d³ configuration. These results show 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, CH₃, OCH₃ 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 ₅ VO ₂ | 67.0 | 4.44 | 8.88 | 66.69 | 4.30 | 8.79 |
| [(2,3-dimePhoH)VO(TPP)] | C ₅₂ H ₃₈ N ₄ VO ₂ | 77.90 | 4.74 | 6.99 | 77.83 | 4.70 | 6.90 |
| [(4-Etpy)VO(TPP)] | C ₅₁ H ₃₇ N ₅ VO | 77.86 | 4.70 | 8.90 | 77.81 | 4.67 | 8.83 |
| [(2-aminoPhoH)VO(p-MeTPP)] | C ₅₄ H ₄₃ N ₅ VO ₂ | 76.77 | 5.09 | 8.29 | 76.73 | 5.01 | 8.20 |
| [(2,3-dimePhoH)VO(p-MeTPP)] | C ₅₆ H ₄₇ N ₄ VO ₂ | 78.41 | 5.48 | 6.53 | 78.40 | 5.47 | 6.50 |
| [(4-EtPy)VO(p-MeTPP)] | C ₅₅ H ₄₅ N ₅ VO | 78.38 | 5.34 | 8.31 | 78.30 | 5.28 | 7.96 |
| [(2-aminoPhoH)VO(p-MeOTPP)] | C ₅₄ H ₄₃ N ₅ VO ₆ | 71.52 | 4.74 | 7.72 | 71.39 | 4.69 | 7.74 |
| [(2,3-dimePhoH)VO(p-MeOTPP)] | C ₅₆ H ₄₇ N ₄ VO ₆ | 72.96 | 5.10 | 6.08 | 72.91 | 5.16 | 6.09 |
| [(4-Etpy)VO(p-MeOTPP)] | C ₅₅ H ₄₅ N ₅ VO ₅ | 72.84 | 4.96 | 7.72 | 72.77 | 4.91 | 7.68 |
| [(2-aminoPhoH)VO(ClTPP)] | C ₅₀ H ₃₁ N ₅ Cl ₄ VO ₂ | 64.79 | 3.34 | 7.55 | 64.72 | 3.30 | 7.51 |
| [(2,3-dimePhoH)VO(ClTPP)] | C ₅₂ H ₃₄ N ₄ Cl ₄ VO ₂ | 66.45 | 3.62 | 5.96 | 66.18 | 3.60 | 5.90 |
| [(4-Etpy)VO(ClTPP)] | C ₅₁ H ₃₃ N ₅ Cl ₄ VO | 66.23 | 3.57 | 7.57 | 66.14 | 3.53 | 7.49 |

Table 2 Elemental analytical data of [CrCl(RTPP)L] where R = H, -CH₃, OCH₃ and L = phenolic and 4-ety py ligands

| Compound | Mol. formula | Calculated percentage | | | Found percentage | | |
|--------------------------------|--|-----------------------|------|------|------------------|------|------|
| | | C | H | N | C | H | N |
| [(2-aminoPhoH)CrCl(TPP)] | C ₅₀ H ₃₅ N ₅ OCrCl | 74.25 | 4.32 | 8.65 | 74.19 | 4.30 | 8.59 |
| [(2,3-dimePhoH)CrCl(TPP)] | C ₅₂ H ₃₈ N ₄ OCrCl | 75.95 | 4.62 | 6.81 | 75.90 | 4.58 | 6.78 |
| [(4-Etpy)CrCl(TPP)] | C ₅₁ H ₃₇ N ₅ CrCl | 75.88 | 4.58 | 8.67 | 75.83 | 4.54 | 6.63 |
| [(2-aminoPhoH)CrCl(p-MeTPP)] | C ₅₄ H ₄₃ N ₅ OCrCl | 74.95 | 4.97 | 8.09 | 74.86 | 4.93 | 8.01 |
| [(2,3-dimePhoH)CrCl(p-MeTPP)] | C ₅₆ H ₄₆ N ₄ OCrCl | 76.58 | 5.24 | 6.38 | 76.52 | 5.18 | 6.29 |
| [(4-EtPy)CrCl(p-MeTPP)] | C ₅₅ H ₄₅ N ₅ CrCl | 76.52 | 5.21 | 8.11 | 76.40 | 5.18 | 8.04 |
| [(2-aminoPhoH)CrCl(p-MeOTPP)] | C ₅₄ H ₄₃ N ₅ O ₅ CrCl | 73.93 | 4.90 | 7.98 | 73.86 | 4.88 | 7.93 |
| [(2,3-dimePhoH)CrCl(p-MeOTPP)] | C ₅₆ H ₄₇ N ₄ O ₅ CrCl | 85.11 | 5.95 | 7.09 | 85.10 | 5.86 | 7.0 |
| [(4-Etpy)CrCl(p-MeOTPP)] | C ₅₅ H ₄₅ N ₅ O ₄ CrCl | 85.12 | 5.18 | 9.03 | 85.03 | 5.76 | 8.9 |
| [(2-aminoPhoH)CrCl(p-ClTPP)] | C ₅₀ H ₃₁ N ₅ Cl ₅ CrO | 63.39 | 3.27 | 7.39 | 63.28 | 3.25 | 7.3 |
| [(2,3-dimePhoH)CrCl(p-ClTPP)] | C ₅₂ H ₃₄ N ₄ Cl ₅ CrO | 65.03 | 3.54 | 5.83 | 64.93 | 3.51 | 5.80 |
| [(4-Etpy)CrCl(p-ClTPP)] | C ₅₁ H ₃₃ N ₅ Cl ₅ Cr | 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 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ | 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 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ | 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-CITPP)] | 15 | 3.69 |
| [(2,3-dimePhoH)CrCl(p-CITPP)] | 20 | 3.75 |
| [(4-Etpy)CrCl(p-CITPP)] | 19 | 3.87 |

Electronic spectra

Free-baseporphyrins display four visible bands and metalloporphyrins exhibit two clear visible bands. The UV and visible spectra of tetraporphyrins 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 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 (bathochromic shift) 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**.

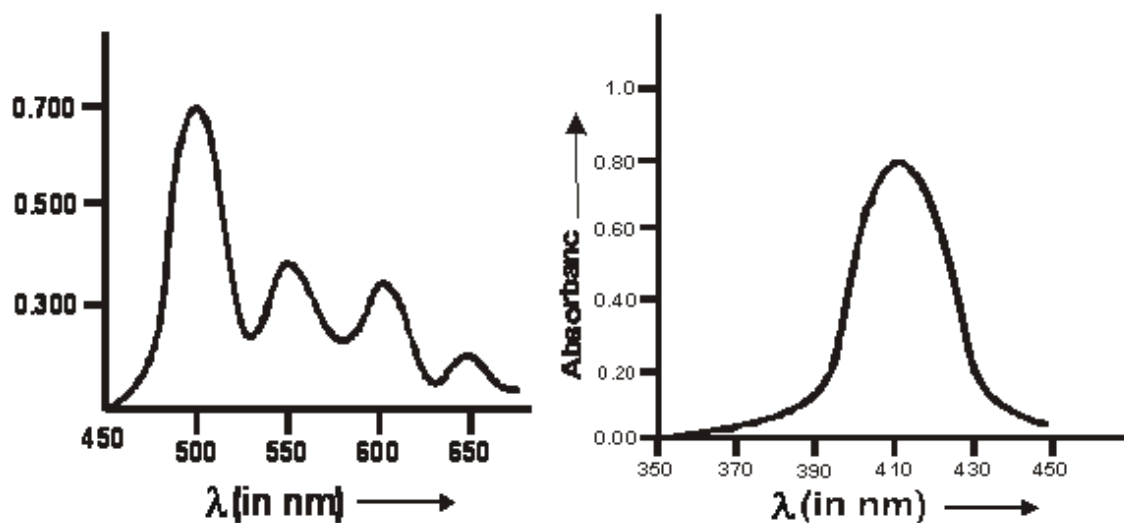
Table 5 Optical absorption spectral data of free baseporphyrins and VO(VI) derivatives in CHCl_3 and CH_2Cl_2 solvents showing λ_{max} together with optical density

| Porphyrins | Solvent | Soret Band (B-Band) | | Q-bands λ_{max} (in nm) abs. | | |
|-----------------------------|--------------------------|-------------------------------------|------------|---|------------|------------|
| | | 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) |
| $\text{H}_2\text{-P-MeTPP}$ | 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(-) |
| $\text{H}_2\text{-P-MeOTP}$ | 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) |
| $\text{H}_2\text{-P-CITPP}$ | 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-CITPP)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 $\log \epsilon$ in CHCl_3

| Compound | B-bands | Q. bands |
|------------------------------|---|---|
| | $\lambda_{\max}(\text{nm})$ ($\log \epsilon \text{ m}^{-1} \text{ cm}^{-1} \nu^{1/2} \text{ cm}^{-1}$) | $\lambda_{\max}(\text{nm})$ ($\log \epsilon \text{ m}^{-1} \text{ cm}^{-1} \nu^{1/2} \text{ cm}^{-1}$) |
| [(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-CITPP)] | 414.7 (4.713), 925 | 536.6 (4.415), 824 |
| [(2,3-dimephoH)VO(p-CITPP)] | 415.8 (4.732), 975 | 538.3 (4.269), 869 |
| [(4-Etpy)VO(p-CITPP)] | 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 spectra are 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-ordinated oxovanadium (IV) porphyrins with phenols as axial ligands are blue shifted relative to their five co-ordinated oxovanadium(IV) porphyrins because of presence of various phenolic ligands attached with VO(IV) which alters the orbital energies 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 hetero atom of the pyridine can be easily donated and hence it requires less energy for transition therefore shows bathochromic shift. On other hand phenols are acidic in nature and phenyl ring present in phenols being electronic withdrawing attracts the lone pair of electrons on oxygen towards itself. With the result its tendency to donate the electrons decreases and therefore requires higher energy for transition and hence shows hypsochromic shift. There is also formation of new band around 610 nm.

**Figure 1** Optical absorption spectra of H_2RTPP in CHCl_3

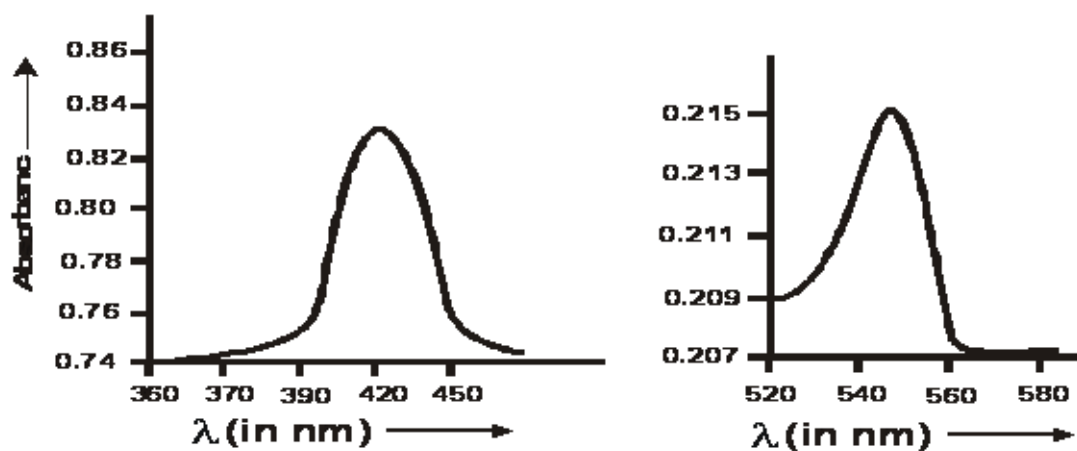


Figure 2 Optical absorption spectra of VO(RTPP) in CHCl_3

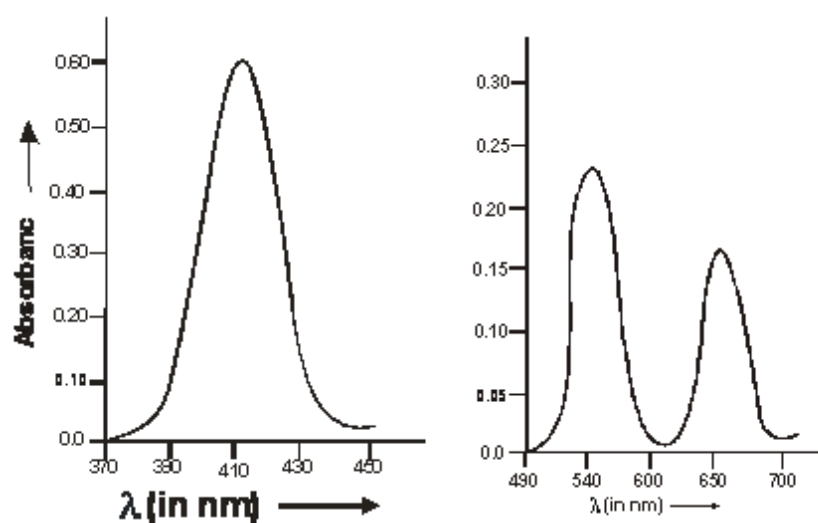


Figure 3 Optical absorption spectra of $[\text{VO}(\text{RTPP})\text{L}]$ where L = 2-aminophoH and 2,3-dimephoH in CHCl_3

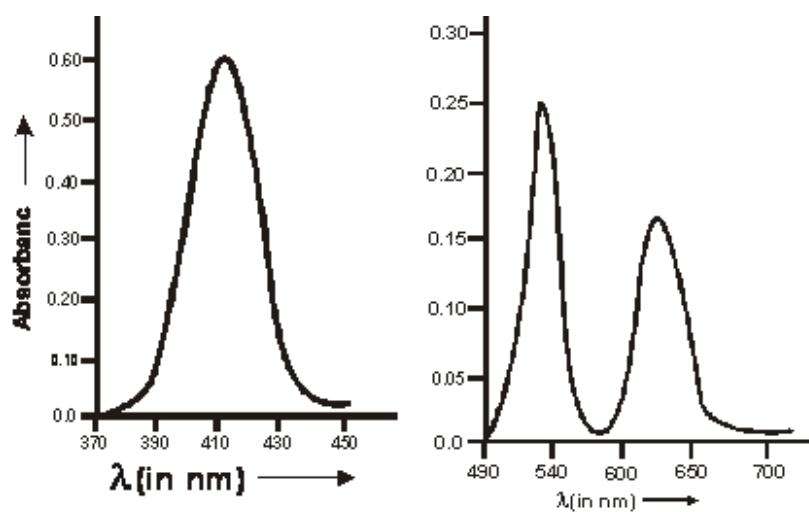


Figure 4 Optical absorption spectra of $[\text{VO}(\text{RTPP})\text{L}]$ where L = 4-Etpy

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-CH₃TPP), Cr(p-OCH₃TPP) and Cr(p-CITPP) exhibits light shift to longer wavelength as compared to CrTPP because of the presence of -CH₃, -OCH₃ and -Cl groups respectively at the p-position of mesophenyl rings of porphyrin moiety. The most pronounced bathochromic shift occurs in chlorochromium(CITPP). The chlorochromium(MeTPP) and chlorochromium (-OCH₃TPP) on the other hand have minor shifts.

The six co-ordinated Cr(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-ordinated chromium(III) porphyrins with 2-aminophenol and 2,3-dimethylphenols and 4-Etpy as the sixth ligand in CHCl₃ 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-ordinated chlorochromium(III) porphyrins because of presence of 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 -NH₂ group and -CH₃ group have electron donating ability and these have Soret and 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 CHCl₃ showing λ_{\max} together with $\log \epsilon$ and $\nu^{1/2}$.

| Compound | B-bands | Q. bands |
|---------------------------------|---|---|
| | $\lambda_{\max}(\text{nm}) (\log \epsilon \text{ m}^{-1}\text{cm}^{-1}\nu^{1/2} \text{ cm}^{-1})$ | $\lambda_{\max}(\text{nm}) (\log \epsilon \text{ m}^{-1}\text{cm}^{-1}\nu^{1/2} \text{ cm}^{-1})$ |
| [(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-MeO)TPP]] | 394.3 (4.017) 450 (4.864) 119.2 | 562.2 (4.309) 998.3 601.4 (4.20) |
| [(2,3-dimePhoH)CrCl(p-MeO)TPP] | 396.2 (3.987) 451.4 (4.889) 1184.2 | 564.1 (4.307) 100.1 603 (4.107) |
| [(4-Etpy)CrCl(p-MeO)TPP] | 3949 (4.053) 449.2 (4.899) 1082.1 | 563 (4.441) 957.6 601.1 (4.086) |
| [(2-aminoPhoH)CrCl(p-CITPP)] | 394.1 (4.0001) 447.1 (4.922) 1062.3 | 562.2 (4.418) 972.6 601 (4.079) |
| [(2,3-dimePhoH)CrCl(p-CITPP)] | 394.2 (4.0003) 446.2 (4.972) 1046.2 | 562 (4.412) 967.3 601.3 (4.809) |
| [(4-Etpy)CrCl(p-CITPP)] | 395.7 (4.007) 450.6 (4.887) 1164 | 563.6 (4.305) 998.8 602.4 (4.199) |

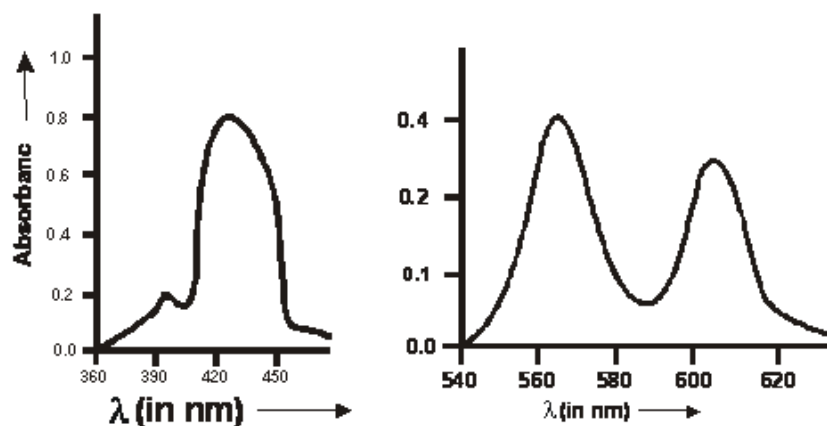


Figure 5 Optical absorption spectra of $[\text{CrCl}(\text{RTTP})\text{L}]$ where $\text{L} = 2\text{-aminophenol}$ and $2,3\text{-dimethylphenol}$

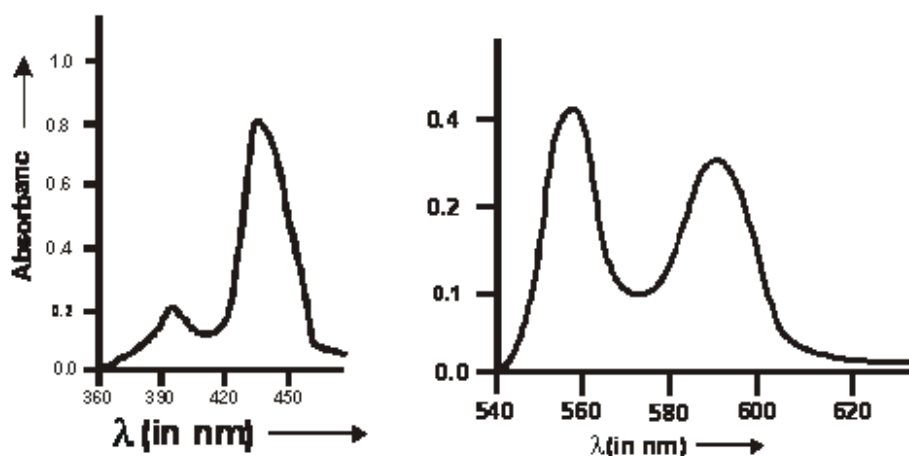


Figure 6 Optical absorption spectra of $[\text{CrCl}(\text{RTTP})\text{L}]$ where $\text{L} = 4\text{-ethylpyridine}$

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 $4000\text{-}400\text{ cm}^{-1}$ 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 $\nu(\text{N-H})$ at 3450 cm^{-1} , aromatic $\nu(\text{C-H})$ at 2963 cm^{-1} , $\nu(\text{C-N})$ at 1095 cm^{-1} , $\nu(\text{C=N})$ at 2360 cm^{-1} and $\nu(\text{C=C})$ at 1637 cm^{-1} . The spectra of $\text{VO}(\text{RTTP})$ 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-TTP and new frequencies occurs at 2961 cm^{-1} for aromatic $\nu(\text{C-H})$ at 1088 cm^{-1} for $\nu(\text{C-N})$ at 2358 cm^{-1} for $\nu(\text{C=N})$ 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-Etpty 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 $\text{VO}(\text{IV})$ porphyrin. Oxovanadium(IV) porphyrin with phenols as axial ligands shows a typical V-O band stretch which usually occurs in the range of $420\text{-}480\text{ cm}^{-1}$. For 2-aminophenol $\text{VO}(\text{IV})$ porphyrin there is additional stretching vibration due to presence of NH_2 group which lies at 3274 cm^{-1} for $\nu(\text{NH}_2)_{\text{sym}}$ and 3362 cm^{-1} for $\nu(\text{NH}_2)_{\text{asym}}$ in addition to vibration for aromatic $\nu(\text{C-H})$ at 2957 cm^{-1} , $\nu(\text{O-H})$ at 3463 cm^{-1} , $\nu(\text{C=C})$ at 1655 cm^{-1} , $\nu(\text{C-N})$ at 1090 cm^{-1} , $\nu(\text{C=N})$ at 2355 cm^{-1} , $\nu(\text{V=O})$ at 1008 cm^{-1} and $\nu(\text{V-O})$ at 470 cm^{-1} respectively. Oxovanadium(IV) porphyrins with 4-Etpty as axial ligand also shows a shift in values of vibrational frequency as compared to $\text{VO}(\text{RTTP})$ where the

vibrational frequencies occur at 2953 cm^{-1} for aromatic $\nu(\text{C-H})$ 1640 cm^{-1} for $\nu(\text{C=C})$, 1095 cm^{-1} for $\nu(\text{C-N})$ 2350 cm^{-1} for $\nu(\text{C=N})$; 1009 cm^{-1} for $\nu(\text{V=O})$, 2920 cm^{-1} for $\nu(\text{C-H})$, 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-base porphyrins 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, OCH₃, Cl and L = 2-aminophOH, 2,3-dimephOH and 4-Ethylpyridine

| Porphyrin | $\nu(\text{N-H})$ cm^{-1} | $\nu(\text{O-H})$ cm^{-1} | $\nu(\text{C-H})$ cm^{-1} | $\nu(\text{C-C})$ cm^{-1} | $\nu(\text{C-N})$ cm^{-1} | $\nu(\text{C=N})$ cm^{-1} | $\nu(\text{V=O})$ cm^{-1} | $\nu(\text{V-O})$ cm^{-1} | $\nu(\text{CH}_2\text{-CH}_3)$ cm^{-1} | $\nu(\text{NH}_2)$ 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 | – | 4 $\nu(\text{NH}_2)$ sym =3274 5 $\nu(\text{NH}_2)$ asym =3362 |
| (2,3-dimephOH) VO(RTPP) | – | 3462 | 2962 | 1630 | 1093 | 2358 | 1010 | 472 | – | – |
| (4-Etpy) VO(RTPP) | – | – | 2953 | 1640 | 1095 | 2350 | 1009 | – | $\nu(\text{C-H})$ 2930 | – |

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

| Porphyrin | $\nu(\text{O-H})$ cm^{-1} | $\nu(\text{C-H})$ cm^{-1} | $\nu(\text{C-N})$ cm^{-1} | $\nu(\text{C=C})$ cm^{-1} | $\nu(\text{C=N})$ cm^{-1} | $\nu(\text{Cr-N})$ cm^{-1} | $\nu(\text{Cr-O})$ cm^{-1} | $\nu(\text{NH}_2)$ cm^{-1} | $\nu(\text{CrCl})$ 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 | $\nu(\text{NH}_2)$ sym 3290.5 $\nu(\text{NH}_2)$ 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 incorporation 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 $\nu(\text{Cr-Cl})$ vibrations and those in the range of 830-890 cm^{-1} are attributed to $\nu(\text{Cr-O})$ vibrations²⁴. 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 $\nu(\text{C-H})$, 1348-1352 cm^{-1} for $\nu(\text{C-N})$, 1590-1592 cm^{-1} and for $\nu(\text{C=C})$, 2346-235 cm^{-1} respectively.

¹H NMR spectral data: The β -pyrrole protons of meso-tetraphenylporphyrin resonate 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 shifts values 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 plane of

macrocycle, they do not rotate freely and mesomeric interaction between the four phenyl groups and the macrocycle 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 deshielded 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 ^1H 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 as 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 deshielded as compared to RTPP due to the presence of electron releasing oxo group. The ^1H NMR spectra of 2-aminophenol VORTPP 2,3-dimethylphenol(RTPP) and 4-Ethyl VO(RTPP) shows that 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(-NH₂) -CH₃ and CH₂-CH₃ groups and p-protons of phenol and pyridine ring. There is an additional peak which resonates as a singlet at 5.3 ppm for OH proton and for CH₂-CH₃ group of 4-Ethylpyridine there is a quartet for -CH₃- proton at 4.15 ppm and triplet for -CH₂ protons at 1.25 ppm. There is a broad singlet for -NH₂ group of 2-aminophenol at 5.6 ppm and 4-Ethyl at 3.4 ppm. All these values show that axially ligated oxovanadium compounds show marginal changes in chemical shift values relative to free-base porphyrins. 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 ^1H NMR data of compounds are expressed in **Table 10**.

Table 10 ^1H NMR data showing chemical shift (δ in PPM) value of the free base and axially ligated VO(IV) porphyrins in CDCl₃

| Porphyrin | β -pyrrole protons | Iminoprotons | Mesoaryl protons | Other protons |
|---------------------------------|--------------------------|--------------|---|---|
| Mesotetraphenylporphyrin (RTPP) | 8.84(s, 8H) | -2.79 (s) | 8.17 (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-aminophenol)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-dimethylphenol)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-Ethyl)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 the other hand in comparison to oxovanadium compounds in axially ligated chromium compounds the resonance also occurs down field as compared to RTPP. The ^1H NMR spectra shows that β -pyrrole protons resonate at 8.95 PPM and ortho and meta protons of mesoaryl rings resonate as doublet at 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-aminophenol and ethyl protons of 4-ethyl pyridine are similar to that of oxovanadium compounds as shown in **Table 11**.

All these values show that axially ligated chromium compounds show 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 ¹H 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 ₅ VO ₂ :788) |
| 2 | [(2,3-dimephoH)]VO(TPP)] ⁺ | 800.06 | (Calc. C ₅₂ H ₃₈ N ₄ VO ₂ : 801.00) |
| 3 | [(4-Etpy)VO(TPP)] ⁺ | 786.01 | (Calc. C ₅₁ H ₃₇ N ₅ VO:786) |
| 4 | [(2-aminophoH)VO(p-MeTPP)] ⁺ | 843.86 | (Calc. C ₅₄ H ₄₃ N ₅ VO ₂ :844) |
| 5 | [(2,3-dimephoH)VO(p-MeTPP)] ⁺ | 856.89 | (Calc. C ₄₈ H ₃₆ N ₄ VO:842) |
| 6 | [(4-Epty)VO(p-MoTPP)] ⁺ | 841.93 | (Calc. C ₅₅ H ₄₅ N ₄ VO:842) |
| 7 | [(2-aminophoH)VO(p-MeOTPP)] ⁺ | 905.91 | (Calc. C ₅₄ H ₄₃ N ₅ VO ₆ : 906) |
| 8 | [(2,3-dimephoH)VO(p-MeOTPP)] ⁺ | 920.89 | (Calc. C ₅₆ H ₄₇ N ₄ VO ₆ :921) |
| 9 | [(4-Etpy)VO(p-MeOTPP)] ⁺ | 905.93 | (Calc. C ₅₅ H ₄₅ N ₅ VO ₅ :906) |
| 10 | [(2-aminophoH)VO(p-CITPP)] ⁺ | 962.03 | (Calc. C ₅₀ H ₃₁ N ₅ Cl ₄ :926) |
| 11 | [(2,3-dimephoH)VO(p-CITPP)] ⁺ | 938.51 | (Calc. C ₅₂ H ₃₄ N ₄ Cl ₄ VO ₂ :939) |
| 12 | [(4-Etpy)VO(p-CITPP)] ⁺ | 923.80 | (Calc. C ₅₁ H ₃₃ N ₅ Cl ₄ VO ₅ :924) |

Table 13 Mass spectra of chlorochromium series compounds

| | | |
|---|--------|---|
| [(2-aminophoH)CrCl(TPP)] ⁺ | 808.46 | (Calc. C ₅₀ H ₃₅ N ₅ OCrCl:808.5) |
| [(2,3-dimephoH)]CrCl(TPP)] ⁺ | 821.48 | (Calc. C ₅₂ H ₃₈ N ₄ OCrCl: 821.5) |
| [(4-Etpy)CrCl(TPP)] ⁺ | 806.47 | (Calc. C ₅₁ H ₃₇ N ₅ CrCl:806.5) |
| [(2-aminophoH)CrCl(p-MeTPP)] ⁺ | 864.46 | (Calc. C ₅₄ H ₄₃ N ₅ OCrCl:864.5) |
| [(2,3-dimephoH)CrCl(p-MeTPP)] ⁺ | 877.47 | (Calc. C ₅₆ H ₄₆ N ₄ OCrCl:877.5) |
| [(4-Epty)CrCl(p-MoTPP)] ⁺ | 862.45 | (Calc. C ₅₅ H ₄₅ N ₅ CrCl:862.5) |
| [(2-aminophoH)CrCl(p-MeOTPP)] ⁺ | 876.43 | (Calc. C ₅₄ H ₄₃ N ₅ O ₅ CrCl: 876.5) |
| [(2,3-dimephoH)CrCl(p-MeOTPP)] ⁺ | 789.39 | (Calc. C ₅₆ H ₄₇ N ₄ O ₅ CrCl:789.5) |
| [(4-Etpy)CrCl(p-MeOTPP)] ⁺ | 774.39 | (Calc. C ₅₅ H ₄₅ N ₅ O ₄ CrCl:774.5) |
| [(2-aminophoH)CrCl(p-CITPP)] ⁺ | 946.47 | (Calc. C ₅₀ H ₃₁ N ₅ Cl ₅ OCr:946.5) |
| [(2,3-dimephoH)CrCl(p-CITPP)] ⁺ | 959.9 | (Calc. C ₅₂ H ₃₄ N ₄ Cl ₅ CrO:959.5) |
| [(4-Etpy)CrCl(p-CITPP)] ⁺ | 944.48 | (Calc. C ₅₁ H ₃₃ N ₅ C ₅ Cr:944.5) |

Antibacterial studies: Antibacterial activity of synthesized complexes was tested by Agar-well diffusion method (Table 14). The samples were tested for antibacterial activity against 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. denitrificans | 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-ety)VO(TPP)] | 12±0.02 | 13±0.01 | 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)CrCl(TP)] | – | – | – | – | – | – |
| [(4-Ety)CrCl(p-MeTPP)] | – | – | – | – | – | – |
| [(2-aminophoH)CrCl(p-MeTPP)] | – | – | – | – | – | – |
| [(2,3-dimephoH)CrCl(p-MeTPP)] | – | – | – | – | – | – |
| [(2-aminophoH)CrCl(p-MeTPP)] | – | – | – | – | – | – |
| [(4-Ety)CrCl(p-MeTPP)] | – | – | – | – | – | – |
| + control | 13±0.40 | 14±0.74 | 22±0.78 | 18±0.92 | 17±0.03 | 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 IC₅₀ values of 36 µg/ml, 37 µg/ml, 45 µg/ml and 48 µg/ml respectively. These complexes showed remarkable scavenging activity with radical scavenging activity with lowest IC₅₀ values whereas 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 soluble materials due to lipophilicity 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 $I = [(C-T)/C] \times 100$ |
|-------|------------------------------|---------------------|----------------------|--|
| 1 | [(2-aminophOH)Vo(TPP)] | 100 | – | – |
| | | 200 | – | – |
| | | 300 | – | – |
| 2 | [(2,3-dimephOH)]Vo(TPP) | 100 | – | – |
| | | 200 | – | – |
| | | 300 | – | – |
| 3 | [(4-etry)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-erty)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 monomeric octahedral 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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