

RESEARCH ARTICLE

Design and Synthesis of Poly Metallic Porphyrin-Schiff's Complex

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ABSTRACT:

A successful synthesis of new *meso*-tetracupratedporphyrin-schiff's complex was achieved from metallo-5,10,15,20-tetrakis(4-hydroxyphenyl) porphyrin (M=Cu(II), VO(II) & Ni(II)) and salicylideneamino-2-(N,N-dimethylamino)ethane copper (II) perchlorate under nitrogen atmosphere. Similarly *meso*-tetracupratedporphyrin-schiff's complex derived from 5,10,15,20-tetrakis(4-hydroxyphenyl) porphyrinato copper (II) and salicylideneamino-2-(N,N-dimethylamino)ethane zinc(II) chloride synthesized as control experiment. Detailed spectral analysis reveal dipolar interaction between the core copper metal ion of the porphyrin and *meso*-copper ions however no interaction between core vanadyl and *meso*-copper ions. Furthermore, the ease with which the copper at the periphery undergoes oxidation and reduction has been understood from the electrochemical investigation. The results also reveal a change in the geometry of the *meso*-copper after coordination to the porphyrin.

KEYWORDS: Porphyrin, tetracuprated, physico-chemical, voltammetry, redox potential.

INTRODUCTION:

Porphyrins are the most versatile ligands among various organic ligands, forming well-defined complexes with essentially all transition metal ions for biological function. They can be used as photosensitizing drugs in photodynamic therapy¹⁻³ when coupled to the unprotected peptide⁴, DNA⁵, etc. Some metalloporphyrins are used as therapeutic drugs to correct the disorder of heme metabolism and suppress tumors^{6,7}. Magnetic resonance imaging of porphyrins and metalloporphyrins is the important characteristic often used in biomedical field, especially in the treatment of cancer⁸. In recent years, peripheral substitution, mostly at *meso*-positions, of platinum group metal ions has been employed in synthesizing dimeric and oligomeric type porphyrins that undergo interesting intramolecular photo processes between the porphyrin sub-units⁹⁻¹².

Even though the existing peripherally metal substituted porphyrins help to understand the interaction between porphyrin rings, such systems are not suitable to study the interaction between the metal centers.

An example in this kind of porphyrins is tetra-ruthenated *meso*-tetrapyrrolyl porphyrin^{13,14}. Its photophysical properties, interaction with calf thymus DNA investigated^{15,16} and the results suggest a strong interaction between ruthenium and porphyrin π -center, resulting in intramolecular energy transfer in excited triplet state^{17,18}. Recently, bimetallic (nickel/palladium) porphyrin monomer has been synthesized¹². However, till date, no study has been conducted with magnetically active paramagnetic metal ions substituted around a porphyrin ring forming *meso*-tetrametallated porphyrin monomers. The coordination of paramagnetic metal ion offers great advantage in probing the interaction between the metal ions. Though author has published mono substitution of the periphery earlier¹⁹ now attempt to make tetramer to see the extent of interaction between the metal centers. Regarding the coordination of paramagnetic metal ion at the peripheral positions of the porphyrin, an earlier report suggests that the coordination of copper (II) at the 8-hydroxyquinoline position of 5,10,15,20-tetrakis(8-hydroxyquinolyl) porphyrin occurs faster than at the central porphyrin core¹⁸. The application of such multi metal complexes could probably lie in synthesizing better catalysts and energy storage systems²⁰. To have an appropriate coordination site, an anionic donor atom, namely hydroxo has been preferred to obtain neutral complexes.

Thus, in the present study, 5,10,15,20-tetrakis(4-hydroxyphenyl) porphyrin has been employed as the base porphyrin. Here in, we report the synthesis, characterization of tetra cooperated porphyrins derived from 5,10,15,20-tetrakis (4-hydroxy phenyl) porphyrinato copper and 5,10,15,20- tetrakis(4-hydroxy phenyl) porphyrinovanadyl and 5,10,15,20-tetrakis(4-hydroxy phenyl) porphyrinato nickel. Also control complex, ie, tetrazincporphyrin derived from 5,10,15,20-tetrakis (4-hydroxy phenyl) porphyrinato copper is also discussed.

MATERIAL AND METHODS:

Instrumentation:

¹H-NMR spectra of free porphyrins were recorded on AMX-400 NMR spectrometer in CDCl₃/DMSO, using TMS as the internal standard. FAB mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer/Data system using Argon/Xenon (6 kV, 10mA) as the FAB gas. Electronic absorption spectra were obtained with Ocean optics optical fiber (400 μm) spectrophotometer SD1000 using 10 mm quartz cell. IR spectra were recorded on ABBBomem MB 104 spectrometer using KBr disks. Elemental (C, H and N) analysis was performed with Heraeus Rapid analyzer. All electrochemical experiments were performed using Ecochemie AUTOLAB PGSTAT 12 controlled by GPES software running under Microsoft Windows. A conventional three-electrode setup was employed in all electrochemical measurements, with tetrabutyl ammonium perchlorate as supporting electrolyte. Generally all the cyclic voltammogram were performed with scan rate, 50mV/s. For recording square wave voltammogram a constant frequency of 8 Hz with step potential of 4mV and pulse amplitude of 10 mV was employed.

Chemicals and reagents:

4-methoxy benzaldehyde, pyrrole and propionic acid were bought from SDFine, India, were used after purification.²¹ All the solvents used were analytical grade and were dried further whenever required. The precursor ligands, *meso*-5,10,15,20-tetrakis-(4-methoxyphenyl) porphyrin (**I**)²², *meso*-5,10,15,20-tetrakis-(4-hydroxyphenyl) porphyrin²³ [**Ia**], 5,10,15,20-tetrakis(4-hydroxyphenyl) porphyrinato copper (**II**)²⁴, 5,10,15,20-tetrakis(4-hydroxyphenyl) porphyrinovanadyl (**III**)²⁴, 5,10,15,20-tetra (4-hydroxyphenyl) porphyrinato nickel (**IV**)²⁴, Salicylideneamino-2-(N,N-dimethylamino) ethane(**L**)²⁵, Salicylideneamino-2-(N,N-dimethylamino) ethane copper (II) perchlorate monohydrate, CuLClO₄.H₂O,(**V**)²⁵ and Salicylideneamino-2-(N,N-dimethylamino) ethane zinc (II) chloride, ZnLCl, (**Va**) were synthesized from the earlier procedures. ¹H NMR was used to confirm the purity of the free base

porphyrins.

Meso-5,10,15,20-tetrakis(4hydroxosalicy lideneamino-2-(N,N-dimethylamino)ethanecopper (II))porphyrinatocopper(II) (VI)

To 75 mL of nitrogen bubbled dry dimethylformamide, **II** (0.5 mmole, 0.37 g) was added. 2.2 mmoles (0.3 g) of anhydrous potassium carbonate was added and purging of nitrogen was continued for further 1 hour. The reaction mixture was then refluxed for 24 hours under nitrogen atmosphere. 2.2 mmoles (0.781g) of **V** was then added and purging was continued for another 30 minutes, followed by refluxion under nitrogen atmosphere for another 24 hours. The volume of the resultant solution was reduced to one fourth under vacuum and then extracted with dichloromethane. The organic layer was washed with water, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified using column chromatography on basic alumina, initially with chloroform and followed by 2% methanol in chloroform as eluent to afford 6% of **VI**. FAB-MS, m/z: calculated for C₉₅H₁₀₇N₁₂O₁₃Cu₅Cl₄: 2082; found: 2083, [M+1]⁺.

Meso-5,10,15,20-tetrakis(4-hydroxosalicy lideneamino-2-(N,Ndimethylamino) ethanecopper (II))porphyrinovanadyl(II) (VII)

Compound **VII** was prepared by adapting a similar procedure described for **VI** except that **III** (0.37 g, 0.5 mmol) was used instead of **II**. Pure **VII** was obtained by column chromatography on basic alumina using 2% methanol in chloroform as eluant. The R_f on an alumina-coated plate was found to be same as that in **VI**. Yield 0.041 g (4%). FAB-MS, m/z: calculated for C₉₄H₁₀₄N₁₂O₁₃Cu₄VCl₄: 2055; found: 2057, [M+2]⁺.

Meso-5,10,15,20-tetrakis(4-hydroxosalicy lideneamino-2-(N,N-dimethylamino) ethanecopper (II) porphyrinatonicel(II) (VIII)

Compound **VIII** was prepared by following a similar procedure given in **VI** except that **IV** (0.38 g, 0.5 mmol) was used instead of **II**. The R_f value was similar in this complex too. Pure **VIII** was obtained by column chromatography on basic alumina using 2% methanol in chloroform as eluant. Yield 0.61 g (6%). FAB-MS, m/z: calculated for C₉₄H₁₀₀O₁₂N₁₂Cu₄NiCl₄: 2041; found: 2041, [M]⁺.

Meso-[5,10,15,20-tetrakis((4-hydroxosalicy lideneamino-2-(N,N-dimethylamino) ethanezinc(II) phenoxo)porphyrinato)copper(II) (IX)

Compound **IX** was prepared by following a similar procedure described for **VI**. However, anhydrous caesium carbonate (0.43 g, 2.2 mmol) was used in the place of anhydrous potassium carbonate. The metal precursor (**Va**, 0.64 g, 2.2 mmol) was used instead of **V**

and the refluxing time was increased to 48 h. The isolation and purification of the complex was as similar as that discussed in VI. The yield was found to be 5%. FAB-MS, m/z: calculated for $C_{88}H_{84}N_{12}O_8CuZn_4$: 1759, found: 1733, $[M-C_2H_2]^+$; 1562, $[M-C_6H_8N_2Cu]^+$; 460, $[M-C_{53}H_{60}N_9O_8CuZn_4]^+$.

RESULTS AND DISCUSSION:

The synthesis of *meso*-tetracopperated and *meso*-tetrazincmetalloporphyrins is achieved by two-step procedure. Firstly, the required metalloporphyrins were prepared and further reaction with the tri-coordinated Schiff's based (copper / zinc) complex, $CuLClO_4 / ZnLCl$, results in coordination of copper / zinc Schiff's base at the *para* position of *meso*-tetrakis-4-hydroxyphenyl group (**Scheme I**). This methodology has afforded us to prepare both homo and hetero metallic molecular systems. In the absence of single crystal structure, scheme I shows a speculative molecular structure. Compounds VI, VII, VIII and IX are stable in air and are soluble in almost all nonpolar organic solvents in contrast to the parent porphyrins, II, III and IV, which are soluble only in polar solvents.

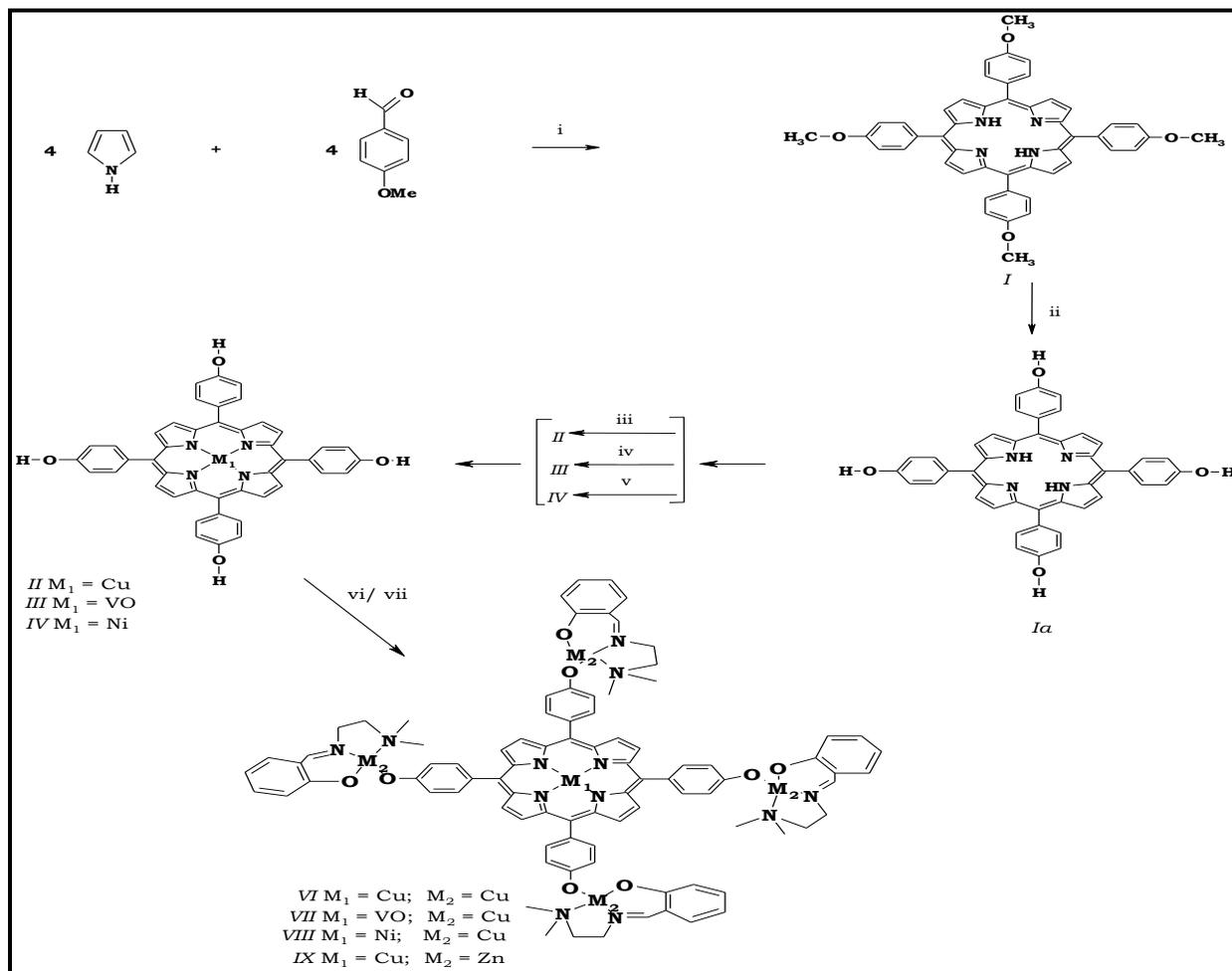
Uv-Vis spectroscopy:

The electronic absorption spectrum of VI, VII, VIII, IX are shown in fig. 1 and the absorption peaks of all the compounds are tabulated in table 1. The electronic absorption spectra of II, III and IV reveal transitions in the expected lines²⁶. On coordination with *VorVa* moiety at the peripheral site, the Soret band maximum of VI, VII, VIII and IX show a red shift with respect to metalloporphyrins and also shows additional broad shoulder like patterns in the blue side of the band maximum. These new shoulders originate due to overlap of charge transfer transitions of CuL / ZnL ²⁷ with the porphyrin transitions. On the other hand the Q band pattern in VI, VII, VIII and IX do not show any marked

change, suggesting that the porphyrin structure has not perturbed drastically. However, the Q band absorption energy is found to shift slightly towards lower energy and with increased broadness. This is due to *meso*-position perturbation of the porphyrin ring²⁶. The coordination of copper at the periphery in the complexes VI, VII and VIII is clearly depicted by the increased intensity in the region greater than 600 nm which arises due to the overlap of ligand field transition of copper in CuL units with the strong Q band of metalloporphyrins as one could see more broadening and also it is not present in either the parent metalloporphyrins or in IX. Since, the electronic transitions of the individual units in VI, VII, VIII and IX neither showed any major change nor new transitions were observed, it is clear that the electronic interactions between porphyrin ring and CuL units are negligible.

Voltammetric study:

The electrochemical behaviour of the complexes from VI to IX can be understood from the electrochemical study of the individual units present in the complexes. Thus the voltammetric study of the precursor's viz., Ia, II, III, IV and V were done to understand the kinetics of the complexes. The electrochemical data obtained are tabulated in table 1. The voltammogram of porphyrin precursors clearly represents two step one electron reversible oxidation and two step one electron reduction²⁸⁻³⁰. On the other hand, the cyclic voltammetric study on V resulted in a single irreversible oxidation process in the potential range of 0 to 1.5 V and the peak at 1.229 V is attributed to the oxidation couple arising due to oxidation of copper(II) to copper(III). Similarly, in the range of 0 to -1.5 V, the metal precursor V shows an irreversible reduction processes at -0.472 V and the reverse scan shows an anodic peak



Scheme I: (i) $\text{CH}_3\text{CH}_2\text{COOH}$, reflux, 30min; (ii) Pyridine hydrochloride, reflux, 130°C , 4h; (iii) $\text{Cu}(\text{OAc})_2$, DMF, heat, 30min; (iv) $\text{VO}(\text{acac})_2$, phenol, reflux, 3h; (v) NiCl_2 , DMF, heat, 30min; (vi) $(\text{CuL})\text{ClO}_4$, DMF/ K_2CO_3 , N_2 atmosphere, 24h, reflux; (vii) ZnLCl , DMF/ Cs_2CO_3 , N_2 atmosphere, 48h, reflux.

[Note: Hydrogen and coordinated solvent molecules are not shown for clarity.]

Table 1: Electronic absorption maximum and voltammetric data of various *meso*-substituted porphyrins (0.1mM)

S. No.	Complex	Absorption maximum (nm)	Oxidation Potential ^a in V			Reduction Potential ^a in V		
			$\text{P} \rightleftharpoons \text{P}^+$	$\text{P}^+ \rightleftharpoons \text{P}^{2+}$	$\text{Cu}^{2+} \rightarrow \text{Cu}^{3+}$	$\text{Cu}^{2+} \rightarrow \text{Cu}^+$	$\text{P} \rightleftharpoons \text{P}^-$	$\text{P}^- \rightleftharpoons \text{P}^{2-}$
1.	Ia	410, 508, 545, 584, 643	0.743	1.178	---	---	-1.260	-1.680
2.	II	406, 530, 569	0.9	1.261	---	---	-1.429	-1.879
3.	III	421, 543, 582	0.849	1.170	---	---	-1.486	---
4.	IV	405, 518	0.986	1.216	---	---	-1.393	-1.966
5.	V	353, 377, 554	---	---	1.229	-0.472	---	---
6.	Va	380	---	---	---	---	---	---
7.	VI	410, 535, 583, 352, 381	0.762	1.0	1.486	-0.653	-0.992	-1.369
8.	VII	419, 540, 581, 358, 377	0.720	1.050	1.334	-0.732	-1.156	---
9.	VIII	410, 520, 347, 376	0.745	0.979	1.345	-0.738	---	-1.7
10.	IX	416, 531, 566, 584	---	---	---	---	---	---

*P = Porphyrin; a: redox potentials are measured with 1mM TBAP as supporting electrolyte in a three electrode system with 2mm Pt disc as working electrode. All potentials are with respect to SCE (0.24 V)

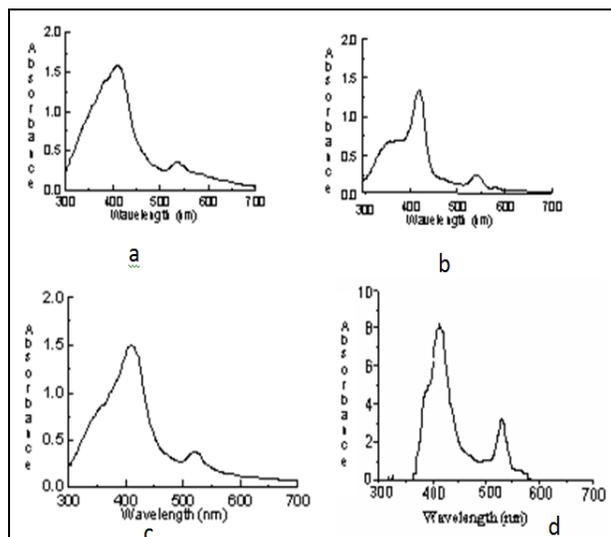


Fig. 1. Electronic absorption spectrum in 10mm pathlength (0.01mM) dichloromethane solution of VI (a) VII (b) VIII (c) and IX (d)

at -0.2 V which is due to re-oxidation of copper(0) to copper(II). It is well known that copper(I) to copper(0) occurs at -0.8 V in acetonitrile³¹. Furthermore, the copper(II) to copper(I) is irreversible due to large geometrical change involved during the process of reduction. The electrochemical study of complexes, see fig 2, shows three one electron oxidation processes in the range of 0.5 to 1.5 V. The oxidation peak at around 0.9 V and 1.0 V are assigned to the oxidation of porphyrin while that around 1.49 V is assigned to the oxidation of copper at the periphery.

Various kinetic criteria are employed to understand the nature of the charge transfer process and are summarized as below

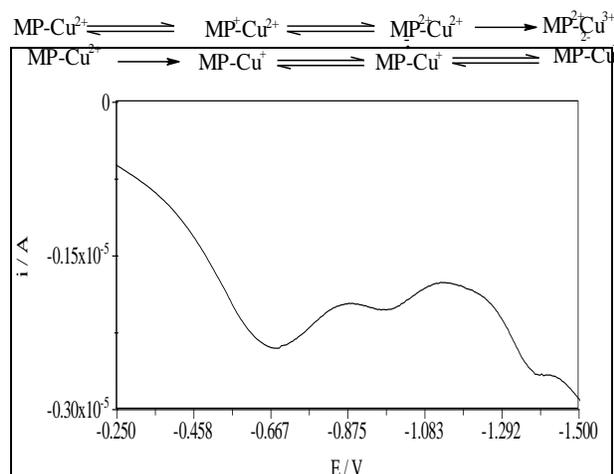


Fig.2. Squarewave voltammogram representing reduction of VI (0.1 mM) at the scan rate of 50mV, in dichloromethane with 1mM TBAP as supporting electrolyte and SCE as the reference electrode

The electrochemical study of the complexes in the range of -0.5 to -1.8 V, result in three cathodic processes. The peak at -0.6 to -0.7 V is assigned to the reduction process taking place in the peripheral copper ion and the while the other two potentials are assigned to the reduction processes taking place at the porphyrin cloud. It is clear from the redox potentials, the oxidation and reduction of the copper(II) at the porphyrin periphery is difficult in VI, VII and VIII in comparison with that of the precursor V. Since on coordination of V to the periphery of any metalloporphyrin resulting in a planar geometry as evidenced from the ESR spectrum¹⁹, the oxidation and reduction processes becomes difficult than in V. On the other hand, the oxidation and reduction of porphyrin ring seems to be easier in the complexes than the corresponding precursors is possibly due to increased distortion of the porphyrin ring on periphery coordination which is also reflected in the covalency character of the Cu-N bond

CONCLUSION:

The availability of replaceable proton in 5,10,15,20-tetrakis(4-hydroxyphenyl) porphyrin allows the preparation of new *meso*-tetracuperated porphyrin monomers. The electronic spectra show red shift and intensity variation due to perturbation at the *meso*- sites. Electronic ground state interactions are negligible. The peripheral copper Schiff's base complex adapts more planar geometry in the tetracuperated systems than in their pure form. The spin-spin interaction seems to be strongly dipolar in nature. The interactions between the *meso*-copper ions are weak due to their large distance. The peripheral copper ion interacts more strongly with the central copper ion than with the central vanadyl ion which also evidenced from the redox potential of the complexes. Also the difficulty in undergoing reduction and oxidation of peripheral copper ions and the easiness to undergo reduction and oxidation in the porphyrin ring rationalize that the peripheral copper reaches more planar geometry and the porphyrin structure distorts on complexation.

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CONFLICT OF INTEREST:

The authors declare no conflict of interest.

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